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ORDERED POROUS STRUCTURES FROM METAL OXIDE NANOCRYSTALS SYNTHESIS, STRUCTURAL CHARACTERIZATION AND APPLICATIONS IN REDOX CATALYSIS

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SUMMARY

The rapid development of civilization and industrial activities has led to a large amount of pollutants being disposed into the environment either intentionally or accidentally, including toxic metals with a great health concern. Chromium is a heavy metal with variable oxidation states and hexavalent chromium, Cr(VI), is the most toxic form. In aquatic systems, chromium exists mostly in the hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) states. Anionic Cr(VI) species are far more mobile and toxic than Cr(III) and difficult to remove from water, since aqueous Cr(III) can be readily precipitated as $Cr(OH)_3$ or Cr_2O_3 in a basic solution. Thus, the presence of Cr(VI) in the aquatic environment is a serious environmental concern because of its high toxic and non-degradable properties. The World Health Organization (WHO) recommended a maximum allowable concentration of 50 µg/L for Cr(VI) in drinking water. Moreover, as a consequence of its toxicity, Cr(VI) has also been categorized as a Group I human carcinogen by the International Agency for Research on Cancer (IARC). Therefore, finding an effective way for remediation of Cr(VI)-contaminated solutions is undoubted of high priority in the field of environmental and health protection.

This thesis focuses on synthesis, structural characterization and environmental applications of high-surface-area mesoscopic architectures composed of tightly connected ultrasmall spinel ferrite nanoparticles. In particular, we found that mesoporous spinel ferrite nanoparticle assemblies (MeFe₂O₄ or MeFO MNAs, Me=Zn, Mn, Ni, Cd and Co) can efficiently suppress electron-hole recombination, manifesting an exceptional activity and magnetic recyclability in photocatalytic reduction of aqueous Cr(VI). Revealed by transmission electron microscopy, N₂ physisorption, and X-ray scattering studies, the resulting materials, which were obtained through a block copolymer-assisted cross-linking aggregation of colloidal nanoparticles, show a 3D interconnected nanoporous structure with large internal surface and exhibit small grain composition (ca. 6-7 nm in size). In addition, a suitable combination of UV-visible/NIR diffuse reflectance spectroscopy and electrochemical impedance spectroscopy (EIS) studies indicated that the electronic band structure of these mesoporous materials fits the electronic requirements for both Cr(VI) reduction and water oxidation under UV and visible light irradiation. Among spinel ferrite nanocrystal assemblies, ZFO MNAs present the highest activity, readily operating without additional sacrificial reagents in photocatalytic detoxification of aqueous Cr(VI), which together with transient gas analysis and fluorescence spectroscopy results suggest a competitive formation of oxygen and hydroxyl radicals at the catalyst surface. These findings provide an essential tool for the delineation of the electronic structure-catalytic property relationship in spinel ferrite nanostructures offering intriguing possibilities for designing new nanoscale photocatalytic systems for efficient environmental pollution purification and energy conversion. Moreover, in an effort to further improve the photocatalytic performance of ZFO assemblies, we suggest the synthesis of binary mesoporous networks consisting of ZFO and MFO (x% MFO-ZFO MNAs, x = 4, 6.5, 8.5and 12.5 wt%) nanoparticles as promising catalysts for detoxification of Cr(VI) aqueous solutions. By tuning the chemical composition and electronic band structure of constituent nanocrystals, the 6.5 wt% MFO-loaded ZFO mesoporous catalyst impart outstanding photocatalytic Cr(VI) reduction activity in the presence of phenol. Mechanistic studies with UV–visible/NIR diffuse reflectance spectroscopy and electrochemical impedance spectroscopy indicate that the performance enhancement of this catalyst predominantly arise from the appropriate band edge positions for Cr(VI) reduction and phenol oxidation. The remarkable activity and durability of the 6.5% MFO-ZFO MNAs implies the great possibility of implementing these new composite catalysts into a realistic Cr(VI) detoxification of contaminated water.

Additional subject of the present research is the synthesis of mesoporous Mn_3O_4 nanoparticle assemblies and investigation of their catalytic activity in oxidation of various saturated and unsaturated hydrocarbons. The successful synthesis of this material highlights the general applicability of the proposed polymer-assisted aggregating self-assembly method to produce highsurface-area mesoporous networks of cross-linked metal oxide nanoparticles. The resulting material possesses a network structure of interconnected 6–7 nm-sized Mn_3O_4 nanoparticles and has a hight accessible surface area (ca. 90 m²/g) and uniform pores (ca. 6.6 in size). These assembled Mn_3O_4 networks demonstrate great potential for application in catalytic oxofunctionalization of various aromatic and cyclic alkenes as well as aryl alkanes with *tert*-butyl hydroperoxide as mild oxidant. Through comparative studies, the high catalytic activity and stability of these Mn_3O_4 assemblies arise from the unique 3D open-pore structure, large internal surface area and uniform mesopores.

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CHAPTER 1 INTRODUCTION TO POROUS SOLIDS

1.1 Porous solids

Porous materials, also called cellular solids, are solids containing in their structure cavities, channels or interstitial voids. Nanoporous materials with pores less than 100 nm have attracted a great deal of technological attention in the past two decades due to their wide range of applications in catalysis, absorption, molecular separation, chemical sensing and electronic and electrochemical devices. In order to describe a porous solid, we have to take into consideration its density, porosity, specific surface area and pore size distribution. Porosity of a material is defined as the ratio of the total pore volume to the apparent volume of the solid. The pore size of a porous material, for example, is an important morphological parameter that greatly affects its catalytic, absorption and gas separation efficiency. In general, the pore shape can be roughly approximated by any of the following three basic pore models [1], see Figure 1: a) cylindrical pores, having a circular cross section, b) ink-bottled pores, having a narrow neck and wide body, and c) slit-shaped pores with parallel plates. According to the size of pores and the International Union of Pure and Applied Chemistry (IUPAC) notation, porous materials are classified into macroporous materials, which have pore diameters of more than 50 nm, *mesoporous* materials, which have pore diameters between 2 nm and 50 nm, and *microporous* materials, which have pore diameters of less than 2 nm (Figure 2) [2].



Figure 1. Pore shapes, (a) cylindrical pores, (b) ink-bottled pores, and (c) slit-shaped pores.



Figure 2. Classification of porous materials according to the pore size.

The most important family of the microporous materials are the zeolites and metal-organic frameworks (MOFs), which have crystalline structure [3]. Shape-selective catalysis and absorption are one of the important functions of these materials which can be tuned by controlling their pore size and chemical composition of inorganic framework. The structural properties of zeolites, for example, enable these porous solids to have ion exchange capabilities and high catalytic functionality [4]. Additionally, the hydrophilic and hydrophobic character of the inorganic zeolitic structure give to these materials the property of being adsorbents for specific organic molecules. However, the small pore size of zeolite materials and microporous crystalline metal-organic frameworks greatly limit their applications. The dimensions and accessibility of pores are limited to sub-nanometer scale and this situation restricts the applicability of these pore structures to only small molecules. To this end, ordered mesoporous materials, which have arisen from the efforts to obtain materials with larger pores than the microporous channels of zeolites, have been synthesized. Specifically, in the early of 90s, Mobil company scientists reported the first ordered and open-framework mesoporous material [5, 6]. The synthesis has been carried out by using cationic surfactants, i.e., cethyltrimethyl ammonium bromide (CTAB), as a template to obtain highly ordered mesoporous silica molecular sieves under hydrothermal basic conditions [7]. This kind of material extends the uniform pore sizes from the range of micropores to mesopores. This new family of materials also initiated the concepts of templating and tuning the pore structure that provide convenience for modification [4, 8]. The first example of mesoporous materials (M41S)

is a two-dimensional (2D) porous structure. In particular, the MCM-41 silicate material has a 2D hexagonal pore structure (**Figure 3**) with uniform pores that may be tuned from ~1.6 nm to 10 nm and exhibits large surface area of above 1000 m²/g and a total pore volume of 0.8–1.0 cm³/g. The MCM-41 is, however, unstable in moisture and temperature due to its thin pore walls, compromising its potential application in catalysis, gas storage and molecular separation [4, 9]. Subsequently, other mesoporous silicas were prepared as well, including the bicontinuous cubic MCM-48 and lamellar MCM-50 [10]. In 1998 a new mesoporous silica SBA-15 was reported using a block copolymer as template [11]. It has the same mesopore symmetry (P6m) as MCM-41, but with larger pores (~ 8 nm in diameter) and thicker pore walls (~3 nm). Unlike MCM-41, SBA-15 exhibits disordered micropore channels in the walls resulting from polymer template embedded in the silica walls during the self-assembly process [12, 13].



Figure 3. Members of the M41S family: MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar with the presence of surfactant molecules between lamellae) [14].

After the discovery of M41S and related solids, an increasing number of research teams has focused on understanding of their formation mechanisms. Scientists have postulated that the formation of these molecular sieve materials is based on the concept of structural directing agent or template. The mesostructure of M41S materials depends greatly on the surfactant concentration and hydrophobic chain length as well as the presence of organic swelling agents dissolved in the hydrophobic spaces. Surfactants are usually organic molecules and have amphiphilic character; they consist of a polar head group and a non-polar hydrocarbon chain in their structure. Because

of this, the surfactant molecules are soluble in organic solvents and water [15, 16]. The amphiphilic properties of surfactants enforce micellization in aqueous media above a critical concentration, known as critical micelle concentration (CMC). The micelles form, in water, by hiding the hydrophobic tails as a core and exposing the hydrophilic head groups outside, forming a core-shell hydrophobic/hydrophilic structure. The interaction between inorganic species and organic molecules includes electrostatic interactions, hydrogen and dative bonding interactions or may be mediated by countercharged ions. The surfactants used in synthesis can be either cationic, anionic, or non-anionic, depending on the charge of inorganic species [17]. The type of surfactant molecules and their concentration and the solution temperature and pH play significant role on the shape and size of micelles. By controlling these parameters, the properties of the micelle, and thus the geometry of inorganic-organic mesostructure, can be readily modified [18, 19].

However, siliceous mesoporous materials possess very low acidity due to the silanol groups and lack of crystallinity in their Al-doped counterparts. Although great process has been made, it is still not easy to apply this method to the preparation of non-silicate mesoporous materials, such as mesoporous transition metal oxides and metal chalcogenides [20, 21]. Mesoporous transition metal oxides have interesting properties owing to their d-shell electrons confined to nanosized pore walls; this feature, for example, allows electron transfer to occur between the reactants and active sites during a given catalytic reaction [22, 23]. Furthermore, they possess a highly redox active surface and a 3D connected pore network arising from template. With these attributes they exhibit many interesting properties in light energy conversion and storage, (photo)catalysis, adsorption, separation, sensing, and magnetic devices [22, 24-27]. A series of transitional metal oxides have now been prepared, including Cr_2O_3 [28], CeO_2 [29], NiO [30], In_2O_3 [31], Fe_3O_4 [32], Co_3O_4 [33], Mn_3O_4 [34], WO_3 [35] etc.

So far, two main synthetic strategies has been established, which are effective in the synthesis of mesoporous structures, these are the *liquid-crystal templating process* and cooperative *self-assembly process*, see **Figure 4** [6, 17]. According to *liquid crystal templating* (LCT) mechanism, the composite mesophase is suggested to be formed by the condensation of inorganic species (by a sol-gel process) around a preformed surfactant array through columbic or other type of interactions. Next the randomly ordered composite species spontaneously pack into a highly ordered mesoscopic phase with an energetically favorable hexagonal or cubic arrangement. This process initiates the hexagonal or cubic ordering in both the surfactant molecules and the final

product as shown in **Figure 4b**. The *cooperative self-assembly* is based on the simultaneous interactions between the surfactant micelles and inorganic species. After polymerization and condensation of inorganic components, the ordered mesostructured inorganic–organic composite structure is eventually formed (**Figure 4a**). Finally, in both (a) and (b) pathways, after removal of templates by solvent extraction or calcination, the mesoporous solids with ordered mesochannels can be obtained.



Figure 4. Formation of mesoporous structures via (A) co-operative self-assembly and (B) via true liquid–crystal templating process [17].

1.2 Templated self-assembly of colloidal nanocrystals into 3D mesoscopic structures

Nanocrystals (NCs) are tiny crystals of metals, metal oxides, semiconductors or magnetic materials consisting of hundreds to a few thousand atoms each. Their size ranges from 2–3 nm to about 50 nm. NCs have a wide variety of potential applications in various technological fields ranging from catalysis and photovoltaic cells to optoelectronic and spintronic devices, due to their size and shape-dependent electronic and optical properties, potentially inexpensive fabrication

process and excellent chemical processability. Over the years, the synthesis of colloidal NCs has evolved to a point that a fine level of control over size, shape, crystallinity, and compositional parameters has finally become possible for many materials systems [36, 37]. Semiconductor materials are particularly useful for photocatalytic processes because of a favorable combination of electronic band structure, light adsorption properties, charge transport characteristics and lifetime of excited states [38]. For instance, the widening of energy bandgap and size-dependent luminescence emission are intrinsic characteristics of semiconductor NCs. Bandgap tuning results in a significant alteration in semiconductor NCs properties, which makes them very important candidates for optoelectronic devices and photocatalysis. As an example, a variety of semiconductor NCs have been proven exceptionally efficient in photocatalytic water splitting applications due to their suitable bandgap and band edge positions.



Figure 5. Schematic of stabilization mechanisms for nanofluids: (A) electrostatic stabilization, (B) steric stabilization, and (C, D) electrosteric stabilization [39].

Despite their predominant properties, individual NCs, however, face several limitations for practical use, especially in catalysis and absorption. A major drawback of isolated NCs is that due to their high surface area and strong attractive interactions between particles, they often tend to agglomerate into larger particles especially during annealing conditions or catalytic processes. The synthesis of colloidal NCs requires the choice of precursor metal salts, reducing agent (usually for synthesis of metal nanoparticles), capping agent (ligand) and solvent to determine the conditions

for the controlled growth of NCs to the desired shape and size. In order to prevent excessive growth by coalescence and/or aggregation, we can utilize certain stabilizing agents like organic ligands since they often remain adsorbed on the NC's surface. Depending on the capping ligand, NCs may be stabilized due to steric or electrostatic interactions (see **Figure 5**), leading to hydrophobic or hydrophilic end-groups that will define in which solvent they will form a stable colloidal solution [39].

Prerequisite for every possible application is the proper surface functionalization of NCs; the functionality of the end-linking agents can determine the interactions of NCs with the environment. Specifically, these interactions may affect the colloidal stability of the particles and may result to a controlled assembly NCs into well-defined architectures with desired complexity and functionality. In order to achieve a continuous network of connected NCs with open pore structure and large internal surface, they have to undergo appropriate surface functionalization. However, several conventional methods have been proved to be ineffective for the construction of porous NC assemblies, since they rely on the weak interparticle interactions (e.g., through hydrogen bonding and van der Waals forces); such weak interactions greatly limit the control over the spatial arrangement of the NCs [40]. In such cases, the resulting NC assemblies are microporous materials with limited mesoporosity. Moreover, due to the strong tendency of NCs to agglomerate, NC aggregates are usually obtained either as close-packed superlattices or random agglomerates with irregular morphology and negligible porosity [41, 42]. Therefore, developing synthetic approaches for the integration of individual NCs into 3D porous structures is an ongoing challenge.

For the synthesis of nanoporous NC assemblies, initially the ligand molecules have to be bound to the particle surface by some attractive interactions most commonly provided by the head group of ligand molecule [43]. By utilizing different kinds of chemically active head groups, such as carboxylic acid, or by introducing other molecules of interest, we can provide several chemical functionalities to the NCs' surface. Depending on the different types of surface ligands [44] (polar, charged or apolar), NCs can be either dispersed in hydrophilic (ethanol, water etc) or hydrophobic (hexane, chloroform, toluene etc) solvents. Therefore, certain amphiphilic ligand molecules, e.g., poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), and NCs capped with these or other ligand molecules can be soluble in a number of solvents with different polarity. Furthermore, the surface ligands contribute to the interparticle interactions and determine the spacing between neighboring NCs in short- and long range ordered NC assemblies [44]. Our group

has recently developed a method to assemble mesoporous networks of connected bismuth ferrite (BiFeO₃) NCs as building blocks (**Figure 6**) [45]. In particular, mesoporous assemblies of BiFeO₃ NCs (denoted as MBFAs) were realized by first surface modification of individual BiFeO₃ nanoparticles with 3-aminopropanoic acid (3-APA) and then using a templated assembly of these nanoparticle colloids in the presence of surfactant aggregates. The specific advantage of using 3-APA as a surface ligand is that its carboxyl (–CO₂H) group can coordinate to the nanoparticle surface, while the amine (–NH₂) end group can prevent nanoparticle aggregation and stabilize the colloidal solution. In addition, the –NH₂ functional group is expected to interact with the polar fragment of the surfactant during the assembly process. Because of the small size, 3-APA could also enable direct NC–NC interactions upon ligand removal at the growth temperature, yielding tightly interconnected NC-based networks. This method offers several advantages, such as a relatively low cost, as well as increased control over pore size, chemical composition and porosity of the assembled structures. In addition, the resulting materials exhibit characteristics that are highly advantageous for catalysis, such as large and accessible pore surface area, tunable visible light response and small grain composition.



Figure 6. Schematic illustration showing possible reaction routes for the formation of mesoporous BiFeO₃ nanoparticle assemblies (MBFAs).

