



Assembly and photochemical properties of mesoporous networks of spinel ferrite nanoparticles for environmental photocatalytic remediation

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ABSTRACT

Spinel ferrite materials have an electronic band structure that is well suited for visible light-induced catalysis, however, their photocatalytic activity remains low due to the daunting charge-carrier separation process. In this article, we report that high-surface-area mesoscopic architectures composed of tightly connected ultrasmall spinel ferrite nanocrystals can efficiently suppress electron-hole recombination, manifesting an exceptional activity and magnetic recyclability in photocatalytic reduction of aqueous Cr(VI). Revealed by 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 a large internal surface area (up to 159 m² g⁻¹) and exhibit small grain composition (ca. 6–8 nm in size). Through a systematic synthesis of various structural analogues to the spinel ferrite family and optical absorption and electrochemical impedance spectroscopy analyses, we demonstrate that the electronic band structure fits the electronic requirements for both Cr(VI) reduction and water oxidation under UV–vis light irradiation. Among spinel ferrites, ZnFe₂O₄ presents 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 photocatalytic systems for efficient environmental pollution purification and energy conversion.

1. Introduction

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 [1]. Cr(VI) is a mutagenic primer and pulmonary carcinogen for living organisms, with an LD50 (lethal dose 50%) value of 50 mg kg⁻¹ [2], which readily invade the human food chains [3]. To this end, the World Health Organization (WHO) recommended a maximum allowable concentration of 50 µg L⁻¹ for Cr(VI) in drinking water [4]. Moreover, as a consequence of its high toxicity, hexavalent chromium has also been categorized as a Group I human carcinogen by the International Agency for Research on Cancer (IARC) [5]. Therefore, finding an effective way for remediation of Cr(VI)-contaminated solutions is undoubtedly 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 [6], TiO₂ [7], CdS [8], WO₃ [9] and SnS₂ [10]. 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 photooxidation) as critical challenges to be addressed for practical applications. To increase the efficiency of photoreactions, recent efforts took advantage

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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) [11,12]. Noble metal nanostructures 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 valence band (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 [13]. 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 and eventually enhance the kinetics of the Cr(VI) reduction [14]. Even though the hybridization of semiconductor structure or introduction of electron donor additives 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+} , 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, lithium-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}) [15–21]. More recently, spinel ferrites, especially zinc ferrite (ZnFe_2O_4 , ZFO), have generated increasing interest as promising photocatalysts due to their narrow band gap ($E_g \sim 1.9\text{--}2.0 \text{ eV}$), favorable conduction band (CB) alignment for water splitting, good photochemical stability, low cost and easy magnetic separation [22–24]. As a consequence, ZFO-based materials have been exploited for photo-Fenton-like degradation of organic dyes [25–27] and photochemical hydrogen production [28,29]. 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 [30–32]. 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 photo-generated excitons would be available for redox reactions.

We have recently developed a method to assemble mesoporous networks of connected metal oxide nanoparticles (NPs). The synthetic procedure involves a polymer-templated self-assembly of colloidal NP building blocks followed by thermal annealing at elevated temperatures. This strategy is straightforward, cost-effective, and, more importantly, offers precise control over pore size, porosity and chemical composition of the assembled structures [33–36]. Of particular interest is that these porous materials exhibit the unique combination of accessible mesopores, small grain composition, and tunable visible light

response – all these characteristics are especially advantageous for constructing high-performance photocatalysts.

In this study, a series of mesoporous architectures of spinel ferrite NPs with an average diameter of 6–8 nm was synthesized using a block copolymer-assisted cross-linking aggregation of colloidal NPs and their impressive performance for photocatalytic detoxification of aqueous Cr(VI) solutions was demonstrated under UV and visible light illumination. In particular, we used different spinel ferrite nanobuilding blocks to construct open-pore network structures of connected NPs with large internal surface area and uniform mesopores. 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, we show that mesoporous zinc ferrite (ZnFe_2O_4) assemblies, due to their unique three-dimensional (3D) porous structure, improved charge transfer along the NP-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 here by performing controlled experiments of fluorescence spectroscopy and oxygen evolution reaction coupled with mass spectrometry. These findings provide an insight into the activation of Cr(VI) detoxification catalysis through the use of suitable electron-donating reagents.

2. Experimental

2.1. Materials

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) block copolymer (Pluronic P123, $M_n \sim 5800 \text{ g mol}^{-1}$), toluene (99.7%), absolute ethanol, sodium dodecylbenzenesulfonate (NaDBS, technical grade) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, > 99.8%) were obtained from Aldrich Chemical Co. Sodium hydroxide (NaOH, 98%) and 3-aminopropanoic acid (3-APA, 99%) were purchased from Acros Organics. Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98%), zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), manganese (II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98%), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), cadmium (II) nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98%), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 97.7%) and phenol (> 99.5%) were acquired from Sigma-Aldrich. All chemicals were used as received without further purification.

2.2. Synthesis of spinel ferrite NPs

Spinel ferrite (MeFO , Me = Zn, Mn, Ni, Cd and Co) NPs with an average diameter of 6–7 nm were prepared according to a modified literature procedure [37]. For a typical synthesis of ZFO NPs, Zn ($\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (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 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 h. 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 $350 \text{ }^\circ\text{C}$ for 12 h. The other spinel ferrite NPs, MnFe_2O_4 (MFO), NiFe_2O_4 (NFO), CdFe_2O_4 (CdFO) and CoFe_2O_4 (CoFO), were synthesized in a similar procedure, using the corresponding metal nitrate precursor.

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