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# Novel Magnetically Hollowsphere Zn-Doped Magnetite for the Efficient Photo-Reduction of Cr(VI)

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## ABSTRACT

Uniform and magnetic recyclable hollowsphere Zn doped $Fe_3O_4$ were successfully synthesized via simple one-pot solvothermal route. Morphology and structure of as-obtained products was characterized by XRD, SEM, HRTEM methods. The Zn-doped $Fe_3O_4$ hollowsphere exhibited high photocatalytic activity for degradation of hexavalent chromium under visible light irradiation. The effects of reaction conditions such as initial pH, photocatalyst dosage and hexavalent chromium contratentation were also studied systematically. The stability of the catalysts and and possible catalytic mechanism was also proposed. The results indicate that Zn doped $Fe_3O_4$ can be promising catalyst for photo-reduction of hexavalent chromium.

## Introduction

Recently, fast development of global industrial and economic is resulting in the great amount of heavy metal pollution in water such as Cd, As, Hg, Cr… Among of these heavy metals, hexavalent chromium is considered as one of reasons for carcinogenic and toxic, while trivalent chromium is friendly-environment and one of trace elements for animal and human. Specially, Cr(III) can be precipitated and separated from solution by adjusting alkaline or neutral pH. Therefore, transformation of Cr(VI) into Cr(III) should be conducted before getting rid of effluents on surface water sources. The traditional routes to eliminate wastewater polluted by Cr(VI) are adsorption by adsorbent [1], precipitation and ion exchange [2], reduction of Cr(VI) with zero-valent aluminum[3]. Recently, using photocatalytic materials for reducing Cr(VI) are getting the great attention due to its low-cost, high efficiency and friendly-environment. The different photocatalysts as $TiO_2$[4], ZnO[5], Ti-Fe kaolinite [6] have been employed to reduce Cr hexavalent. However, some problems is still remaining while using semiconduction catalyts to photo-reduce Cr(VI) such as low potential adsorption light, low efficiency, complexity in preparing and separation and recycling.

Recent years, metal doped oxide, spinel oxide nanopartlicles have attracted much more attention due to their enhanced electrical conductivity, interesting magnetic properties and high photocatalyst activities. Among the spinel oxides, $Fe_3O_4$ nanoparticles with a cubic spinel structure where a half of $Fe^{3+}$ ions occupy in all the tetrahedral sites, a half of the $Fe^{3+}$ ions and all the $Fe^{2+}$ ions local on the octahedral sites, are considered as promising materials in many fields owing to its abundant, low-cost, friendly-environment, easy controllable synthesis and interesting magnetic properties.

Herein, we successfully prepared uniform Zn doped $Fe_3O_4$ hollowpheres via a simple solvothermal route in absence of any surfactants. The as-obtained products showed porosity hollow properties. The catalytic property of the as-obtained products in photo-reduction Cr(VI) was evaluated by under visible light irradiation.

## Experimental

### *Materials*

All chemicals used in this work were from Sinopharm Chemical Reagent Co., Ltd, China without further treatment and purification. De-ionized water was used in the whole experiments.

### *Mesocrystal preparation*

Zn-doped $Fe_3O_4$ hollow were prepared by a simple hidrothermal approach with ethylene glycol as solve [7]. Brief, among of Zin chloride and iron (III) chloride hexahidrate and amoniacetate were putted in 100 ml of ethylene glycol followed by stirring for 0.5h. After that, the solution was treated by ultrasonic (at 59 Hz) for 30 mins. The solution was transferred to autoclave and heated at 200 °C for 24h. The black materials was recovered by a magnet then washed with ethanol and deionized water for several times. Finally, product powder was dried at 80 ºC for 12h before further usage.

### *Characterization*

X-ray diffraction (XRD) analysis was carried out using a X-ray powder diffractometer with Cu Kα radiation at 40 kV and 50 mA. The morphology and internal structure of the prepared samples were further checked by transmission electron microcopy (TEM), high-resolution transmission electron microcopy (HRTEM) using a JEOL JEM-2010 HR electron microscope operated at a voltage of 200 kV and equipped with a Gatan GIF Tridiem system.

### *Photo-Reduction Cr(VI) activity*

The photocatalytic activity of the as synthesized product was investigated by the Cr(VI) photo-reduction from aqueous solution under the visible light irradiation (300W Dy lamp with a 400 nm cut-off filter). In a typical experiment, 2 mg of the as-prepared photocatalyst was dispersed in 100 mL of 50 mg/L Cr(VI). During irradiation, 2 mL of sample was taken at different time intervals and centrifuged immediately to remove the composite particles. The residual concentration of Cr(VI) in the supernatant was measured by UV-Vis spectrophotometry at 540 nm after complexation with DPC.