Another approach to modify the surfaces of NCs is to replace the pre-existing long organic ligands with smaller molecules. The most common class of surface ligands used for synthesis of NCs is represented by molecules having a head group with high affinity to the NC surface and an aliphatic tail that provides sterical stabilization of the colloidal solution in nonpolar solvents such as hexane, toluene etc [44]. Oleic acid, trioctylphosphine oxide (TOPO), dodecanethiol, oleylamine, hexadecylamine, and phosphonic acids are examples of the most frequently used

surface ligands [46]. However, the presence of such bulky capping molecules creates an insulating barrier around each NC and blocks the access of molecular species to the NC surface, which are detrimental for electronic [47, 48] and catalytic [49] applications as well as for templated NC assembly processes. These problems can be addressed by utilizing a ligand-exchange method, where the original ligands are replaced with specifically target species which could be used for carrier transport and conjugation with other molecules and surfaces. Nitrosonium tetrafluoroborate (NOBF₄) or diazonium tetrafluoroborate salts are usually employed to replace the native ligands and stabilize the NCs in various polar solvents, such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), water and acetonitrile. This exchange process gives ligand-stripped NCs with open coordination sites (cationic sites) at their surface, which are charge-stabilized by BF_4^- ions [46]. Based on the ligand-exchange process by NOBF₄, our group has recently reported the synthesis of new mesoporous CoO materials isolated from the polymer-assisted cross-linking polymerization of CoO NCs, and demonstrated for the first time the application of these single-component assemblies in photocatalytic reduction of aqueous Cr(VI) under UV and visible light irradiation (**Figure 7**) [50].



Figure 7. Surface modification of NCs by NOBF₄ treatment [46]. In this case, the NCs are transferred from toluene to the DMF phase accompanied by the binding of the BF_4^- ions to the NC surface.

1.3 Oxidation of alkenes and aryl alkenes

Oxidation reactions are among the most elementary of organic transformations and are essential in chemical industry. Olefinic hydrocarbons, which are main constituents of oil and natural gas,

are excellent feedstocks for chemical industry. Catalytic oxo-functionalization of aromatic and aliphatic alkenes towards the production of more valuable products, such as alcohols, ketones, acids and peroxides, is one of the most important transformations in organic chemistry [51]. Aldehydes and ketones, that is, the oxidized products of alcohols are used largely not only in perfumes and dye industries but also in a wide number of other chemical industries, such as rubber and polymer, pharmaceutical and agrochemical industry. Selective oxidation of olefins, for example styrene, is an important chemical reaction as the products of this reaction (epoxide and aldehyde) can be used as starting materials for the manufacture of plasticizers, perfumes and pharmaceuticals. Also, styrene oxide is mainly used in the epoxy resins industry as a plasticizer and as a raw material for phenethyl alcohol and styrene glycol synthesis. It is also used as a chemical intermediate for cosmetics, surface coatings, treatment of fibers and textiles, and agricultural and biological chemicals and is, therefore, an important product for pharmaceutical and fine chemical synthesis [52]. Currently, epoxides are conventionally prepared by the epoxidation of alkenes with organic peracid as oxidant, which is unsafe and generate a large quantity of waste with a heavy environmental burden with respect to its disposal [53]. Therefore, it is important to selectively oxidize styrene to styrene oxide or epoxide products with an ecofriendly and cost-effective route, while achieving high styrene conversion. In this regard, significant advancements have been made in the use of solid, recyclable catalysts, in respect of environmental friendly conditions using molecular oxygen or hydrogen peroxides as mild oxidants [54-56]. The use of solid catalysts offers several advantages over homogeneous systems, including catalyst recovery and controlled regio- and chemo-selective transformations [57]. So far, although a diverse range of supported transition-metal oxides, such as CuO, ZnO, CeO₂, Fe₂O₃ and WO₃, [58-62] metal nanoparticles, such as Pd and Ru, [63, 64] and polyoxometalate clusters, such as $[W_{10}O_{32}]^{4-}$, $[Mn_2ZnW(ZnW_9O_{34})_2]^{10-}$ and $[XW_{12}O_{40}]^{n-}$ (X = P, Si), [65-68] have been applied to these reactions, the selective oxidation of olefins with high associated product yield still remains a challenge.

Manganese oxides, especially Mn_3O_4 , have attracted particular attention in catalysis because of their intriguing oxidation–reduction (redox) properties and excellent chemical stability. As a result, in recent years, a number of Mn_3O_4 -containing materials have been successfully used in various catalytic applications, including degradation of phenols [69, 70], reduction of nitrobenzenes [71], and oxidation of arenes [72], alcohols [73, 74] and alkyl-substituted alkenes [75, 76]. In addition,

hausmannite Mn₃O₄ has received a considerable interest as electrode material for lithium-ion batteries and supercapacitors owing to its low cost, good electrochemical performance, and most importantly excellent cycling stability even at high current rates [77, 78]. Earlier studies have shown that Mn₃O₄ nanostructures with a large number of exposed catalytically active sites, such as nanoparticles, nanorods and nanosheets, are particularly effective for a variety of redox reactions. For example, these materials displayed exemplary activity in oxidation of volatile organic compounds (VOCs) [79], such as benzene, toluene and o-xylene, and electrocatalytic reduction of oxygen [80]. In principle, small-sized Mn₃O₄ nanoparticles and one dimensional (1D) nanorods might exhibit distinctive functionalities owing to the high reactivity, large exposed surface area and adequate interactions between the active sites and reactants, portending great potentials for use in future catalytic applications [69, 81]. However, despite these promising advances, thermodynamic factors favour the excessive agglomeration of such nanomaterials in large close-packed superstructures (e.g., bulk-like structures and densely packed nanoparticle aggregates) with irregular shape and low porosity. Consequently, the integration of these nanoscale building blocks into high surface-to-volume ratio architectures with internal porosity is a promising approach to address these limitations [41, 82-85].

Our group recently demonstrated the synthesis of ordered mesoporous iron oxide architectures using ligand-stripped γ -Fe₂O₃ NCs as primary building blocks [40, 86]. For the construction of these materials, the NOBF₄ salt was utilized to gently strip the native ligands (oleyl alcohol) from the surface of γ -Fe₂O₃ nanoparticles and charge stabilized them by BF₄⁻ anions. This procedure was necessary to obtain ligand-free nanoparticles that preferentially segregate to the polar domains of the polymer template (through electrostatic or hydrogen-bonding interactions) during synthesis. Thermal annealing is then used to decompose the polymer and fuse the nanoparticles into a rigid mesoporous network. As a result of the accessible pore channels and large surface area, mesoporous γ -Fe₂O₃ NC assemblies have been shown to be highly effective for reduction of nitroarenes into the corresponding aryl amines and oximes, using methylhydrazine or hydrazine as reducing agents [86].

1.4 Heterogeneous photocatalysis

Photocatalysis is a promising method in the field of green technology, which can be used for

various purposes like degradation of various organic pollutants in wastewater, production of hydrogen, purification of air, and antibacterial activity. When compared with other methods, photocatalysis is rapidly growing and gaining more attention from the researchers due to following advantages [87]: (i) Photocatalysis offers a good substitute for energy-intensive conventional methods with the capacity for using renewable and pollution-free solar energy. (ii) Unlike conventional treatment measures, which transfer pollutants from one medium to another, photocatalysis leads to the formation of innocuous products. (iii) This process can be used to decompose a variety of hazardous compounds in different wastewater streams. (iv) It can be applied to aqueous and gaseous-phase treatments, as well as solid-phase treatments to some extent. (v) The reaction conditions for photocatalysis are mild, the reaction time is modest, and a lesser chemical input is required. (vi) Secondary waste generation is minimal. (vii) The option for recovery can also be explored for metals, which are converted to their less-toxic/nontoxic metallic states. Summing up all these benefits and advantages, heterogeneous photocatalysis provides a cheap and effective alternative to clean water production, environmental remediation, fine organic synthesis and energy conversion applications. However, charge recombination is believed to be a major loss of the excited charge carriers and a critical factor that limits the solar-to-chemical energy conversion efficiency for semiconductor photocatalysts. The photocatalytic activity of semiconductors greatly depends on the effective charge carrier separation and suppression of electron-hole recombination. These are essential factors for enhancing the efficiency of the photocatalytic process.

During the photocatalytic process, the illumination of a semiconductor photocatalyst with ultraviolet (UV) and/or visible light radiation activates the catalyst. The valence band (VB) is the band made up of the completely occupied molecular orbital, low in energy. On the other hand, the conduction band (CB) is the band of the molecular orbital that are high in energy, sufficient to accept electrons and make them free to move throughout the structure under the influence of applied energy. The energy difference between the valence and conduction bands is called the band gap (E_g). As depicted in **Figure 8**, the semiconductor photocatalyst absorbs photons with energies equal to or higher than its band gap. This process creates an electronic vacancy or hole (h^+) at the valence band and a photogenerated electron (e^-) in the conduction band edge of the semiconductor.



Figure 8. Schematic diagram of semiconductor photocatalysis.

1.5 Electronic structure of semiconductor photocatalysts

The electrons of a single, isolated atom occupy atomic orbitals each of which has a discrete energy level. When two or more atoms join together to form into a molecule, their atomic orbitals overlap. So, if two identical atoms combine to form a diatomic molecule, each atomic orbital split into two molecular orbitals of different energy, allowing the electrons to occupy the new orbital structure. The Pauli exclusion principle dictates that no two electrons can have the same quantum numbers in a molecular orbital. When molecular orbitals are formed from N atoms, atomic orbital combined to form N molecular orbitals. In solids, N is very large (N ~ 10^{22}), resulting in a large number of orbitals. The overlap of a large number of orbitals leads to closely spaced (of the order of 10^{-22} eV) molecular orbitals. The energy band. **Figure 9** shows the change of the electronic structure of a semiconductor compound as the number N of monomeric units present increases from unity to clusters of more than 2000 units [88].



Figure 9. Change of the electronic structure of a semiconductor compound as the number N of monomeric units present increases from unity to clusters of more than 2000 units [88].

1.6 Basic principle of photocatalysis

The first step in the heterogeneous photocatalysis of organic and inorganic compounds is the interaction of semiconductor with light which results in the generation of electron-hole pairs in the semiconductor structure. Photoexcitation of the semiconductor particles creates mobile electrons and holes (free excitons) in the CB and VB, creating pathways as depicted in **Figure 10** [89]. In particular, two disadvantageous recombination processes, i.e., photogenerated electrons and holes are recombine on the surface (pathway A) or in the bulk (pathway B) structure of the semiconductor within a few nanoseconds, can be realized deteriorating the photocatalytic activity [90]. Simultaneously, the photogenerated electrons and holes can be transferred to the semiconductor surface by spontaneous migration. The photogenerated electrons/holes can further transfer to organic or inorganic species or the solvent molecules, which are pre-adsorbed on the semiconductor surface [91]. While the semiconductor can donate electrons to reduce an electron

acceptor (pathway C), a hole can migrate to the surface and oxidize an electron donor (pathway D) [92]. Thereby, subsequent anodic and cathodic redox reactions can be initiated. These constitute the basic principle of semiconductor based photocatalysis toward light energy conversion.



Figure 10. Schematic photoexcitation in a semiconductor photocatalyst followed by deexcitation pathways [89].

Fundamentally, the overall efficiency of a semiconductor is dictated by three key intrinsic characteristics [93]: (i) the energy difference between the conduction band minimum (E_{CB}) and valence band maximum (E_{VB}), that is, the band gap, (ii) the absolute potentials of the E_{CB} and E_{VB} (i.e., the band position), and (iii) the dynamics of the photogenerated electrons and holes, such as diffusion length, mobility, lifetime, rate of surface charge recombination, and interfacial charge transfer. The band gap limits the portion of the solar spectrum that can be utilized to activate the semiconductor; for example, semiconductors with $E_g > 3.0$ eV are only responsive toward UV light, whereas those with smaller band gaps are favorable for more proficient solar energy harvesting. Another crucial parameter is the knowledge of the band positions or flat band potentials. The potential of the band edges indicates the thermodynamic limitations for the photoreactions that can be carried out with the charge carriers. The energy level at the bottom of the CB is actually the reduction potential of photoelectrons and the energy level at the top of the

VB determines the oxidizing ability of photogenerated holes; these values reflect the ability of the system to promote reductions and oxidations, respectively. From a thermodynamic point of view, adsorbed couples can be reduced photocatalytically by CB electrons if they have redox potentials more positive than the potential of the CB and can be oxidized by VB holes if they have redox potentials more negative than the potential of the VB. The flat band potential (E_{FB}), which is the result of the surface exchange equilibria of the material, dictates the energy of the two charge carriers at the solid/liquid interface. Therefore, the ability of a semiconductor to undergo charge carrier transfer to adsorbed species on its surface is determined by the energy levels of the CB (reduction) and VB (oxidation) edges. Based on the above, we can conclude that knowledge of flat band potentials or band positions is very useful since they serve as an indicator of the thermodynamic limitations for the photoreactions. Among the semiconductors shown in **Figure 11**, some oxides and chalcogenides have enough band gap energies to be excited by UV or visible light and the redox potentials of their VB and CB edges can promote a series of oxidative and reductive reaction.



Figure 11: Band position of commonly used semiconductors in aqueous electrolyte at pH = 0 [94].

Based on the energy band structure, we can now understand the differences among semiconductors, insulators, and conductors. A semiconductor has a nearly filled valence band and a nearly empty conduction band separated by a band gap as illustrated in **Figure 12**. The band diagram of an insulator is similar to that of a semiconductor except for a larger E_g (more than 4

eV), which separates a completely filled band and a completely empty band (see **Figure 12**). Totally filled bands and totally empty bands do not contribute to current conduction, just as there can be no motion of electrons. A conductor has a quite different energy band diagram. As depicted, a conductor has a partially filled band. Hence, the electrons can access empty levels within the CB and move freely across all atoms of the solid. The abundance of the conduction electrons makes the resistivity of a typical conductor much lower than that of a semiconductor and insulator. In a semiconductor, some electrons can jump to the empty CB by thermal or optical excitation. Basically, the Fermi level represents the average work done to remove an electron from the material (work function). In other words, levels below this value tend to be filled with electrons and levels above tend to be empty. If the Fermi level lies within a band, the material will be good conductor. On the other hand, if the Fermi level is between two widely separated bands, the material will be a good insulator. If the Fermi level is between bands that are relatively close, the material is a semiconductor.



Figure 12: Energy band diagrams for a (a) semiconductor, (b) insulator and (c) conductor material.

1.7 Wastewater treatment

Water is the most precious natural resource in the world embracing over 70% of the earth surface. The rapid development of civilization and industrial activities has led to a series of environmental problems. Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries [95]. Since they are non-biodegradable and can accumulate in living tissues cause various diseases and disorders [96]. The removal of toxic metals in an effective and economic way has been a critical issue for environment improvement and health protection. An ideal water treatment process should have the capability to mineralize all the toxic organic and inorganic components completely without leaving behind any harmful byproducts. The main techniques which have been utilized to reduce the heavy metal ion content of effluents include chemical precipitation, ion-exchange, adsorption and electrolytic reduction [96]. However, these methods have been found to be limited since they often involve high operational costs and may also be associated with the generation of secondary wastes which present treatment problems, such as the large quantity of sludges generated by precipitation processes. The choice of the proper treatment process depends on the nature of the pollutants present in water, and on the allowable contamination level in the treated water.

1.8 Hexavalent chromium

Currently, contamination of natural water sources with hexavalent chromium, Cr(VI), arising from various industrial activities such as electroplating, metal finishing, and pigments, is an essential issue in environmental remediation field [97]. Cr(VI) is a mutagenic primer and pulmonary carcinogen for living organisms, with an LD50 (lethal dose 50%) value of 50 mg/kg [98], which readily invade the human food chains [99]. To this end, the World Health Organization (WHO) recommended a maximum allowable concentration of 50 μ g/L for Cr(VI) in drinking water [100]. Moreover, as a consequence of its high toxicity, Cr(VI) has also been categorized as a Group I human carcinogen by the International Agency for Research on Cancer (IARC) [101]. In aquatic environments, chromium exists mostly in the hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) states [102]. Anionic Cr(VI) is far more mobile and toxic than Cr(III) and more difficult to remove from water. Similar to many other metal ions, however, aqueous Cr(III) can be readily precipitated as $Cr(OH)_3$ or Cr_2O_3 in alkaline solutions or can be removed by adsorption and ion exchange. Therefore, finding an effective way for remediation of Cr(VI)-contaminated solutions is undoubted of high priority in the field of environmental and health protection.

Towards this goal, semiconductor photocatalysis constitutes an intriguing technology to attain low-cost sustainable detoxification of Cr(VI) aqueous solutions using just the sunlight as an energy source. In this process, Cr(VI) oxyanions, such as monovalent HCrO₄⁻ and divalent CrO₄²⁻, will be reduced to the less toxic Cr(III) cations by photoexcited electrons over a light-irradiated semiconductor catalyst. Simultaneously, the photogenerated holes on the surface of catalysts will be consumed in oxidation reactions. So far, a diverse set of semiconductor materials have been explored as Cr(VI) reduction photocatalysts, including ZnO [87], TiO₂ [103], CdS [104], WO₃ [87] and SnS_2 [105]. Although promising, studies on these systems, however, signifies the high recombination rate of photoexcited electron-hole pairs, low visible-light absorption in wide gap semiconductors and poor cyclic stability (e.g., metal sulfide catalysts are susceptible to photocorrosion) as critical challenges to be addressed for practical applications. To increase the efficiency of photoreactions, recent efforts took advantage from the modification of the semiconductor band structure by forming Schottky junctions with a narrow-bandgap semiconductor or a noble metal cocatalyst. In particular, these supplemental components can improve the charge-transfer separation processes within the semiconductor particles by acting as electron or hole collectors (through a band-edge potential gradient) [106, 107]. Noble metal nanoparticles could also provide access to redox pathways with low overpotential, thus further contributing to the high photocatalytic performance. Meanwhile, since most of the visible-light semiconductors have a VB edge potential well above the water oxidation level, thermodynamic constraints may impede Cr(VI) photoreduction without the aid of suitable hole scavengers. Thus, several studies make use of sacrificial reagents, such as ethylenediaminetetraacetate (EDTA), ascorbic acid and ammonium compounds, to provoke Cr(VI) photocatalysis [108]. Since oxidation of these organic compounds is thermodynamically more favorable than water oxidation reaction, this process may overcome the competitive four-electron conversion of water to dioxygen [2H₂O

 \rightarrow O₂ + 4H⁺ + 4e⁻] and eventually enhance the kinetics of the Cr(VI) reduction [109]. Even though the hybridization of semiconductor structure or introduction of electron donor additives in the solution would exert efficient photocatalysis, these processes can impart an additional cost for the fabrication and operation of catalysts, which is a critical issue. Thus, it is highly desirable to develop a photocatalyst to achieve high Cr(VI) reduction efficiency at low cost, using the sunlight.

 $Spinel \ ferrite \ oxides \ (MeFe_2O_4, where \ Me \ is \ a \ divalent \ metal \ ion \ such \ as \ Mn^{2+}, \ Co^{2+}, \ Fe^{2+}, \ Ni^{2+}, \ Ni^{2+},$ Zn^{2+} , etc.), due to their unique electronic and magnetic properties, are considered as a class of very promising materials for various technological applications. They have demonstrated great promise for applications in high-density magnetic storage devices, Li-ion batteries, electrochemical capacitors and absorption of toxic metals (e.g., As(III), Pb(II), Hg(II)) because of their excellent redox behavior, high chemical stability (especially in acidic media), room temperature superparamagnetic or ferromagnetic activity, and large saturation magnetization (more than 50 emu g⁻¹) [110-116]. More recently, spinel ferrites, especially zinc ferrite (ZnFe₂O₄, ZFO), have generated increasing interest as promising photocatalysts due to their narrow band gap ($E_g \sim 1.9$ -2.0 eV), favorable conduction band alignment for water splitting, good photochemical stability, low cost and easy magnetic separation [117-119]. As a consequence, ZFO based materials have been exploited for photo-Fenton-like degradation of organic dyes [120-122] and photochemical hydrogen production [123]. Unfortunately, inherent problems of ZFO such as short hole diffusion length (ca. 10 nm), thus rapid recombination of photoexcited charges (electron-hole pairs), and low absorption coefficient still persist serious problems for its potential use in photocatalysis and energy conversion [124-126]. To address these limitations, the design and synthesis of spinel ferrite materials at the nanoscale featuring a large solid/liquid interface constitutes an efficient way. In principle, a semiconductor catalyst with small grain size composition can minimize the distance for photogenerated charges to transfer to the surface, and thereby to increase the separation efficiency of the free electron-hole pairs. On the other hand, since the optical absorption in most semiconductor materials (like metal ferrites) declines rapidly within about 15–20 nm, small-sized particles can absorb photons near the surface region and, thereby, facilitate charge separation at the catalyst/electrolyte interface. This means that a significant fraction of the photogenerated excitons would be available for redox reactions.

1.9 Thesis statement and contributions

The rapid development of civilization and industrial activities has led to a series of environmental problems. For decades, large amount of pollutants has been discharged into the environment intentionally or accidentally, including toxic metals in water with a great health concern. Different from the organic components, toxic metallic ions such as Cr(VI) generally are not degradable and have an infinite lifetime, thus they may be accumulated in living tissues, causing various diseases and environmental problems. The conventional approach for the reduction or removal of Cr(VI) includes electrochemical precipitation, adsorption, bacterial reduction and ion exchange processes. Compared to the above methods, photocatalytic reactions are considered a clean and promising technology owing to its highly efficient photoreduction of Cr(VI) to the less harmful Cr(III).

The scope of this doctoral dissertation is to produce a series of mesoporous architectures of spinel ferrite (MeFe₂O₄ or MeFO, Me=Zn, Mn, Ni, Cd and Co) NCs and to investigate their photocatalytic activity for detoxification of aqueous Cr(VI) solutions under UV and visible light illumination . In particular, we used different spinel ferrite nanobuilding blocks to construct openpore network structures of connected NCs with large internal surface area and uniform mesopores. The synthesis of these materials was accomplished using a block copolymer-assisted cross-linking aggregation of colloidal nanoparticles, followed by thermal decomposition of the organic components. Systematic studies were conducted to elucidate the effect of morphology, electronic band structure and electrochemical properties of metal ferrite nanostructures on the Cr(VI) photoconversion efficiency. The photocatalytic reduction property of metal ferrites, especially Cr(VI) reduction, is rarely investigated. Herein, it is shown that mesoporous zinc ferrite (ZnFe₂O₄) assemblies, due to their unique three-dimensional (3D) porous structure, improved charge transfer along the NC-linked framework and proper matching of band-edge positions with respect to the Cr(VI) reduction and water oxidation potentials, exert outstanding performance in photocatalytic detoxification of Cr(VI). Furthermore, a possible mechanism for the overall photoreduction reaction of Cr(VI) is presented by performing controlled experiments of fluorescence spectroscopy and oxygen evolution reaction coupled with mass spectrometry. The results demonstrate spinel ferrite NC assemblies as a highly efficient and stable photocatalytic system for solar light-driven environmental pollution purification and energy conversion.

An advantage of the proposed synthetic route is that it allows the construction of extended 3D porous networks from metal oxide NCs as building blocks in contrast to the preparation of isolated nanoparticles and nanorods and close-packed thin films [127, 128]. To demonstrate the general applicability of our synthetic strategy, we produce mesoscopic assemblies of well-defined metal oxide nanoparticles for practical use in catalysis. Specifically, in this study, we present the synthesis of a new mesoporous network consisting of interconnected Mn₃O₄ NCs through a polymer-assisted self-assembly method and demonstrate its high activity for the catalytic oxofunctionalization of aliphatic and aromatic alkenes as well as aryl alkanes using *tert*-butyl hydroperoxide as a mild oxidant. The resulting material possesses a network structure of interconnected 6-7 nm-sized Mn₃O₄ nanoparticles and shows highly accessible surface area and narrow pore-size distribution. We show that, compared to other morphologies of Mn_3O_4 such as bulk microparticles, individual nanoparticles and random nanoparticle aggregates, mesoporous assemblies of Mn₃O₄ NCs have the potential to provide more exposed active sites between the nanoparticles, leading to improved catalytic performance. Furthermore, we demonstrate that although these Mn₃O₄-catalyzed reactions proceed under mild conditions, they are particularly selective towards saturated and unsaturated carbonyl compounds [83].

CHAPTER 2 EXPERIMENTAL SECTION

2.1 Synthesis of spinel ferrite NCs

Spinel ferrite (MeFe₂O₄ of MeFO, Me=Zn, Mn, Ni, Cd and Co) NCs with an average diameter of 6-7 nm were prepared according to a modified literature procedure [129]. For a typical synthesis of ZFO NCs, Zn(NO₃)₂·6H₂O (5 mmol) and Fe(NO₃)₃·9H₂O (10 mmol) were dissolved in 25 mL of deionized (DI) water at room temperature, forming a clear solution. Next, 25 mL of 0.4 M sodium dodecylbenzenesulfonate (NaDBS) aqueous solution and 500 mL of toluene were added under vigorous stirring, and the resulting turbid solution was left overnight at room temperature, giving a clear solution. After that, 40 mL of 1 M NaOH aqueous solution was added dropwise to the above solution, which was stirred for another 2 hours. Concentrated solution with suspended colloids was obtained by distilling out water and most of the toluene solvent, which then washed with water and ethanol several times to remove excess of surfactant. Subsequently, the product was isolated by centrifugation and then annealed under a nitrogen atmosphere at 350 °C for 12 hours. The other spinel ferrite nanoparticles, MnFe₂O₄ (MFO), NiFe₂O₄ (NFO), CdFe₂O₄ (CdFO) and CoFe₂O₄ (CoFO), were synthesized in a similar procedure, using the corresponding metal nitrate precursor (i.e., Mn(NO₃)₂·4H₂O, Ni(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O and Co(NO₃)₂·6H₂O for MFO, NFO, CdFO and CoFO respectively).

2.2 Preparation of colloidal metal ferrite NCs

The surface of spinel ferrite NCs was modified with 3-aminopropanoic acid (3-APA) according to a previously reported method [45]. Briefly, as-made MeFO NCs (230 mg) were added in 4 mL of DI water containing 3-APA (45 mg), and the pH of the solution was adjusted to 4.0 with 2 M HCl. The resulting mixture was then vigorously stirred at room temperature to assure that NCs will transfer to the liquid phase and form a stable suspension, typically within 24 hours. The dispersion was initially assisted with sonication for about 20 min. The 3-APA-capped spinel ferrite NCs were

isolated by centrifugation, rinsed several times with DI water, and finally dispersed in ethanol to form a stable colloidal solution of 120 mg/mL.

2.3 Synthesis of mesoporous spinel ferrite NC assemblies

The mesoporous spinel ferrite NC assemblies (MeFO MNAs) were synthesized as follows: 0.2 g of Pluronic P123 (EO₇₀PO₂₀EO₇₀) block copolymer was dissolved in 1 mL of anhydrous ethanol at room temperature. Then, 1 mL of colloidal MeFO NCs solution (120 mg/mL) was slowly added to the surfactant solution under continuous stirring. The resulting mixture was kept at room temperature for 2 hours and then stored in an oven at 40 °C for about 2–3 days under static condition. Mesoporous solids were prepared by heating the dry product in air for 4 hours at 350 °C, using a 0.5 °C/min heating rate. For comparison, untemplated ZFO material was also prepared by a similar procedure without the addition of polymer template. Bulk-like ZFO solid was also produced by thermal decomposition of $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ salts (in a molar ratio of 1:2, respectively) in air at 1100 °C for 2 hours. The purity and crystal structure of as-prepared materials were confirmed with powder XRD.

2.4. Synthesis of mesoporous binary MFO-ZFO NC assemblies

The mesoporous MFO-ZFO NC assemblies (denoted as x% MFO-ZFO MNAs, where x% is the weight percent of the MFO phase in the product) were synthesized as follows: 0.2 g of Pluronic P123 (EO₇₀PO₂₀EO₇₀) block copolymer was dissolved in 1 mL of anhydrous ethanol at room temperature. Then, 1 mL of colloidal ZFO NC solution (120 mg/mL) and appropriate amount of MFO NC solution (120 mg/mL) were slowly added to the surfactant solution. The resulting mixture was kept under sonication for 10 min and then stored in an oven at 40 °C for about 2–3 days under static condition in order mesostructured NC/polymer composites to be formed. Mesoporous solids were prepared by heating the dry product in air for 4 hours at 350 °C, using a 0.5 °C/min heating rate. The amount of 3-APA-capped MFO NCs used in reactions was varied between 5, 8, 11 and 17 mg to gives a series of mesoporous binary x% MFO-ZFO materials with different loading amount of MFO, i.e., x = 4, 6.5, 8.5 and 12.5 wt%, respectively. For comparison, untemplated 6.5% MFO-ZFO material was also prepared by a similar procedure without the

addition of polymer template. The purity and crystal structure of as-prepared materials were confirmed with powder XRD.

2.5 Synthesis of Mn₃O₄ NCs

Mn₃O₄ NCs (6–7 nm in size) stabilized with oleic acid were prepared according to a literature procedure[130]. In detail, 1 mmol of Mn(CH₃CO₂)₂ and 2 mmol oleic acid dissolved in 10 mmol of oleylamine were added in 15 mL of xylene in air atmosphere. After slowly heating to 90°C, 1 mL of deionized water was injected into the solution under vigorous stirring, and the resulting solution was aged at 90 °C for 3 hours. A total of 100 mL of ethanol was added to precipitate the NCs, which was followed by centrifugation to retrieve the NCs in powdery form. The NCs synthesized were dispersed in *n*-hexane to form a stable colloidal solution (10 mg/mL).

2.6 Ligand-exchange of Mn₃O₄ NCs

The ligand-exchange process was carried out according to a previously reported method[46]. In a typical reaction, 5 mL of Mn_3O_4 NC dispersion in *n*-hexane was added in 5 mL of a solution of NOBF₄ in N,N-dimethylformamide (DMF) (10 mg/mL) and the mixture was kept stirring at room temperature until the NCs were transferred to the DMF phase. The Mn_3O_4 NCs were then collected by precipitation with toluene followed by centrifugation at 13000 rpm for 15min. The ligand-stripped Mn_3O_4 NCs were dispersed in DMF to give a final concentration of 240 mg/mL.

2.7 Synthesis of mesoporous Mn₃O₄ NC assemblies

The mesoporous Mn_3O_4 NC assemblies (Mn_3O_4 MNAs) were synthesized as follows: 0.2 g of Pluronic P123 ($EO_{70}PO_{20}EO_{70}$) block copolymer was dissolved in 1.5 mL of anhydrous ethanol at room temperature. Then, 0.5 mL of colloidal Mn_3O_4 NC solution was slowly added dropwise to the surfactant solution with continuous stirring. The resulting mixture was kept at room temperature for 2 hours and then stored in an oven at 40 °C for about 6 to 7 days under static condition. Removal of the template between the Mn_3O_4 NCs as well as interparticle connection was achieved by heating the dry product at 350 °C for 4 hours in air, using a 0.5 °C/min heating rate. For comparison, random aggregates of Mn_3O_4 NCs (Mn_3O_4 RNAs) were also prepared by a similar procedure without the addition of polymer template. Bulk-like Mn_3O_4 solid was also prepared by thermal decomposition of $MnCO_3$ in air at 950 °C for 2 hours. Powder XRD confirms the formation of single phase Mn_3O_4 .

2.8 Catalytic oxidations of aliphatic and aromatic hydrocarbons

In a typical experiment, a mixture of hydrocarbon (0.4 mmol) and catalyst (0.04 mmol) in 2 mL of acetonitrile was placed in a 4 mL glass reactor closed with a Teflon cap. The reaction was initiated by adding TBHP (3 equiv.) and the mixture was vigorous stirred at 70 °C. The reaction conversion and the products characterization were realized by a combination of gas chromatography – mass spectrometry (Shimadzu GCMS-QP2010 Ultra) and 1H NMR spectroscopy (Bruker AMX 300 MHz) by withdrawing small aliquots from the reaction mixture. The spectroscopic data of the products are in agreement with the corresponding commercially available.

2.9 Photocatalytic Cr(VI) reduction reactions

The photocatalytic Cr(VI) reduction was carried out in a Pyrex glass cell (100 mL capacity) containing 50 mL of Cr(VI) aqueous solution and different concentrations of catalyst (0.3–0.7 g/L). The Cr(VI) solution (50 mg/L) was prepared by dissolving K₂Cr₂O₇ in DI water, and the pH of the solution was adjusted to the desired values with dilute sulfuric acid. Before irradiation, the reaction solution was stirred in the dark for 30 min to ensure adsorption/desorption equilibrium and then exposed to UV and visible light, using a 300W Xe lamp (Variac Cermax) equipped with cut-off filters (360 nm and 420 nm cut-off, respectively). All the experiments were carried out at 20 ± 2 °C using a water bath cooling system. During the reaction, the concentration of Cr(VI) in the solution was monitored via 1,5-diphenylcarbazide (DPC) colorimetric method, using a Perkin Elmer Lambda 25 UV–vis spectrometer. The normalized concentration (Ct/Co) of Cr(VI) solution at different illumination times was calculated as proportional to the absorbance of DPC-Cr(VI) complex at 540 nm.



Figure 13. Set-up of photocatalytic Cr(VI) reduction experiments with a 300-W Xe lamp.

For the photocatalytic water oxidation reaction, 25 mg of ZFO MNAs catalyst and 50 mL of 50 mg/L Cr(VI) aqueous solution (pH = 2) were placed into a 100-mL airtight quartz tube. The temperature of the suspension was maintained at 20 ± 2 °C by using an external water-cooling system. The reaction solution was first purged with argon for 40 min under atmospheric pressure to remove any dissolved air and then irradiated with a 300W Xe lamp ($\lambda > 360$ nm). The produced O₂ was analyzed by gas chromatography with a Shimadzu GC-2014 instrument equipped with a thermal conductivity detector, using Ar as a carrier gas.

2.10 Physical characterization

Thermogravimetric (TG) analysis was performed on a Perkin Elmer Diamond instrument in an air atmosphere (~200 mL/min flow rate) with a heating rate of 5 °C/min.

Small-angle X-ray scattering (SAXS) measurements were performed on a Xenocs Nano-inXider system using Cu K α radiation (λ =1.54189 Å). Scattering data were corrected for dark current and empty tube scattering.
Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro MPD X-ray diffractometer (45 kV and 40 mA) using Cu K α (λ =1.5406 Å) radiation (45 kV, 40 mA). Diffraction data were recorded in the 2 θ range of 20–80° with a 2 θ step size of 0.01° and a scanning speed of 0.1°/min in Bragg–Brentano geometry.

Elemental microprobe analyses were performed by a JEOL JSM-6390LV scanning electron microscope (SEM) equipped with an Oxford INCA PentaFETx3 energy dispersive X-ray spectroscopy (EDS) detector (Oxfordshire, UK). Data acquisition was performed at least five times for each sample using an accelerating voltage of 20 kV and a 100-s accumulation time.

Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 electron microscope equipped with a LaB_6 filament and operated at 200 kV accelerating voltage. Samples were prepared by suspending fine powders in anhydrous ethanol and then drop casting on a copper grid covered with carbon film.

Nitrogen adsorption and desorption isotherms were measured at -196° C on a Quantachrome NOVA 3200*e* sorption analyzer. Before measurement, samples were degassed at 100 °C under vacuum ($<10^{-5}$ Torr) for 12 hours. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method [131] on the adsorption data in the relative pressure range of 0.05–0.22. The total pore volumes were estimated from the adsorbed amount at the relative pressure (P/Po) of 0.98 by applying the Gurvich rule, and the pore size distributions were obtained from the adsorption branch of the isotherms, using the nonlocal density functional theory (NLDFT) method [132].

UV–vis/near-IR diffuse reflectance spectra were recorded with a Perkin Elmer Lambda 950 optical spectrophotometer, using BaSO₄ powder as a 100% reflectance standard. The energy bandgap (E_g) of the samples were estimated from Tauc plots of (Fhv)² as a function of photon energy (hv), where F is the Kubelka–Munk function of the reflectance (R): F = $(1-R)^2/(2R)$ [133].

The Raman spectra were collected at room temperature on a Nicolet Almega XR micro-Raman spectrometer equipped with a 473 nm blue laser (15 mW) as an excitation source.

Fluorescence spectra were obtained at room temperature on a Lumina Fluorescence spectrometer (Thermo scientific) equipped with a 150W Xe lamp.

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was performed on a Perkin Elmer NexION 300X instrument. For ICP-MS analysis, 1 mL of the sample solution was evaporated to dryness, followed by the addition of 100 mL of 2% HNO₃.

The reaction conversion and the products characterization were realized by a combination of gas chromatography – mass spectrometry (Shimadzu GCMS-QP2010 Ultra) and ¹H NMR spectroscopy (Bruker AMX 300 MHz) by withdrawing small aliquots from the reaction mixture. The spectroscopic data of the products are in agreement with the corresponding commercially available.

2.11 Electrochemical measurements

Mott–Schottky plots were collected with an electrochemical workstation (CHI 660E). A threeelectrode set-up, with a platinum plate $(1.0\times2.0 \text{ cm}^2)$ and a silver–silver chloride (Ag/AgCl, 3M KCl) as the counter and reference electrodes, respectively, was adopted to study the samples. The capacitance of the semiconductor/electrolyte interface was obtained at 1 kHz, with 10 mV AC voltage amplitude in 0.5 M Na₂SO₄ aqueous solution (pH = 7). Working electrode for impedance potential measurements was fabricated as follows: ~10 mg of spinel ferrite catalyst was dispersed in 1 mL DI water and the mixture was subjected to sonication in a water bath until a uniform suspension was formed. After that, 40 µL of the suspension was loaded on the surface of fluorine-doped tin oxide (FTO, 10 Ω /sq) substrate, which was masked using 3M scotch tape with an effective area of 1 cm². The sample was dried in a 60 °C oven for 30 min. The donor density (N_d) of the semiconductors was calculated according to the Mott–Schottky equation:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon \varepsilon_0 e N_d} \left(E - E_{FB} - \frac{k_B T}{e} \right) \sim \frac{2(E - E_{FB})}{\epsilon \varepsilon_0 e N_D}$$
(1)

where C_{SC} is the space-charge capacitance, E is the applied potential, E_{FB} is the flat-band potential, N_d is the donor density of electrode material, ε_0 is the vacuum permittivity (8.8542×10⁻¹⁰ F/cm), ε is the material's relative dielectric constant, e is the elementary charge (1.602×10⁻¹⁹ C), k_B is Boltzmann's constant and T is the temperature in Kelvin.

The donor density (N_d) of the semiconductors was calculated according to the Mott–Schottky equation:

$$N_{\rm D} = \frac{2(E - E_{\rm FB}) \cdot C_{\rm SC}^2}{\epsilon \varepsilon_{\rm o} e}$$
(2)

where the term (E –E_{FB}) \cdot $C_{sc}{}^2$ is the reciprocal of the slope of the Mott-Schottky plot.

CHAPTER 3

MESOPOROUS SPINEL FERRITE NANOCRYSTAL ASSEMBLIES AS EFFICIENT CATALYSTS FOR PHOTOCATALYTIC REDUCTION OF Cr(VI)

3.1 Structure and morphology of MeFO MNAs

The synthesis of mesoporous assemblies of spinel ferrite NCs (hereafter denoted as MeFO MNAs, Me = Zn, Mn, Ni, Cd and Co) was accomplished by first modifying the surface of individual MeFO NCs with 3-aminopropanoic acid (3-APA) and then cross-linking the NC colloids in the presence of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (Pluronic P123, BASF) block copolymer. We confirmed the coordination of 3-APA to the nanoparticles surface with Fourier transform infrared (FT-IR) spectroscopy.



Figure 14. FT-IR spectra of (a) ZFO NCs capped with 3-aminopropanoic acid (3-APA) and (b) pure 3-APA compound. The assignment of IR peaks of 3-APA to various vibration modes was based on that of ref. [134] (v - stretching, δ - bending, w - wagging, ρ - rocking, s - symmetric, as - asymmetric).

Figure 14 present typical FT-IR spectra of 3-APA–capped ZFO NCs and pure 3-APA compound. The hybrid nanoparticles revealed the carbonyl (C=O) stretching vibration bands of 3-APA at ~1635 cm⁻¹ and ~1382 cm⁻¹ region, which are slightly red-shifted by ~5 cm⁻¹ compared to that of pure 3-APA. Furthermore, there was no significant shift in the resonance of C–N (~853 cm⁻¹) and $-NH_2$ (~1542 cm⁻¹) bonds of 3-APA after surface modification. The IR analysis thus leads to a conclusion that the 3-APA ligands are being tethered to the nanoparticle surface through the carboxylate (–COO[–]) groups, while the amine (–NH₂) functional groups are available to interact with the polar domains of the polymer template during synthesis.

Mesoporous architectures of connected NCs with open-pore structure then obtained by annealing the polymer/NC composite samples in air at 350 °C to remove the polymer template and cross-link the NCs (through covalent bonding) into extended 3D networks. Evidence that the template was entirely removed by calcination was obtained by thermogravimetric (TG) analysis. A typical TG curve of the mesoporous ZFO sample is shown in **Figure 15**, where a weight loss of about 3.4% from 230 to 500 °C can be attributed to the hydroxylation of the particle surface.



Figure 15. TG profiles of as-prepared containing surfactant (black line) and mesoporous (red line) ZFO MNAs recorded under air flow (~150 mL/min). The differential thermogravimetric (DTG) curve (dashed line) for as-prepared material is also given.

The nanostructure of as-prepared spinel ferrite mesoporous materials was characterized by small-angle X-ray scattering (SAXS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). A typical SAXS pattern of the mesoporous ZFO shows a weak broad scattering peak centered at $q (= 4\pi \cdot \sin \theta / \lambda)$, where 2θ is the scattering angle) range of ~0.47 nm⁻¹ (**Figure 16**), which corresponds to an average repeat distance (d = $2\pi/q$) of about 13.5 nm. The presence of this scattering peak indicates mesoscopic order, although with small coherent domain size, and corresponds to the center-to-center interparticle distance in the sample. Analysis of the scattering data with Guinier approximation [135] showed that the average diameter of constituent nanoparticles is about 8 nm (**Figure 16, inset**).



Figure 16. SAXS pattern (inset: Guinier plot, $\ln[I(q)] \propto q^2 \cdot R_g^2/3$, where R_g is the radius of gyration obtained from analysis of the low-*q* scattering data. The red line is fit to the data) of mesoporous assemblies of ZFO NCs.

XRD measurements revealed that the crystallinity of the precursor nanoparticles, established through colloidal synthesis, well persists thought assembly and annealing process. In **Figure 17**, all the XRD diffraction peaks of mesoporous materials correlate well with the reference data for cubic metal ferrites. No peaks from impurity phase like ZnO or Fe_2O_3 had been detected in XRD patterns, indicating the phase purity of the samples. Using the Scherrer's equation and peak width of the (311) reflection, the average domain size of spinel ferrite crystallites in various mesoporous samples was calculated. In agreement with SAXS results, through this analysis, we obtained a grain size of about 6–8 nm (**Table 1**), which is very close to that of the respective precursor nanoparticles (~6–7 nm, see **Figure 18** and **Figure 19**). These results reflect a minimal grain growth of crystallites during the high-temperature treatment. Further, energy dispersive X-ray spectroscopy (EDS) microanalysis of the inorganic network showed consistent results of the XRD and SAED (see below). In **Figure 20**, EDS analysis of the ZFO MNAs indicated a stoichiometric ratio of Zn/Fe ~ 1:2 for constituent nanoparticles, reaffirming a single-phase composition.



Figure 17. Powder XRD patterns of different mesoporous spinel ferrite materials. All the diffraction peaks are consistent with the cubic spinel phase of metal ferrites. Analysis of the (311) reflection with the Scherrer equation gives an average grain size of about 6–8 nm.



Figure 18. XRD patterns of the mesoporous assemblies of ZFO MNAs (black line) and precursor ZFO NCs (red line).



Figure 19. Powder XRD patterns of different spinel ferrite nanoparticles. Analysis of the (311) reflection with the Scherrer equation gives an average grain size of about 6–7 nm.



Figure 20. Typical EDS spectrum of mesoporous assemblies of ZFO NCs (ZFO MNAs).

Catalyst	Surface area (m²/g)	Pore volume (cm ³ /g)	Pore width (nm)	Crystalline size ^[a] (nm)
ZFO	105	0.15	5.8	6.2 (6.0)
NFO	159	0.18	5.4	8.2 (6.1)
CdFO	118	0.19	5.6	6.1 (5.9)
CoFO	134	0.18	5.6	7.1 (6.8)
MFO	106	0.23	6.1	6.7 (6.5)

Table 1. Textural properties of MeFO MNAs materials.

[a] Average crystalline size of MeFO particles calculated by the Scherrer formula: $d_p = 0.9\lambda/B \cos\theta$, where λ is the source wavelength ($\lambda_{Cu} = 0.154$ nm) and B is the full-width half-maximum of the diffraction peal centered at 2 θ degrees. In parenthesis: the average crystalline size of starting MeFO NCs.

TEM imaging has been used to investigate the morphology and microstructure of the assembled materials and typical results for mesoporous ZFO are shown in **Figure 21a** and **21b**. The TEM images depict a highly porous network composed of reasonably monodisperse nanoparticles with an average diameter of 6–7 nm, which is in good accordance with the SAXS and XRD analyses. As shown in **Figure 21b**, the nanoparticles are interconnected forming a continuous structure, which allows a direct NC-to-NC contact for efficient charge transport. A typical high-resolution TEM (HRTEM) image displayed in inset of **Figure 21b** further confirms the cubic spinel structure of the constituent NCs, showing distinct lattice fringes with ~3.0 Å spacing throughout the nanoparticles that could be assigned to the (220) planes of cubic ZnFe₂O₄ structure. Meanwhile, selected-area electron diffraction (SAED) pattern taken from a part of the mesoporous network shows a series of broad concentric diffraction rings (**Figure 22**), signifying multiple orientations of small NCs. All the electron diffraction rings can be readily assigned to cubic spinel phase of ZnFe₂O₄ with a lattice constant of a = 8.429 Å (space group: Fd-3m), again supporting the single-crystalline nature of the ZFO MNAs.



Figure 21. Typical TEM images and a high-resolution TEM image of an individual ZFO NC (inset of panel b) of the ZFO MNAs.



Figure 22. Selected-area electron diffraction (SAED) pattern of the ZFO MNAs sample.

Nitrogen physisorption measurements revealed that our assembled structures have a high porosity with regular mesopores between the NCs. As shown in **Figure 23** and **24**, all samples exhibit typical type IV adsorption and desorption isotherms with distinct H₃-type hysteresis loop at a relative pressure (P/P_o) range of 0.45–1.0, which is characteristic of mesoporous solids with interconnected porosity. The Brunauer–Emmett–Teller (BET) specific surface areas and total pore volumes of mesoporous spinel ferrite materials were estimated to be 105–159 m²/g and 0.15–0.23 cm³/g, respectively. These surface areas are very high if we account for their massive framework structure (mass density ~5–5.6 g/cm³). The pore size distribution plots derived from adsorption data using the nonlocal density functional theory (NLDFT) model (based on slit-like pores) was found to be quite narrow with an average pore diameter of about 5 to 6 nm. The very similar pore size of the MeFO MNAs materials indicates proper replication of the assembled networks around the polymer template. Given an average SAXS repeat distance of 13.5 nm for ZnFO MNAs, from the difference between the interparticle distance and the pore size, we calculated a framework wall thickness of about 7.7 nm, which is highly consistent with the diameter of the constituent nanoparticles (~8 nm, as obtained from SAXS analysis). This implies that the walls of MeFO

MNAs consist of a single layer of nanoparticles. **Table 1** summarizes the textural properties of the mesoporous samples. Note that the open mesopores and high surface area of the assembled structure of the MeFO MNAs offer a large catalyst/electrolyte interface area for fast mass-transfer kinetics and rapid electrochemical reactions, which are beneficial for the photocatalytic performance. With the purpose of elucidating the role of polymer template in the synthesis of spinel ferrite MNAs, untemplated ZFO sample has also synthesized by direct self-assembly of colloidal 3-APA capped ZFO NCs and its textural properties were characterized by N_2 physisorption. This material exhibits a lower BET surface area (81 m²/g), pore volume (0.14 cm³/g) and average pore diameter (ca. 3.9 nm) than ZFO MNAs (**Figure 23**), indicating that the proposed method is a typical template-driven synthesis process.



Figure 23. Nitrogen adsorption (solid symbols) and desorption (open symbols) isotherms at -196° C and the corresponding NLDFT pore-size distributions calculated from the adsorption branch of the isotherms (inset) for the ZFO MNAs (black symbols) and untemplated ZFO material (orange symbols). The N₂ isotherms of the ZFO MNAs are offset by 5 cm³/g for clarity (STP: standard temperature and pressure).



Figure 24. N_2 adsorption-desorption isotherms and the corresponding NLFDT pore-size distribution (inset) for the MeFO MNAs samples.

3.2 Photocatalytic study of MeFO MNAs

3.2.1. Photocatalytic activity

The photocatalytic activities of mesoporous spinel ferrite assemblies were assessed in the photoreduction of aqueous Cr(VI) solutions under UV and visible light irradiation. In **Figure 25**, the evolutions of Cr(VI) photoreduction are plotted for the five different spinel ferrite catalysts. Compared to other samples, ZFO MNAs is the most active catalyst toward Cr(VI) reduction giving a respective conversion level of ~81% in 3 hours. As we shall discuss below, the high reactivity of ZFO relates to its highly porous structure and suitable electronic band structure for Cr(VI)

reduction and water oxidation. Therefore, we focused on reactions with this catalyst during our further studies. First, we proceeded to optimize the reaction conditions by changing the catalyst loading and pH of the solution. **Figure 26** shows the evolution of the photocatalytic reduction of Cr(VI) over time for different concentrations of ZFO MNAs catalyst. It can be seen that, with increasing catalyst concentration, the conversation of Cr(VI) is increased and reaches a maximum at 0.5 g/L. The increase photoactivity with the catalyst loading is due to the increased number of photons absorbed by the catalyst nanoparticles and the high density of surface active sites that are available for reaction [136]. However, excess amount of catalyst (0.7 g/L) may counter this effect, leading to a slight decrease in Cr(VI) reduction efficiency, presumably due to the light scattering effect from the particles surface. Meanwhile, control experiments showed that no obvious reduction or adsorption of Cr(VI) occurs in the absence of light even after 3 hours, demonstrating the photocatalytic nature of the reactions (see **Figure 26**).



Figure 25. Photocatalytic reduction of aqueous Cr(VI) over different spinel ferrite catalysts. The standard deviation of all measurements is about 3%. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, pH = 2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.



Figure 26. Effect of the ZFO MNAs catalyst concentration. Reaction conditions: 300–700 mg/L catalyst, 50 mg/L Cr(VI) aqueous solution, pH = 2, UV–visible light ($\lambda > 360$ nm) irradiation, 20 °C.

Next, a series of catalytic experiments were performed to investigate the effect of pH on ZFO photocatalytic activity. As shown in **Figure 27**, the Cr(VI) reduction photocatalysis by ZFO MNAs remarkably was increased as the solution pH decreases from 6 to 2. Notably, in a pH 2 solution, the ZFO catalyst achieves a Cr(VI) reduction level of ~81% in 3 hours. We interpret the dependence of photoreduction rate on pH to the change in the Cr(VI) adsorption on the catalyst surface. The Cr(VI) species in low pH solution (precisely, less than 4) predominantly exist as $HCrO_4^-$ anions, while in this environment the catalyst surface is positively charged; the point of zero charge (pH_{pzc}) of ZnFe₂O₄ is reported to be 4.6 [137]. This means that under acidic conditions (pH < pH_{pzc}) the surface of photocatalyst becomes positive (=M–OH₂⁺) due to the excess of H⁺ ions, which tends to adsorb more HCrO₄⁻ ions, thereby increasing the Cr(VI) photoreduction rate. As for the lower Cr(VI) reduction activity obtained at pH = 1, this could be attributed to the firm binding of reactants (HCrO₄⁻ anions) by the catalyst surface.



Figure 27. Time courses of photocatalytic reduction of Cr(VI) over ZFO MNAs catalyst in pH 1– 6. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) aqueous solution, pH = 1–6, UV– visible light ($\lambda > 360$ nm) irradiation, 20 °C. The pH of the solution was adjusted with 1 M H₂SO₄.

3.2.2. Effect of morphology on the photocatalytic activity

In addition to the oxidation kinetics at the ZFO/solution interface, morphological effects may also contribute to the high photoactivity of ZFO MNAs. This can be investigated by comparing photocatalytic data for Cr(VI) reduction by individual (3-APA–capped) ZFO NCs, random aggregates of ZFO NCs (untemplated ZFO) and bulk ZFO The photocatalytic activity of ZFO MNAs remarkably exceeds that of the isolated ZFO NCs as depicted in **Figure 28**. The photocatalytic Cr(VI) reduction was investigated using similar amounts of catalysts (0.5 g/L) under identical conditions. Assuming that the reaction rate is proportional to the concentration of Cr(VI), the photocatalytic reaction can be expressed by the first-order kinetics of Langmuir-Hinshelwood model. Thus, analysis of the temporal evolution of Cr(VI) concentration using the pseudo-first-

order reaction rate (1) reveals a rate constant k of $6.6 \times 10^{-4} \text{ min}^{-1}$ for ZFO NCs and $2.4 \times 10^{-3} \text{ min}^{-1}$ for mesoporous ZFO assemblies (**Figure 28b**).

$$\ln(C_t/C_o) = -k \cdot t \tag{3}$$

where, C_0 and C_t is the concentration of Cr(VI) at initial time and time t, respectively, and *k* is the apparent reaction rate constant .

The lower photoactivity of isolated NCs might be ascribed to the agglomeration of NCs, which could form close-packed microstructures with a limited number of exposed surface active sites. Also, the untemplated ZFO sample, although has a sufficiently large surface area (81 m²/g), gave a lower conversion yield to Cr(III) (about 46% in 4 hours, $k = 7.8 \times 10^{-4}$ min⁻¹). Presumably, a deterioration of Cr(VI) diffusion within the small interstitial voids (ca. 3.8 nm in size) may contribute to the slow reaction kinetics of untemplated material. Consequently, all these results suggest that incorporation of small grain composition and high mesoporosity into ZFO catalyst has a beneficial effect in enhancing photocatalytic efficiency. In agreement to this, bulk-like ZFO particles (surface area < 1 m²/g), prepared by the direct calcination of Zn(NO₃)₂ and Fe(NO₃)₃ compounds at 1100 °C, show almost five times lesser photoreduction rate ($k = 5.1 \times 10^{-4}$ min⁻¹) than mesoporous ZFO assemblies.



Figure 28. (a) Photocatalytic reduction of aqueous Cr(VI) as a function of irradiation time (standard deviation = 3%) and (b) plot of kinetic rate constants (*k*) of mesoporous ZFO assemblies (ZFO MNAs), ZFO NCs, bulk-like ZFO solid and untemplated ZFO material. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr (VI) solution, pH = 2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.

Besides, the superior reactivity of the mesoporous ZFO assemblies as compared to isolated ZFO NCs could be attributed to the efficient separation of photoinduced electron-hole pairs within the semiconductor network. This can be confirmed by comparing the photoluminescence (PL) spectra of colloidal ZFO NCs and ZFO MNAs. As seen from **Figure 29**, the ZFO NCs exhibit an intense emission in the 390–500 nm range at room temperature when excited with photons of wavelength 325 nm. The PL peak at 380 nm corresponds to the interband electron-hole radiative transitions, while the weak shoulder peak at ~480 nm arises from localized mid-gap states to the carrier relaxation processes due to intrinsic defects (particularly, interstitial Zn defects) [138]. Importantly, compared to isolated NCs, mesoporous ZFO assemblies show a dramatic decrease of the photoemission signal, indicating that recombination of photogenerated electrons and holes has been efficiently repressed. These results suggest that the mesoporous framework of linked ZFO NCs has the potential to exhibits efficient charge transport between adjusted nanoparticles, facilitating the electron-hole dissociation along the assembled structure.



Figure 29. Room-temperature PL spectra of isolated ZFO NCs and mesoporous assemblies of ZFO NCs (ZFO MNAs). PL measurements were performed in water (1 mg/mL) at an excitation wavelength of 320 nm.

Notably, the photocatalytic activity of ZFO MNAs is superior or even comparable to that of other high-performance catalysts studied under similar conditions. A comparison of the photocatalytic Cr(VI) reduction activities of different catalysts from the literature is shown in **Table 2**.

Table 2. Comparison of Cr(VI) reduction activity of different photocatalysts studied under similar experimental conditions.

Photocatalyst	Reaction conditions Light source		Cr(VI)	Ref.
			reduction	
			activity	
$La_2Ti_2O_7$	1 g/L catalyst, 50 mg/L	300-W Hg lamp	~75%, 3 h	[139]
particles	Cr(VI) solution, $pH = 2$	(UV light)		
MIL-68(In)-NH ₂	0.4 g/L catalyst, 20 mg/L	300-W Xe lamp	~97%, 3 h	[140]
particles	Cr(VI) solution, $pH = 2$	(λ>420 nm)		
CoO _x /TiO ₂	1 g/L catalyst, 50 mg/L	300-W Xe lamp	~70%, 140 min	[141]
nanosheets	Cr(VI) solution, $pH = 3$	(λ>420 nm)		
Cu ₂ ZnSnS ₄	0.5 g/L catalyst, ~5 mg/L	40-W Hg lamp	~60%, 2.5 h	[142]
nanoparticles	Cr(VI) solution	$(\lambda > 400 \text{ nm})$		
ZnO	12 g/L catalyst, 80 mg/L	100-W Hg lamp	~50%, 2 h	[143]
microparticles	Cr(VI) solution	(UV light)		
CdS/RGO	1 g/L catalyst, 10 mg/L	400-W Hg lamp	~92%, 4 h	[144]
composite	Cr(VI) solution	$(\lambda > 400 \text{ nm})$		
TiO ₂ (Degussa	1 g/L catalyst, 10 mg/L	500-W Hg lamp	~70%, 4 h	[145]
P25)	Cr(VI) solution	$(\lambda > 365 \text{ nm})$		
TiO ₂ /WO ₃	0.1 g/L catalyst, 4 mg/L	150-W lamp	~80%, 5 h	[146]
nanoparticles	Cr(VI) solution,	$(\lambda > 365 \text{ nm})$		
_	pH = 3.7			
α-FeOOH/RGO	1 g/L catalyst, 10 mg/L	125-W Hg lamp	~94%, 3 h	[147]
composite	Cr(VI) solution, $pH = 2$	(λ>400 nm)		
-				
Amino-	6 g/L catalyst, 50 mg/L	15-W LED lamp	~65%, 24 h	[148]
functionalized	Cr(VI) solution, $pH = 2$	(Vis light)		
Fe ₃ O ₄ /WO ₃				
nanoparticles				
NaTaO ₃ particles	1 g/L catalyst, 10 mg/L	450-W Hg lamp	~30%, 2 h	[149]
	Cr(VI) solution, $pH = 7$	(λ>260 nm)		
SnS ₂	1 g/L catalyst, 50 mg/L	250-W Xe lamp	~97%, 2 h	[105]
nanoparticles	Cr(VI) solution	(λ>420 nm)		
CoO NC	0.3 g/L catalyst, 50 mg/L	300-W Xe lamp	~92%, 3 h	[50]
assemblies	Cr(VI) solution, $pH = 2$	(λ>360 nm)		
ZFO MNAs	0.5 g/L catalyst, 50 mg/L	300-W lamp	~81%, 3 h;	In this
	Cr(VI) solution, pH = 2	(λ>360 nm)	~98%, 4h	study

3.2.3. Mechanism of photocatalytic Cr(VI) reduction

To better understand the hole transfer processes in spinel ferrite NCs, we also tested the photooxidation activity of ZFO MNAs under UV and visible light illumination. The photocatalytic water oxidation was carried out in an air-tight quartz cell, and the evolved oxygen was analyzed by gas chromatography (Shimadzu GC-2014). As shown in Figure 30, ZFO MNAs catalyst is effective to oxidize water to dioxygen from an aqueous solution containing 50 mg/L Cr(VI). This confirms that the photoreduction of Cr(VI) is largely associated with O₂ production; an average O_2 evolution rate of ~2.6 µmol/h was obtained with 25 mg of ZFO MNAs catalyst (in 50 mL of Cr(VI) solution) after 3 hours of irradiation. To further verify that the detected oxygen was indeed generated by water oxidation reaction, we conducted the photocatalytic experiment, as described above, in a vacuum-tight cell and the generated oxygen was monitored in situ with a gas analyzer (Hiden HPR-20 QIC). Figure 31 displays the transient photocatalytic O₂ evolution response of ZFO MNAs under light on and off conditions. It shows that oxygen quickly formed under UV-vis light irradiation, while no oxygen evolution is detected when the light was turned off. In conjunction with the results above, this study provides unequivocal evidence for the spontaneous water oxidation on the zinc ferrite surface, leading to the production of molecular oxygen. Thus, the overall reaction in acid conditions can be described in the followings Eqs. (4)–(6).

$$2HCrO_{4}^{-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 8H_{2}O(l) \text{ (cathode)}$$
(4)

$$3H_2O(1) + 6h^+ \rightarrow \frac{3}{2}O_2(g) + 6H^+(aq) \text{ (anode)}$$
 (5)

$$2\text{HCrO}_4^{-}(\text{aq}) + 8\text{H}^+(\text{aq}) \to 2\text{Cr}^{3+}(\text{aq}) + \frac{3}{2}\text{O}_2(\text{g}) + 5\text{H}_2\text{O}(1)$$
(6)



Figure 30. Photocatalytic oxygen evolution (standard deviation = 2.5%) for ZFO MNAs catalyst under $\lambda > 360$ nm light irradiation.



Figure 31. Oxygen evolution transient with light on/off for ZFO MNAs catalyst under $\lambda > 360$ nm light irradiation.

The photocatalytic Cr(VI) reduction activity of ZFO MNAs was also tested in an N₂-purged reaction cell (instead of under air atmosphere) to gain information about the effect of oxygen on the Cr(VI) reduction kinetics. As seen from **Figure 32**, after 4 hours of illumination, the conversion level of Cr(VI) reach ~99% (corresponding to an average Cr(VI) reduction rate of 3.9 µmol/h), which is very similar to that obtained from the air-equilibrated system (ca. 98% conversion, 4.0 µmol/h Cr(VI) reduction rate). These results clearly show that presence of oxygen has no influence on the reduction of Cr(VI), indicating that HCrO₄⁻ species preferentially accept electrons during the catalytic process, as anticipated from the higher (more positive) redox potential of HCrO₄^{-/}Cr³⁺ (0.94 V vs NHE, pH = 7) compared to O₂/O₂⁻⁻ pair (-0.33 V vs NHE, pH = 7) [150].



Figure 32. Influence of oxygen on the photocatalytic reduction of Cr(VI). The mean standard deviation for catalytic measurements is about 3%.

Also, aside from the oxygen evolution reaction, photooxidation of surface hydroxyl groups may also proceed by a direct hole-transfer mechanism. In fact, in photocatalytic Cr(VI) reduction process, the photogenerated holes migrate to the surface of the catalyst, where they may react with hydroxyl (–OH) groups or adsorbed water molecules to form hydroxyl radicals (•OH). Recently, we have demonstrated that this is a viable possibility for CoO catalyst in the photocatalytic reduction of Cr(VI) [50]. To examine whether •OH radicals are produced during the photocatalytic process, fluorescence spectroscopy was conducted using coumarin as a fluorophore. Coumarin is an excellent probe for monitoring the formation of hydroxyl radicals in a solution; it reacts with •OH to produce umbelliferone which emits a characteristic fluorescence signal at 455 mn under 332 nm excitation. **Figure 33** displays the time-dependent emission spectra of the reaction solution, showing the progressive decrease in the emission of coumarin and the appearance of the emission band of umbelliferone.



Figure 33. Fluorescence spectra of coumarin in water for ZFO MNAs catalyst. The emission peak at 395 nm and 455 nm corresponds to the coumarin and umbelliferone, respectively. Reaction conditions: 500 mg/L catalyst, 10 mM coumarin, 50 mg/L Cr (VI) solution, pH = 2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.

These results agree against the formation of •OH under the photocatalytic Cr(VI) reduction conditions, which can be ascribed to the favorable oxidation of surface hydroxyl groups $(E_0(OH/OH^-) = 1.58 \text{ V})$ [151] and absorbed water molecules $(E_0(•OH/H_2O) = 1.92 \text{ V})$ [152] by the photogenerated holes. Given the Cr(VI) reduction (4.0 µmol/h) and O₂ evolution (2.6 µmol/h) rate efficiency of the ZFO MNAs catalyst and that the reaction proceeds through Eq. (6), we found that during UV–vis illumination an ~85% of surface-reaching holes are participated in water oxidation reaction to produce oxygen, while the remainder react with surface hydroxyl groups and absorbed water molecules (–OH/H₂O_{abs}) to produce •OH radicals.

To explain the observed variation in the Cr(VI) photoconversion activity presented in Figure 25, the position of the conduction band and valence band edges of each catalyst were estimated based on electrochemical impedance spectroscopy (EIS) and optical absorption measurements. Figure 34 displays the Mott-Schottky plots obtained at a frequency of 1 kHz and the corresponding fits of the linear regime of the inverse square capacitance $(1/C_{sc}^2)$ versus applied potential (E) curves for the mesoporous spinel ferrite assemblies. Using extrapolation to $1/C_{sc}^2$ = 0, the flat-band potential (EFB) of ZFO, NFO, CdFO, CoFO and MFO catalysts was calculated to be -0.17 V, 0.05 V, 0.14 V, 0.08 V and -0.31 V vs NHE (pH = 7), respectively. The electron donor density (N_d) of these catalysts deduced from the slope of the $1/C_{sc}^2 - E$ curves range between 3.61×10^{16} and 1.12×10^{17} cm⁻³, see **Table 3**. Noted that the positive slope of the Mott–Schottky plots indicates that all catalysts have n-type properties. In Figure 36, the energy band diagram for each catalyst is illustrated. Considering a heavily n-doped semiconductor (such as the spinel ferrite materials), it seems reasonable to assume that the E_{FB} potential is located very close to the CB edge (typically, E_{FB} is 0.1–0.3 eV lower than the bottom of the CB) [153, 154]. The VB maximum was thus determined by subtracting the energy band gap (E_g) from the E_{FB} value of the semiconductors. We used diffuse reflectance UV-vis absorption spectroscopy to investigate the optical absorption properties of the MeFO MNAs. The energy band gap values were determined by Tauc's plots, i.e., (Fhv)² versus photon energy, where F, h, and v are the Kubelka-Munk function of the reflectance, Plank constant, and light frequency, respectively, and was found to be 2.17, 1.93, 1.87, 1.34 and 1.45 eV for ZFO, NFO, CdFO, CoFO and MFO MNAs, respectively (Figure 35).

Catalyst	Band gap (Eg) (eV)	Flat-band potential (E _{FB}) (V vs NHE)	VB potential (EvB) ^[a] (V vs NHE)	Donor density (N _d) (cm ⁻³)
ZFO	2.17	-0.17	2.00	$3.63 imes 10^{16}$
NFO	1.93	0.05	1.98	6.39×10^{16}
CdFO	1.87	0.14	2.01	$7.16 imes 10^{16}$
CoFO	1.34	0.08	1.42	$3.61 imes 10^{16}$
MFO	1.45	-0.31	1.14	$1.12 imes 10^{17}$

Table 3. Optical and electrochemical data (pH = 7) of MeFO MNAs.

[a] The VB maximum potential (E_{VB}) of the semiconductors was estimated from $E_{FB} + E_g$.



Figure 34. Mott-Schottky plot of the MeFO MNAs catalysts.



Figure 35. Tauc plots $((\alpha hv)^2$ versus photon energy) derived from UV–vis/NIR optical absorption data for MeFO MNAs catalysts.



Figure 36. Energy band diagrams of mesoporous spinel ferrite (MeFO MNAs) catalysts. The red lines show the energy bandgap of the semiconductors.

The energy diagrams show that the CB of all the spinel ferrite MNAs is positioned well above the reduction level of Cr(VI), thus collaborating the feasibility of these materials for multi-electron reduction of Cr(VI) to Cr(III). Of particular note, the photoactivity of spinel ferrite mesoporous, except for MFO, seems to correlate with the E_{FB} onset potential and obeys the order: ZFO > NFO > CdFO ~ CoFO. Meanwhile, Figure 36 shows that all the catalysts meet the electrochemical requirement for splitting water to oxygen, that is, the position of VB in these materials is lower than the oxidation potential of water (0.82 V vs NHE, pH = 7). Nonetheless, the photocatalytic activity for Cr(VI) reduction from MFO MNAs is considerably low that one would expect from reduction ability of the CB electrons. In particular, MFO MNAs has the most negative flat-band potential (-0.31 V vs NHE, pH = 7) of all examined catalysts, which reflects a higher reducing property. We attribute this difference in activity to the lower water-oxidation efficiency of the MFO catalyst. Although, the high lying E_{FB} level makes MFO a good electron donor for Cr(VI) reduction, its VB edge states very close to the thermodynamic oxygen evolution potential, and therefore, it is possible a significant portion of surface-reaching holes to be lost by recombination, instead of engaging in water reduction reaction. Also, the VB maximum of this material, like in the case of CoFO, is more negative than the electrode potential of •OH/H₂O_{abs} and •OH/OH⁻ pairs, which means that MFO (and similarly the CoFO) cannot oxidize water or surface hydroxyl groups to discharge •OH (Figure 36). Overall, such kinetic and thermodynamic constraints can deteriorate the photoactivity of the catalyst.

To elucidate this possibility, we examined the Cr(VI) photoreduction activity of zinc ferrite and manganese ferrite mesoporous catalysts in the presence of phenol as a sacrificial electron donor. Since phenol exhibits a lower oxidation potential than water (precisely, the redox potential of phenol and water oxidation is 0.96 V and 0.82 V vs NHE at pH = 7, respectively), it would be reasonable to expect that phenol oxidation reaction may facilitate an efficient utilization of surface reaching holes. This means that oxidation of phenol can overcome the kinetic limitation of the oxygen evolution reaction (i.e., $2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$), and therefore, in this case, the contribution from the direct electrochemical oxidation of water by the VB holes of the catalyst could be considered negligible. **Figure 37** shows the comparison of the Cr(VI) reduction time courses for ZFO and MFO MNAs photocatalysts with 10 equivalents of phenol (with respect to HCrO₄⁻ concentration). It can be observed that, in the presence of phenol, MFO behave as a more active catalyst than ZFO for Cr(VI) reduction (the rate constant (*k*) derived from the data in **Figure** **37** is $5.3 \times 10^{-3} \text{ min}^{-1}$ for MFO and $3.6 \times 10^{-3} \text{ min}^{-1}$ for ZFO, see **Figure 37**), which is in accord with the increasing E_{FB} potential of the semiconductors. Additionally, results of these experiments also indicated that the performance of both ZFO and MFO MNAs catalysts was further improved with addition of phenol; under $\lambda > 360$ nm light irradiation, a quantitatively (> 99%) conversion of Cr(VI) was achieved within 3 hours. The rate enhancement in the photoreduction of Cr(VI) can be explained by the fast hole-transfer kinetics for phenol oxidation, suggesting that the photogenerated electrons govern the overall photocatalytic process.



Figure 37. Photocatalytic reduction of aqueous Cr(VI) with ZFO and MFO MNAs catalysts in the presence of phenol under UV–vis and visible light irradiation. (The inset show the corresponding kinetic plots of the pseudo-first-order reaction rates. The red lines are fit to the data. The mean standard deviation for catalytic measurements is about 3%. All photocatalytic reactions were performed as follows: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, 400 mg/L phenol (for control experiments), pH = 2, 20 °C, UV–vis ($\lambda > 360$ nm) or visible light ($\lambda > 420$ nm) irradiation.

It should be stressed that Cr(VI)-bearing wastewater solutions often contain organic dyes, pesticides, and phenolic compounds and therefore their simultaneous redox degradation is an interesting task. The ZFO and MFO MNAs materials are proven to perform as efficient photocatalysts with reasonable Cr(VI) reduction activity in these conditions. Because of the visible light response of zinc ferrite and manganese ferrite NCs ($E_g \sim 2.17$ eV and ~ 1.45 eV, respectively, as estimated by optical absorption spectra), ZFO and MFO MNAs catalysts can also perform Cr(VI) photoreduction with reasonable activity under visible light illumination. As shown in **Figure 37**, under $\lambda > 420$ nm light, a $\sim 70\%$ and a $\sim 76\%$ Cr(VI) conversion level was obtained with ZFO ($k = 2.3 \times 10^{-3} \text{ min}^{-1}$) and MFO ($k = 3.5 \times 10^{-3} \text{ min}^{-1}$) MNAs catalyst in 4 hours, respectively.



Figure 38. Recycling study of the ZFO MNAs catalyst in the absence (closed symbols) and presence (open symbols) of phenol (Inset photographs: initial solution of Cr(VI) and separation of the ZFO MNAs catalyst using an external magnet after reaction). The inset show the corresponding kinetic plots of the pseudo-first-order reaction rates. The red lines are fit to the data. The mean standard deviation for catalytic measurements is about 3%.

Moreover, the ZFO MNAs catalyst is operationally stable over the course of the photoreduction. The stability of the ZFO MNAs was assessed within three recycling experiments in the absence and presence of 0.4 g/L phenol (Figure 38). The catalyst was isolated by centrifugation or using an external magnet after completion of the reaction (inset photos in Figure 38), washed with water, and then reused for the next catalytic run. All these photocatalytic reactions conducted under similar conditions, i.e., using 0.5 g/L ZFO MNAs catalyst and 50 mg/L Cr(VI) solution, manifested almost the same photoconversion yield. Evidently, the ZFO MNAs catalyst showed an improved stability with no signs of decreasing the catalytic activity after 12 hours of irradiation; the rate constants (k) of the repeated reactions were determined to be 2.3×10^{-3} (3.6×10^{-3} with phenol), 2.4×10^{-3} (4.1 × 10⁻³) and 2.3×10^{-3} (4.7 × 10⁻³) min⁻¹ for the 1st, 2nd and 3rd run, respectively, see upper inset of Figure 38. Further, XRD and N₂ porosimetry characterizations of the reused sample indicated that its crystallinity and porous structure are widely retained after catalysis, see Figures 39 and 40, respectively. Also, EDS analysis on the retrieved catalyst (collected using a magnet without washing) indicated the nominal composition of the sample (ZnFe₂O₄), with almost no sign of Cr deposition (Figure 41). This result, along with the control experiment (without irradiation) in Figure 26, suggests that adsorption of Cr(VI) ions on the catalyst's surface plays a negligible role in the photocatalytic reaction.



Figure 39. Powder XRD pattern of the ZFO MNAs catalyst retrieved after the cycling test with the cycling test without phenol.



Figure 40. Nitrogen adsorption-desorption isotherms at -196 °C (Inset: the corresponding poresize distribution calculated from the adsorption branch of isotherm according to the NLDFT method (based on slit-like pores), indicating an average pore size of about 6 nm) of the ZFO MNAs catalyst retrieved after the cycling test without phenol. Analysis of the adsorption data indicate a BET surface area of 101 m²/g and a pore volume of 0.15 cm³/g.



Figure 41. Typical EDS spectrum of the ZFO MNAs catalyst retrieved after the cycling test without phenol (isolated using an external magnet without washing). The EDS results show a Zn:Fe atomic ratio of ~1:2. The Cr content is less than the analytical detection limit (~0.4%).



Figure 42. Schematic representation of the Cr(VI) photoreduction mechanism over mesoporous network prepared from ZFO NCs with a diameter of 6–7 nm (ZFO MNAs).

Based on the above results, we propose a reaction mechanism for the photocatalytic Cr(VI) reduction over spinel ferrite catalysts. Figure 42 illustrates the mechanistic model behind the ZFO MNAs-catalyzed Cr(VI) photoreduction. Briefly, upon UV and visible light irradiation, photoexcited electrons and holes are generated in the CB and VB, respectively, of the spinel ferrite NCs. Because of the favorable electrochemical potential of the CB edge, the photoexcited electrons can be readily transferred to the catalyst surface, where they will react with harmful Cr(VI) species; as shown in Figure 36, the CB edge of all catalysts is more negative than the $HCrO_4^{-}/Cr^{3+}$ redox couple. On the other hand, since the VB level of the catalyst is more positive than the O₂/H₂O redox potential, the photogenerated holes react with surface adsorbed water to produce oxygen. This can be explicitly supported by results in Figures 30 and 31, which show that UV-vis light illumination of the ZFO MNAs leads to an explicit evolution of oxygen gas. Also, during the reaction, a fraction of surface-trapped holes also reacts directly with -OH/H2Oabs to produce •OH radicals. The production of •OH radicals in the Cr(VI)/ZFO MNAs catalytic system has been elucidated earlier by intercepting photochemically produced umbelliferone with fluorescence spectroscopy (Figure 33). It should be noted that, although •OH radicals can form H₂O₂, i.e., by the reaction $\bullet OH(aq) + \bullet OH(aq) \rightarrow H_2O_2(aq)$, the production of H_2O_2 is not expected or would be minimal in this system due to the strong peroxidase-like activity of ZFO [155]. Meanwhile, the in situ generated •OH radicals can also be considered as a strong oxidant for the photodegradation of organic pollutants, such as phenol. Since phenol is a better hole scavenger as compared to water, the addition of such molecules to the reaction mixture can remarkably enhance the intrinsic hole transfer efficiency, thus accelerating the overall photocatalytic process.

3.3 Structure and morphology of binary MFO-ZFO MNAs

The synthesis of mesoporous binary assemblies of spinel ferrite MnFe₂O₄ (MFO) and ZnFe₂O₄ (ZFO) NCs (denoted as x% MFO-ZFO, x = 4, 6.5, 8.5, 12.5 wt%) was accomplished by crosslinking polymerization of NC colloids in the presence of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) block copolymer, followed by calcination at 350 °C. The crystallinity and phase purity of the composite materials were confirmed by XRD measurements. **Figure 43** illustrates the XRD patterns of the x% MFO-ZFO MNAs. All XRD diffraction peaks can be assigned to the spinel structure of ZFO and MFO ((220), (311), (400), (511) and (440)), and no other peak from impurity phases, like MnO, ZnO or other metal oxide phases, had been detected. These results clearly indicate the phase purity of the resulting materials.



Figure 43. Powder XRD patterns of ZFO MNAs and binary x% MFO-ZFO MNAs. All the diffraction peaks are consistent with the cubic spinel phase of metal ferrites.

The mesoporosity of the composite materials was determined by nitrogen physisorption measurements. **Figure 44** depicts typical N₂ adsorption–desorption isotherms and the corresponding pore size distribution plots for the binary x% MFO-ZFO MNAs. All the isotherms feature typical type IV curves, according to the IUPAC classification, with a distinct H₃-type hysteresis loop at a relative pressure (P/P₀) range of 0.45–1.0, being characteristic of mesoporous solids with slit-like pores. The BET surface areas and total pore volumes of mesoporous composite materials were measured to 66–91 m²/g and 0.08–0.14 cm³/g, respectively. The pore size in these materials was derived from the adsorption branch of isotherms using the NLDFT method (based on slit-like pores) (**Figure 44**, **insets**). The NLDFT analysis indicated quite narrow size distributions of pores with an average pore diameter of ~ 5 to 6 nm, which is very close to the pore size of the single-component MeFO MNAs materials.



Figure 44. Nitrogen adsorption (solid symbols) and desorption (open symbols) isotherms at -196° C and the corresponding NLFDT pore-size distribution plots calculated from the adsorption branch of the isotherms (inset) for the binary x% MFO-ZFO MNAs catalysts.

Catalyst	Surface area (m²/g)	Pore volume (cm ³ /g)	Pore width (nm)
4% MFO-ZFO	91	0.14	5.8
6.5% MFO-ZFO	66	0.08	5.7
8.5% MFO-ZFO	78	0.13	5.8
12.5% MFO-ZFO	81	0.12	5.8

Table 4. Textural properties of binary x% MFO-ZFO MNAs catalysts.

3.4 Photocatalytic study of binary ZFO-MFO MNAs

3.4.1. Photocatalytic activity

In general, recalcitrant dyes and organic contaminates were frequently observed in Cr(VI)containing wastewaters and the presence of these organic compounds may increase the difficulty of pollutant abatement. However, organic matter may supply electrons to the photocatalytic system, acting as a scavenger of VB holes of the photocatalyst. Even though the adsorption of Cr(VI) onto the catalyst surface could be obstructed by the organics, enhanced photocatalytic efficiency and reduction rate may be resulted from the reduced recombination between the photogenerated electrons and holes. As a proof of concept, the Cr(VI) photoreduction activity of binary x% MFO-ZFO MNAs was investigated in the presence of phenol as organic pollutant under $\lambda > 360$ nm light irradiation. Figure 45 illustrates the normalized temporal concentration of changes (C/C_o) of Cr(VI) during the photocatalytic process with different MFO, ZFO and x% MFO-ZFO catalysts. The comparison shows that 6.5% MFO-ZFO MNAs exhibit better catalytic performance for Cr(VI) reduction, achieving a ~85% Cr(VI) conversion in 2 hours. Comparatively, under identical conditions, single-components MFO and ZFO MNAs achieve ~60% and ~57% conversion of Cr(VI), respectively. Similar to MFO and ZFO MNAs, the high reactivity of 6.5% MFO-ZFO MNAs composite is related to its high surface area and, most importantly, to its suitable electronic band structure for Cr(VI) reduction and phenol oxidation (see below). Accordingly, we focused on Cr(VI) reduction reactions with this catalyst during our further studies.


Figure 45. Photocatalytic reduction of aqueous Cr(VI) over different MFO, ZFO and x% MFO-ZFO MNAs catalysts. The standard deviation of all measurements is about 3%. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, 400 mg/L phenol, pH = 2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.

Figure 46 shows comparison results of the Cr(VI) photoreduction over 6.5% MFO-ZFO MNAs catalyst in the presence and without phenol. It can be observed that, without phenol, the Cr(VI) photoreduction rate of 6.5% MFO-ZFO MNAs is considerably low (~25% Cr(VI) conversion level in 2 hours) under the examined conditions. Unlike water, phenol seems to enable efficient utilization of VB holes, leading to an improvement for the oxidation efficiency. The oxidation of phenol is kinetically more favourable than the oxidation of water and, therefore, this process can accelerate the overall photocatalytic reaction. In general, the photooxidation of water to dioxygen is a sluggish reaction that involves several uphill reaction steps such as dissociation of –OH species and formation of O–O bonds. This study clearly suggests that the photocatalytic reduction of Cr(VI) and oxidation of phenol are collaborative over mesoporous MFO-ZFO NC assemblies and this process can enhance the photoreduction effect.



Figure 46. Photocatalytic reduction of aqueous Cr(VI) as a function of irradiation time (standard deviation = 3%) of 6.5% MFO-ZFO MNAs and untemplated 6.5% MFO-ZFO (6.5% MFO-ZFO RNAs) catalysts in absence and presence of phenol. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, 400 mg/L phenol (PhOH), pH = 2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.

In addition to chemical composition, morphological effects may also contribute to the high photocatalytic activity of 6.5% MFO-ZFO MNAs. To elucidate this possibility, we also prepared random aggregates of MFO and ZFO NCs (6.5% MFO-ZFO RNAs), using a similar procedure to that describe above for MNAs, but without template. Results shown in **Figure 46** indicate that, although the untemplated sample has a similar chemical composition as 6.5% MFO-ZFO MNAs and exhibits a sufficiently large surface area (ca. 88 m²/g), achieve a significant lower conversion yield to Cr(III) (~53% in 3 hours) than that obtained for Cr(VI) photoreduction over mesoporous analogous. Presumably, the untemplated sample contains a random distribution of small-sized pores between the NCs, which results in slow diffusion kinetics of Cr(VI) ions. Therefore, from these results, it can be inferred that the material's surface area and pore volume play an important role in the reduction rate of Cr(VI).

The reusability of the 6.5% MFO-ZFO MNAs catalyst was investigated by conducting three recycling experiments in the presence of 400 mg/L phenol. The catalyst was isolated by centrifugation after completion of the reaction, washed with water, and re-dispersed in a fresh Cr(VI) aqueous solution. As shown in **Figure 47**, the 6.5% MFO-ZFO MNAs retain more than 94% of its initial activity after recycling. Moreover, XRD and N₂ porosimetry characterizations of the reused sample indicated that its crystal structure and porous structure is well maintained after catalysis, substantiating high durability, see **Figures 48** and **49**, respectively.



Figure 47. Recycling study of 6.5% MFO-ZFO MNAs catalyst. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, 400 mg/L phenol, pH=2, UV–vis light ($\lambda > 360$ nm) irradiation, 20 °C.



Figure 48. Powder XRD pattern of the 6.5% MFO-ZFO MNAs catalyst retrieved after the cycling test.



Figure 49. Nitrogen adsorption and desorption isotherms at -196 °C (Inset: the corresponding pore-size distribution calculated from the adsorption branch of isotherm according to the NLDFT method, indicating an average pore size of about 6 nm) of the 6.5% MFO-ZFO MNAs catalyst retrieved after the cycling test. Analysis of the adsorption data indicate a BET surface area of 66 m²/g and a pore volume of 0.09 cm³/g.

3.4.2. Effect of coexisting organic compounds

To assess the effect of organic compounds on the photocatalytic reduction of Cr(VI), constant amounts of citric acid (CA), phenol and ethylenediaminetetraacetic acid (EDTA) were added to the photocatalytic reactor before beginning the process. Since oxidation of these organic compounds is kinetically more favorable than water oxidation (Eox for phenol, citric acid, EDTA and water is 0.96 V, 1.2 V, 1.17 V and 0.82 V vs NHE at pH = 7, respectively), it is anticipated that this process will enhance the kinetics of the Cr(VI) reduction. The concentration of each organic compound was adjusted to 3 equivalents, while the initial Cr(VI) concentration, photocatalyst dosage, and pH of solution were fixed at 50 mg/L, 500 mg/L and 2, respectively. From Figure 50 it can be observed that the Cr(VI) reduction rate in the presence of citric acid and EDTA is remarkably faster than with phenol. The increased photocatalytic reduction of Cr(VI) in the presence of these compounds can be attributed to the fact that, unlike phenol, citric acid and EDTA can be effectively act as hole scavengers (accelerating the oxidation reaction) because of their enhanced absorption on the catalyst surface. In particular, under acidic conditions (pH \sim 2), there are electrostatic attractions between the positively charged = $M-OH_2^+$ surface and negatively charged EDTA (in the form of H_3EDTA^- (pKa₁ = 1.99) and H_2EDTA^{2-} (pKa₂ = 2.67)) and CA (in the form of H_2CA^- pKa₁ = 3.1) ions, which result in an increased concentration of these species near the catalyst's surface [156, 157]. Comparatively, in acidic solutions, phenol predominately exists as neutral molecular form (it has a pKa of about 9.88), which is absorbed by the catalyst through weak van der Waals and hydrogen bonds.



Figure 50. Photocatalytic reduction of aqueous Cr(VI) over 6.5% MFO-ZFO MNAs catalyst in the presence 3 equivalents of phenol (PhOH), citric acid and EDTA under $\lambda > 360$ nm light irradiation. Reaction conditions: 500 mg/L catalyst, 50 mg/L Cr(VI) solution, pH = 2, UV–vis, 20 °C.

3.4.3. Mechanism of photocatalytic Cr(VI) reduction over MFO-ZFO MNAs

To explicate the observed variation in the Cr(VI) photoreduction activity shown in **Figure 45**, the electrochemical behavior of the as-prepared composite materials was delineated with electrochemical impedance spectroscopy (EIS) and optical absorption measurements. The optical properties of binary x% MFO-ZFO MNAs were measured by UV–vis/NIR diffuse reflectance spectroscopy. The optical band gap (E_g) of the catalysts was determined from Tauc plots for a direct band-gap semiconductor (i.e., $(\alpha hv)^2$ versus hv plots derived from the UV–vis/NIR spectra) as shown in **Figure 51**. The E_g was estimated to be 2.00, 2.18, 2.00 and 2.13 eV for 4%, 6.5%, 8.5% and 12.5% MFO-loaded ZFO MNAs catalysts, respectively. Presumably the observed energy band gap is related to the band structure of the ZFO due to the low loading of MFO NCs in binary assemblies.



Figure 51. Tauc plots derived from UV–vis/NIR diffuse reflectance spectra of the binary x% MFO-ZFO MNAs catalysts.

Figure 52 displays the Mott–Schottky plots obtained at a frequency of 1 kHz and the corresponding fits of the linear regime of the inverse square capacitance $(1/C_{sc}^2)$ versus applied potential (E) curves for the mesoporous x% MFO-ZFO catalysts. Using extrapolation to $1/C_{sc}^2 = 0$, the E_{FB} potential of x% MFO-ZFO MNAs was calculated to be -0.19 V, -0.33 V, -0.32 V and -0.30 V vs NHE, respectively. The electron donor density (N_d) of these catalysts deduced from the slope of the $1/Csc^2 - E$ curves range between 9.71×10^{15} and 1.12×10^{17} cm⁻³ (see **Table 5**). It is apparent that all the $1/Csc^2$ versus E plots of mesoporous x% MFO-ZFO samples show positive linear slope, indicating n-type conductivity.



Figure 52. Mott-Schottky plots of the binary x% MFO-ZFO MNAs catalysts.

Catalyst	Band gap (Eg) (eV)	Flat-band potential (E _{FB}) (V vs NHE)	VB potential (EvB) ^[a] (V vs NHE)	Donor density (Nd) (cm ⁻³)
4% MFO-ZFO	2.00	-0.19	1.81	9.71×10^{15}
6.5% MFO-ZFO	2.18	-0.33	1.85	$1.79 imes 10^{16}$
8.5% MFO-ZFO	2.00	-0.32	1.68	$1.88 imes 10^{16}$
12.5% MFO-ZFO	2.13	-0.30	1.83	$1.46 imes 10^{16}$

Table 5. Optical and electrochemical data (pH = 7) for x% MFO-ZFO MNAs catalysts.

[a] The VB maximum potential of the semiconductors was estimated from $E_{FB}+E_g. \label{eq:estimate}$



Figure 53. Energy band diagrams of binary x% MFO-ZFO MNAs catalysts. The red lines show the energy bandgap of the semiconductors.

Based on the E_{FB} values and optical band gaps (see **Table 5**), the energy diagrams for each composite catalyst are illustrated in **Figure 53**. Here we assumed that the E_{FB} potential is very close to the CB edge position of the MFO-ZFO MNAs samples (typically, the E_{FB} potential is about 0.1 – 0.3 V lower than the CB edge), which is quite reasonable for heavily doped n-type semiconductor, such as ZnFe₂O₄. The results in **Figure 53** show that the CB edge of binary x% MFO-ZFO MNAs is positioned well above the reduction level of Cr(VI), thus collaborating the feasibility of these materials for multi-electron reduction of Cr(VI) to Cr(III). Meanwhile, all the catalysts meet the electrochemical requirement for oxidation of phenol, that is, the position of VB in these materials is lower than the oxidation potential of phenol. Among the studied catalysts, 6.5% MFO-ZFO MNAs have a relatively more negative E_{FB} potential (-0.33 V), which reflects a higher reducing ability of CB electrons, and a more positive VB potential (1.85 V), which favors the oxidation of organic molecules (e.g., phenol) by the surface-reaching holes. Moreover, among the composite structures, 6.5% MFO-ZFO MNAs have a relatively high electron donor density of

about 1.8×10^{16} cm⁻³. Taken together, these thermodynamic effects definitely impact the overall photocatalytic performance of the 6.5% MFO-ZFO MNAs catalyst.

CHAPTER 4 MESOPOROUS ASSEMBLED Mn₃O₄ NANOCRYSTAL NETWORKS AS EFFICIENT CATALYSTS FOR SELECTIVE OXIDATION OF ALKENES AND ARYL ALKANES

4.1 Catalysts synthesis and characterization

A schematic overview of mesoporous Mn_3O_4 NC assemblies (Mn_3O_4 MNAs) synthesis by the polymer-templated aggregating self-assembly (ASA) method is shown in **Figure 54**. Briefly, for the synthesis of Mn_3O_4 MNAs, a dimethylformamide (DMF) solution containing BF_4^- -coated Mn_3O_4 NCs was added to an ethanol solution of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀) block copolymer. The reaction mixture was then placed in an oven to boost the aggregation process.



Figure 54. Schematic illustration of the synthesis of Mn₃O₄ MNAs (ASA: Aggregating Self-Assembly, Cal: Calcination, MNAs: Mesoporous Nanocrystal Assemblies).

We observed that the initial concentration of Mn_3O_4 NCs and the evaporation time of solvents have a considerable influence on the porosity of the products. We obtained optimal results (on the basis of the surface area and total pore volume of the final products) with a slow evaporation of solvents (within ~6–7 days, at 40 °C) and using a copolymer: Mn_3O_4 :ethanol:DMF molar ratio of 0.07:1:49.7:12.3. In these conditions, as the reaction progresses, the Mn_3O_4 NCs co-assemble with the liquid crystalline block copolymer, and eventually formed a hybrid polymer–NC supramolecular mesostructure. This intermediate product was then calcined in air at 350 °C for 4 hours to yield a Mn_3O_4 NC-linked mesoporous network with 3D interconnected porosity. The complete elimination of the polymer template was confirmed by thermogravimetric (TG) analysis, where the mesoporous sample did not show any appreciable weight loss up to 600 °C (**Figure 55**).



Figure 55. TG profiles for as-prepared containing surfactant (black line) and mesoporous (red line) Mn₃O₄ NC assemblies recorded under air flow. The differential thermogravimetric (DTG) curve (dashed line) for as-prepared materials is also given.

The porous structure of the as-obtained Mn₃O₄ MNAs material was characterized by smallangle X-ray scattering (SAXS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and N₂ physisorption. The SAXS pattern is shown in **Figure 56**, where a relative broad but resolve scattering peak at 0.49 nm⁻¹ q (=4 π ·sin θ/λ , where 2 θ is the scattering angle and λ is the wavelength of Cu irradiation) range can be observed. The peak position of this reflection corroborates to the NC aggregates with an average interparticle spacing (from d = $2\pi/q$) of 12.8 nm. Moreover, analysis of the scattering data by the Guinier equation [135] showed that the constituting nanoparticles have an average particle size of about 6.9 nm (**Figure 56, inset**). As we will show below, this particle size is very close to the diameter of the starting materials (ca. 7 nm, as determined from XRD data, see below), which implies minimal grain coarsening of Mn_3O_4 NCs during synthesis.



Figure 56. SAXS pattern of the mesoporous assemblies from Mn₃O₄ NCs. Inset: Guinier plot $(\ln[I(q)] \propto q^2 \cdot R_g^2/3)$, where R_g is the radius of gyration $(q \cdot R_g < 1)$ for the Mn₃O₄ MNAs sample derived from the low *q*-region of the scattering curve. The red line is fit to the data.

Typical TEM images of the Mn_3O_4 MNAs are shown in **Figures 57a** and **57b**. The images reveal a disordered porous network that is constructed solely by individual nanoparticles with grain sizes 6.7 ±0.9 nm (see the inset in **Figure 57a**), in agreement with SAXS results. To probe the crystal structure of the mesoporous framework, we utilized high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). The HRTEM image, in inset of **Figure 57b**, displays a portion of the porous structure and demonstrates the high crystallinity of constituting nanopartilces; it shows distinct lattice fringes with 2.9 and 4.9 Å interplanar spacings, which

correspond to the (200) and (101) crystal planes (along the [010] direction) of tetragonal Mn_3O_4 , respectively. Besides, the SAED pattern, in **Figure 58**, reveals that the Mn_3O_4 NCs embedded in the pore walls are randomly oriented, showing a series of Debye-Scherrer diffraction rings that can be assigned to the hausmannite structure of Mn_3O_4 (JCPDS card no. 24-0734).



Figure 57. (a, b) Representative TEM images (inset of panel a: particle-size distribution histogram showing an average particle diameter of 6.7 ± 0.9 nm) and high-resolution TEM image of an individual Mn₃O₄ NC (inset of panel b).



Figure 58. SAED pattern for the Mn₃O₄ MNAs sample.

Consistent with electron microscopy studies, the wide-angle XRD pattern of the Mn₃O₄ MNAs material revealed its highly crystalline nature as shown in **Figure 59**. All of the diffraction peaks can be readily indexed to the hausmannite phase of Mn₃O₄ with a tetragonal lattice structure (space group: I41/amd). It is worth noting that the XRD pattern of Mn₃O₄ MNAs is identical to that of the precursor nanoparticles, and no other diffraction peaks were detected for impure crystalline phases (e.g., Mn_2O_3 and MnO_2 oxides). This is collaborated with Raman spectroscopy results, which indicates only the characteristic shifts of hausmannite structure for the Mn₃O₄ MNAs, see Figure 60. The prominent peak at ~647 cm⁻¹ and three weak features at 281, 304, and 362 cm⁻¹ in the Raman spectrum are indicative of the Ag symmetry stretching mode and out of plane bending modes of Mn₃O₄ in the sample[158, 159]. In addition, the Raman spectrum also confirms the high pure phase of the Mn_3O_4 since no other peaks, which could be assigned to any other oxide of Mn, were detected. Also, the broadening of the XRD peaks suggests that Mn₃O₄ occurs as very finegrained particles. On the basis of Scherrer analysis [160] of the (211) reflection, the average domain size of Mn_3O_4 crystallites was estimated to be ~7 nm for both mesoporous Mn_3O_4 assemblies and precursor (BF_4 -capped) Mn_3O_4 NCs. Taken together with TEM images, these results verify that the constituting Mn₃O₄ nanoparticles prevent, to a great extent, interparticle sintering and maintain their initial nanostructure during heating treatment.



Figure 59. XRD patterns of (i) mesoporous Mn₃O₄ assemblies (Mn₃O₄ MNAs) and (ii) isolated BF₄⁻-capped Mn₃O₄ NCs.



Figure 60. Raman spectrum of the Mn₃O₄ MNAs.



Figure 61. N₂ adsorption–desorption isotherms at -196 °C and the corresponding NLDFT poresize distribution plots (inset) of the polymer templated mesoporous assemblies (Mn₃O₄ MNAs) (i) and random aggregates (Mn₃O₄ RNAs) (ii) of Mn₃O₄ NCs (STP: standard temperature and pressure).

The porosity of the template-free material was examined by nitrogen physisorption measurements. Figure 61 shows N₂ adsorption–desorption isotherms and the corresponding pore size distribution plot for mesoporous Mn₃O₄ assemblies (Mn₃O₄ MNAs) along with those of nontemplated analogous. The adsorption isotherm of the Mn₃O₄ MNAs sample is of type IV with a combination of H₂ and H₃-type hysteresis loop (according to IUPAC classification), which is ascribed to an interconnected mesoporous structure with slit-like pores [161]. The Brunauer-Emmett-Teller (BET) surface area and total pore volume assessed from the adsorption branch of the isotherms are 90 m²/g and 0.19 cm³/g, respectively. The mesoporous Mn_3O_4 assemblies feature a narrow non-local density functional theory (NLDFT) pore-size distribution with the maximum of the peak centered at ~6.6 nm (Figure 61, inset). This pore size is related to the void space among the assembled nanoparticles. Given an average interparticle distance of 12.8 nm (determined by SAXS), the difference between the repeat distance and the pore size gives an estimate of the wall thickness at 6.2 nm. This value corresponds well with the diameter of the Mn₃O₄ nanoparticles obtained by TEM (ca. 6.7 nm) as well as SAXS analysis (ca. 6.9 nm). Thus, it appears that the layers of interconnected nanoparticles that comprise the walls of Mn₃O₄ MNAs are single.

Crucially, the polymer-templated ASA process yielded porous network of assembled Mn_3O_4 NCs with mesoscale porosity. For comparison, in the absence of template, the BF_4^- -capped Mn_3O_4 NCs are randomly aggregated into close-packed structures. This is illustrated by the N₂ adsorptiondesorption isotherms shown in **Figure 61**; the shape of which confirms the difference in morphology between the templated and nontemplated NC assemblies. The N₂ adsorptiondesorption isotherms of the random aggregates of Mn_3O_4 NCs (Mn_3O_4 RNAs) are of type IV with a H₃-type hysteresis loop, typically found with random porous networks with slit-like pores [161]. Analysis of the adsorption data reveals that this sample has a BET surface area of 107 m²/g and a total pore volume of 0.10 cm³/g. In addition, the estimated NLDFT pore-size distribution plot (assuming slit-shaped pores) indicates the formation of NC aggregates with ca. 2.7 nm-sized interstitial voids. In order to estimate the micropore volume in these materials, we performed CO₂ physisorption measurements at 0 °C and the obtained isotherms were analyzed by the Dubinin-Radushkevich (DR) method (**Figure 62**). The DR plot for the Mn₃O₄ assemblies prepared with polymer template shows a micropore volume of 0.02 cm³/g (corresponding to a microporosity of ~11%), while random aggregates of Mn₃O₄ NCs show a micropore volume of 0.05 cm³/g (corresponding to a microporosity of about 50%). On the basis of the above results, it can thus be concluded that the polymer-templated sample mainly contains mesopores within the assembled structure, while the randomly agglomerated nanoparticles adopt a more densely packed structure with significant fraction of micropores (d < 2 nm).



Figure 62. (a) CO_2 adsorption isotherms measured at 0 °C and (b) Dubinin-Radushkevich (DR) plots for mesoporous assemblies (Mn₃O₄ MNAs, green symbol) and random aggregates (Mn₃O₄ RNAs, orange symbol) of Mn₃O₄ NCs.

4.2 Catalytic activity of Mn₃O₄ MNAs

To assess the catalytic activity of the Mn_3O_4 MNAs and to determine the optimum reaction conditions, the oxidations of styrene (1) using different oxidants and solvents was initially study. Following various catalytic experiments, an almost quantitatively conversion of 1 (ca. 93%) was observed in the presence of 10 mol % (based on 1) Mn_3O_4 MNAs catalyst and 3 equivalents of *tert*-butyl hydroperoxide (TBHP) in 2 mL of CH₃CN, within 3 hours (Table 1, entry 3). In all cases, the corresponding benzaldehyde (1a) was observed as the major product accompanying with small amounts of phenyl acetaldehyde (1b), epoxystyrene (1c) and double oxidative product 2oxo-2-phenylacetaldehyde (1d), see Table 6.



Figure 63. Catalytic oxidation of styrene (**1**) to benzaldehyde (**1b**) over Mn₃O₄ MNAs catalyst in different solvents. Reaction conditions: 0.4 mmol **1**, 0.04 mmol catalyst, 3 equivalents TBHP, 2 mL solvent, 70 °C, 3 hours.

Noted that addition of equimolar amount of TBHP (with respect to 1) resulted in incomplete oxidation of 1, while in the presence of 2 equivalents of TBHP, a 60% conversion of 1 was observed in 3 hours (**Table 6**, entries 1 and 2). The increase of the TBHP amount (5 equiv.) did

not result in a significant enhancement of the transformation of **1**, while the selectivity to **1a** notably decreased (**Table 6**, entry 4). Among the solvents studied, the catalytic performance of Mn_3O_4 MNAs can be improved when the reaction is carried out in acetonitrile, affording 61% yield of **1a** in 3 hours; comparatively, methanol and ethanol resulted in a lower oxidation activity, giving **1a** in 49% and 22% product yield, respectively, under similar conditions (**Figure 63**). This is probably due to the efficient coordination of **1** to the surface-active sites of Mn_3O_4 in polar solvents.

Meanwhile, no appreciable oxidation of **1** takes place when molecular oxygen (1 atm) and hydrogen peroxide (H₂O₂) were used as oxidants under the same conditions (**Table 6**, entries 5 and 6). Besides, in the case of H₂O₂ oxidation (3 equiv.), a large amount of gas bubbles appeared as soon as the oxidant was injected into the reactor, implying a fast catalytic decomposition of H₂O₂ by the Mn₃O₄ nanoparticles. The reaction activity also strongly depends on the catalyst loading and reaction temperature. We found that the optimum catalyst loading for **1** oxidation was attained at 10 mol % (see **Table 6**, entries 7 and 8). At 50 °C, the conversion to **1a** was moderate (ca. 46%, **Table 6**, entry 9), while upon increasing the temperature at 70 °C, **1** was selectivity oxidized to **1a** with 61% yield. Higher reaction temperature (90 °C), however, did not result in significant improvement of **1a** formation (**Table 6**, entry 10). Moreover, control experiments showed that in the absence of catalyst or TBHP oxidant, no oxidation of **1** occurred (even over a 4-hour reaction period), indicating that oxidation reaction is really a catalytic process.

It is notably that Mn_3O_4 MNAs shows higher catalytic activity than individual Mn_3O_4 NCs and random aggregates of Mn_3O_4 NCs. In particular, when BF_4 -capped Mn_3O_4 NCs were introduced as catalyst, they afforded a **1** conversion of 53% in 3 hours (**Table 6**, entry 11), which is remarkably lower than that of Mn_3O_4 MNAs. This may be attributed to the aggregation of NCs, resulting in a decreased number of active sites available for catalysis. Also, random Mn_3O_4 NC aggregates (Mn_3O_4 RNAs), although possess higher surface area, gave a lower conversion of **1** (ca. 65%), under identical conditions (**Table 6**, entry 12). Overall, these findings suggest that the high activity of the Mn_3O_4 MNAs can be attributed to the small grain size of Mn_3O_4 particles, which provides a large number of surface-active sites, and the 3D mesoporous structure, which facilitates reactant contact with the nanoparticle surface. In agreement to this, we also found that use of Mn_3O_4 micropowder (BET surface area < 1 m²/g) resulted in approximately two times lower activity than that found for mesoporous assemblies of Mn_3O_4 NCs (see **Table 6**, entry 13).

Table 6. Conditions evaluation in the oxidation of styrene (1) using various Mn_3O_4 -based catalysts and oxidants.



Entry	Catalyst	Oxidant	Conv. (%) ^[b]	Yield (%) ^[b]			
				1a	1b	1c	1d
1 ^[c]	Mn ₃ O ₄ MNAs	TBHP	38%	27%	4%	3%	4%
2 ^[c]	Mn ₃ O ₄ MNAs	TBHP	60%	38%	7%	9%	6%
3	Mn ₃ O ₄ MNAs	ТВНР	88%	61%	7%	12%	8%
4 ^[c]	Mn ₃ O ₄ MNAs	TBHP	93%	50%	10%	24%	9%
5	Mn ₃ O ₄ MNAs	O_2	Nr ^[d]				
6	Mn ₃ O ₄ MNAs	H_2O_2	<1%	<1%			
7 ^[e]	Mn ₃ O ₄ MNAs	TBHP	64%	42%	5%	12%	5%
8 ^[e]	Mn ₃ O ₄ MNAs	TBHP	74%	49%	6%	14%	5%
9 ^[f]	Mn ₃ O ₄ MNAs	TBHP	70%	46%	8%	9%	7%
10 ^[f]	Mn ₃ O ₄ MNAs	TBHP	92%	62%	9%	13%	8%
11	Mn ₃ O ₄ NPs	TBHP	53%	34%	4%	12%	3%
12	Mn ₃ O ₄ RNAs	TBHP	65%	40%	6%	9%	9%
13	Mn ₃ O ₄ bulk	TBHP	45%	31%	3%	6%	5%

[a] Reaction conditions: **1** (0.4 mmol), catalyst (0.04 mmol, 10 mol % with respect to **1**), TBHP (3 equiv.), CH₃CN (2 mL), for 3 hours at 70 °C. [b] Based on the consumption of **1** determined by GC-MS. [c] These experiments were performed with 1 equivalent (entry 1), 2 equivalents (entry 2) and 5 equivalents (entry 4) of TBHP. [d] No reaction. [e] These experiments were performed with 0.02 mmol (entry 7) and 0.06 mmol (entry 8) of catalyst. [f] These reactions were carried out at 50 °C (entry 9) and 90 °C (entry 10).

Remarkably, the catalytic activity of Mn_3O_4 MNAs compared higher or even comparable to that of other commonly used metal oxide catalysts. For example, Mn_3O_4 MNAs catalyst outperforms the catalytic activity of MoO_3 [162], MoO_2 [163], Fe_3O_4 [164], $NiFe_2O_4$ [165] and $Mg_{0.4}Fe_{2.6}O_4$ [165] nanoparticles, NiCoFe spinel-type oxide nanosheets [166], NiO and CoO microparticles [167] and mesoporous vanadium silicate-1 zeolites [168], while it nearly as effective as the Co₃O₄ [169] and CuO [170] nanoparticles and Zr-doped CeO₂ nanorods [171] studied under similar reaction conditions (see **Table 7**).

Catalyst	Styrene (mmol)	Catalyst (mol%)	TBHP (equiv.)	Conv. (%) (Select. (%)) ^[a]	Temp. (°C) /Time (h)	Ref.
MoO ₃ NPs	1	1	2	85% (23%)	80 °C/24 h	[162]
MoO ₂ NPs	1	1	2	71% (71%)	80 °C/24 h	[163]
Fe ₃ O ₄ NPs	10	~4	1 ^[b]	37% (68%)	60 °C/12 h	[164]
NiFe ₂ O ₄ NPs	10	~4	1 ^[b]	31% (56%)	60 °C/12 h	[165]
Mg _{0.4} Fe _{2.6} O ₄ NPs	10	~5	1 ^[b]	41% (67%)	50 °C/24 h	[165]
NiCoFe ^[c]	10	100 mg	1.2	77% (64%)	80 °C/12 h	[166]
NiO	10	~13	1.5	55% (90%) ^[d]	83 °C/3 h	[167]
CoO	10	~13	1.5	47% (73%) ^[d]	83 °C/3 h	[167]
VS-1 ^[e]	1	~20	1	85% (50%)	100 °C/12 h	[168]
Co ₃ O ₄ NPs	10	1.2	3 ^[b]	97% (88%) ^[d]	60 °C/8 h	[169]
CuO NPs	1	6	2.5	87% (82%)	70 °C/3 h	[170]
Zr/CeO2 NRs[f]	4.35	~7	2	78% (79%) ^[d]	80 °C/12 h	[171]
Mn3O4 NCAs	0.4	10	3	88% (70%)	70 °C/3 h	This work

Table 7. Comparison of catalytic data for styrene oxidation by mesoporous Mn_3O_4 NC assemblies (Mn_3O_4 MNAs) and other reported catalysts from the literature.

[a] Selectivity $[100 \times (\% \text{ yield})/(\% \text{ conversion})]$ to benzaldehyde, [b] With H₂O₂ as the oxidant, [c] NiCoFe spinel-type oxide nanosheets, [d] Selectivity to styrene epoxide, [e] Mesoporous vanadium silicate-1 zeolite (0.37 wt.% V), [f] Zr-doped CeO₂ nanorods (10 mol % Zr).

The Mn_3O_4 MNAs also demonstrated exceptionally high stability under the examined conditions. The reusability of the catalyst was assessed by performing repeated catalytic tests, in which **1** was oxidized under the reaction conditions described above. After each test, the catalyst was recovered from the reaction mixture by filtration, washed several times with deionized water and used for the next catalytic run. Catalytic results, shown in **Figure 64**, indicated that the conversion level of **1** remains as high as 88–90% (at 3 hours reaction time) after five catalytic runs, reflecting excellent reusability.



Figure 64. Recycling study of Mn_3O_4 MNAs in the oxidation of styrene (1). Reaction conditions: 0.4 mmol of substrate, 0.04 mmol of catalyst, 3 equivalents of TBHP, 2 mL of CH₃CN, 70 °C.

Characterization of the regenerated catalyst by XRD showed that the phase remained Mn_3O_4 and the crystallite size did not change (ca. 7 nm, as determined by Scherrer analysis), **Figure 65**. However, N₂ physisorption measurements revealed that the retrieved sample has a BET surface area of 68 m²/g, which is lower than that of the fresh catalyst (ca. 90 m²/g), and a pore volume of 0.12 cm³/g. In addition, pore size analysis points to the formation of a slightly wider pore-size distribution with a peak maximum at 6.3 nm (**Figure 66**). These preliminary studies indicate a

structural deformation (i.e., small shrinkage of the pore structure) of the Mn₃O₄ NC assemblies during catalysis. To check the possibility of leaching Mn from catalyst, ICP-MS analysis was performed on the solution following a 15-hours reaction time (after the catalyst was removed by centrifugation). The results indicated that there is no leaching of Mn to the solution phase; the metal content was below the detection limit of 0.3 ng/L.



Figure 65. Powder XRD pattern of five times reused Mn_3O_4 MNAs catalyst. Scherrer analysis on the (211) reflection indicates a Mn_3O_4 crystalline size of about 7 nm.



Figure 66. N₂ adsorption–desorption isotherms at -196 °C and the corresponding NLDFT pore size distribution (inset) of the regenerated Mn₃O₄ MNAs catalyst.

To study the general applicability of the above oxidation process, various *para*-substituted styrenes (2 and 3) and cyclic alkenes (4 and 5) were examined. Figure 67 summarizes the results obtained from these oxidation reactions using Mn₃O₄ MNAs catalyst and TBHP oxidant. As can be seen, both methyl (2) and chloro (3) *para*-substituted styrenes were selectively oxidized by the Mn₃O₄ MNAs, yielding the corresponding aldehydes (2a and 3a) as the only products. However, oxidation of electron-deficient aromatic styrene 2 (*p*-Cl-substituted) proceeded faster than electron-rich styrene 3 (*p*-Me-substituted), giving the respective aldehyde in 98% and 90% yield, respectively, in 3 hours. Furthermore, an almost quantitative consumption (ca. 95%) of cyclohexene (4) was observed by GC-MS under the conditions described above, in which the corresponding conjugated cyclohexenone (4a) was obtained at 90% relative yield with a small amount of the allylic cyclohexanol (4b, 5% yield) in 2 hours. However, in contrast to cyclohexene, cyclooctene (5) was oxidized to cyclooctene oxide (5a) and cyclooctene (5b) at 31% and 12%

relative yields, respectively. Noted that aliphatic 1-octene does not oxidized under the present conditions (results not shown).



Figure 67. Time profiles of *para*-substituted styrenes and cycloalkenes (2–5) oxidation over Mn_3O_4 MNAs catalyst.

Regarding the mechanism of these organic transformations, we believe that a radical process probably is involved in the oxidation of alkenes to carbonyl compounds; although the formation of a metal dioxirane-type intermediate due the interaction of TBHP with the Mn_3O_4 catalyst cannot be excluded. This hypothesis found support from above oxidation reactions in which electron-rich aryl alkenes (styrenes) were oxidized faster than cyclic and aliphatic alkenes. In addition, further evidence could be obtained by the oxidation of a series of aromatic saturated hydrocarbons, such as ethyl benzene (**6**), diphenylmethane (**7**), fluorene (**8**) and cumene (**9**). In general, the oxidation of saturated α -carbon C–H bonds in aromatic alkanes, under mild oxidative conditions, represents one of the most important and synthetically useful reactions [172]. Such organic transformations usually suffer from very low selectivity and proceed under harsh reaction conditions, like high temperature and pressures or high-energy radiation. Surprisingly, under the examined conditions, the aromatic hydrocarbons **6–8** were selectively oxidized to the desired carbonyl compounds (**6a–8a**) in appreciable yields, as shown in Scheme 2. While very small amounts (~1–5% product yields) of the corresponding secondary alcohols **6b–8b** were detected among the reaction mixture by GC-MS. This observation indicates that the oxidation reaction proceeds through the initial formation of the corresponding alcohols, which rapidly oxidized to ketones **6a–8a**. In order to support this assumption, we examined the oxidation of 1-phenylethanol (**6b**) under the same conditions. Indeed, within 3 hours, acetophenone (**6a**) was obtained as the only product in 91% yield (**Figure 68**). In the case of cumene (**9**), acetophenone (**9a**) was observed by GC-MS and 1H NMR as the major product, accompanying with a significant amount of the corresponding tertiary alcohol (**9b**, ~9% product yield). Acetophenone is a C–C bond cleavage product which is formed from the corresponding peroxy- or alcoxy radical intermediate during the oxidation process [173-175].



Figure 68. Oxo-functionalization of aromatic hydrocarbons **6–9** into the corresponding carbonyl compounds catalyzed by Mn_3O_4 MNAs. In parentheses: the corresponding isolated yield and selectivity. Reaction conditions: 0.4 mmol substrate, 0.04 mmol catalyst, 3 equivalents TBHP, 2 mL CH₃CN, 70 °C.

Of particular note, Mn₃O₄ MNAs catalyst also exhibited very good catalytic activity and chemoselectivity in oxidation of aliphatic cycloalkanes, such as cyclooctane (**10**), with TBHP. Catalytic results showed that **10** oxidized to the corresponding cyclooctanone (**10a**) in 51% yield, accompanied with cyclooctanol (**10b**) in low yield (6%) within a 3-hours reaction period. To the best of our knowledge, there is no report that describes cyclooctane oxidation with such a high relative yield (89%) to cyclooctanone using Mn-based catalyst. Overall, these findings suggest that the present Mn₃O₄ MNAs/TBHP catalytic system represents an expeditious approach towards a lab as well as a large-scale production of carbonyl compounds from styrenes or aromatic hydrocarbons in high yields and selectivity.

CHAPTER 5 CONCLUSIONS

Summing up, high-surface-area mesoporous networks of spinel ferrite NCs from a block copolymer-directed aggregating self-assembly of colloidal NCs have been prepared. These nanoarchitectures are solely constructed of a continuous mesoporous network consisting of connected nanoparticles (ca. 6-8 nm in average diameter), which provides a spatial delocalization of charge-carriers and exhibits a high surface area (ca. $105-159 \text{ m}^2/\text{g}$) accessible to the reactants. We for the first time show that mesoporous assemblies made of zinc ferrite (ZnFe₂O₄) NCs perform as a viable photocatalyst, attaining improved Cr(VI) reduction photocatalysis and excellent cyclic stability without the additional use of additives (hole scavenges). Indeed, the unprecedented activity of ZFO MNAs towards Cr(VI) photoreduction is attributed to its suitable band edge positions, 3D interconnected porous structure, large internal surface area (up to 159 m^2/g), and small grain composition. Control catalytic experiments coupled with transient gas analysis and fluorescence spectroscopy data showed that Cr(VI) photoreduction reaction proceeds simultaneously with the competitive formation of oxygen and hydroxyl (•OH) radicals via a holemediated oxidation of adsorbed water or hydroxyl groups on the catalyst surface. Moreover, an addition of phenol favors the oxidation half-reaction through an efficient utilization of surfacereaching holes, which is beneficial to the acceleration of the photocatalytic reaction. The results demonstrate spinel ferrite NC assemblies as a highly efficient and stable photocatalytic system for solar light-driven environmental pollution purification and energy conversion.

Additionally, high-surface area mesoporous binary x% MFO-ZFO NC assemblies were also successfully synthesized via a polymer assisted co-assembly of colloidal ZFO and MFO nanoparticles and amphiphilic block copolymer aggregates. These samples were used as photocatalysts for the detoxification of Cr(VI) aqueous solutions in the presence of phenol. Results indicated that the high photocatalytic activity of 6.5% MFO-ZFO MNAs catalyst compared to single-components MFO and ZFO MNAs is presumably a result of the combined effect of accessible pore volume and appropriate band edge positions for Cr(VI) reduction and phenol oxidation. The remarkable activity and durability of the 6.5% MFO-ZFO MNAs implies the great possibility of implementing this new catalyst into a realistic Cr(VI) detoxification of contaminated water.

Finally, mesoporous assemblies of Mn₃O₄ NCs (Mn₃O₄ MNAs) with accessible pores can be synthesized through a polymer-assisted aggregating self-assembly method. The successful synthesis of this material highlights the general applicability of the proposed method to produce high-surface-area mesoporous networks of cross-linked metal oxide nanoparticles. Structural characterization with SAXS, TEM, XRD and N₂ physisorption indicated that Mn₃O₄ MNAs material consists of an interconnected network of 6–7 nm-sized hausmannite (Mn₃O₄) NCs and exhibits a large surface area of 90 m^2/g with a narrow range of pore sizes (with a peak maximum centered at about 6.6 nm). These mesoporous Mn_3O_4 assemblies demonstrate great application perspectives in catalytic oxo-functionalization of various aromatic and cyclic alkenes as well as aryl alkanes with tert-butyl hydroperoxide (TBHP). As compared to individual Mn₃O₄ NCs, randomly aggregated Mn₃O₄ NCs and bulk Mn₃O₄ solid, the higher reactivity of Mn₃O₄ MNAs is attributed to the 3D open-pore structure and large accessible surface area, which allow facile mass transport throughout the assembled structure. Moreover, product analysis indicated that the reaction between the selected alkenes and the TBHP-Mn₃O₄ catalyst proceeds via an allylic oxygenate intermediate obtained by a radical process. These results open up the possibility of using mesoporous assembled structures of small-sized Mn₃O₄ NCs for selective alkene and aryl alkane oxidations.

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