## Results and discussion

### *Characterization of hollowsphere Zn-doped $Fe_3O_4$*

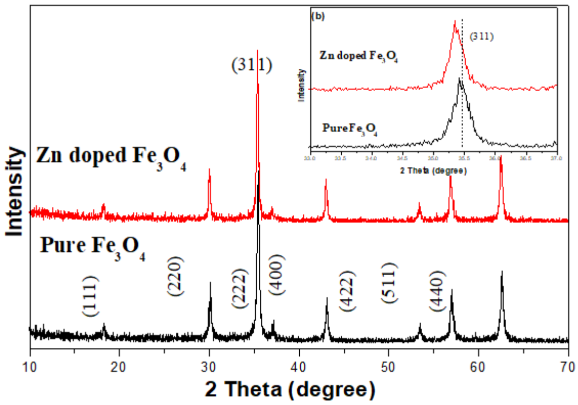

Figure 1: XRD pattern of pure $Fe_3O_4$ and Zn doped $Fe_3O_4$ at 200 °C for 24 h; the highlighted (311) diffraction peak of pure $Fe_3O_4$ and Zn doped $Fe_3O_4$ at 200 °C for 24 h (inserted)

The XRD patterns of the pure $Fe_3O_4$ and Zn-doped $Fe_3O_4$ hollowsphere are showed in Figure 1. Both the patterns indicate that all reflection peaks could be indexed to magnetite with cubic spinel structure (JCPDS 77-1545). No diffraction peaks of zinc oxide were observed, suggesting that crystalline zinc oxides did not form during the synthesis process. However, it can be learned from patterns inserted in Fig.1 that the (311) crystal plane of Zn-doped $Fe_3O_4$ slightly shifted to smaller angle and the corresponded lattice constant increased from 0.8395 nm to 0.8406 nm, which could be ascribed to the substitution of a small amount of $Fe^{2+}$ (ion radius =0.61 nm) and $Fe^{3+}$ (ion radius = 0.49 nm) in the magnetite by $Zn^{2+}$ with a larger ion radius of 0.74 nm. The results suggest that Zn has been successfully doped into the crystal structure of $Fe_3O_4$, in which doped $Zn^{2+}$ ion may tend to substitute $Fe^{3+}$ ion in tetrahedral sites and a small amount $Fe^{2+}$ ion located on octahedral sites [8,9].

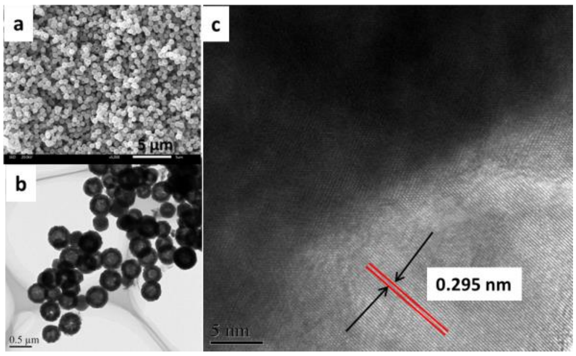

Figure 2: (a) SEM, (b) TEM images of the as-synthesized sample, (c) HRTEM image

Morphology and crystalline structure of the as prepared products were investigated by SEM, TEM and HRTEM. As depicted in Figure 2a-b, the products exposed uniform submicrosphere shape with an average size of 400 nm. The TEM image of Zn-doped $Fe_3O_4$ in Figure 1b confirms its hollow and high porosity structure by dark shell and bright center observed. The structure of the as-synthesized hollowspheres was observed by HRTEM images (Figure 2c). The lattice fringes of 0.295 nm between two adjacent lattice planes of inner core match well with the crystallographic planes (220) of magnetite with cubic spinel structure [10]. From the results, it can see that Zn doped $Fe_3O_4$ hollowsphere with internal sub-micro hole was prepared successfully.

### *Photocatalytic reduction of Cr(VI)*

#### *Cr(VI) adsorption isotherms*

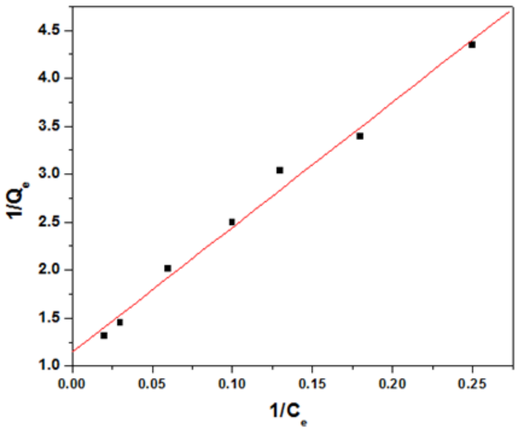

Figure 3: Lnear plot of 1/Qe versus 1/Ce.

As well-known, in heterogeneous systems, the catalytic sites often occupy on the surface of catalysts. Therefore, the adsorption of reactants on the surface plays a very important role in the hetero-catalytic reaction. It was reported that most of photocatalytic reactions followed Langmuir–Hinshelwood model in which the adsorption capacity of photocatalysts could significantly effect on the reaction efficiency[4]. To address further the photocatalytic performance of as-prepared Zn doped $Fe_3O_4$, Cr(VI) adsorption isotherms at pH 3 and room condition are conducted, which used the well-known isotherms Langmuir model as shown in Fig 3. The isotherms models can be describe in linear form by following equations:

$$\frac{Ce}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)Ce$$

$Q_e$: the equilibrium adsorption amount (mg/g); $C_e$: the equilibrium concentration of Cr (VI) (mg/l); $Q_m$: the maximum adsorption amount (mg/g); b: the adsorption constant (l/mg)

The plot of $1/Q_e$ values versus $1/C_e$ is presented in the Figure 3. The results were well fitted on the basis of high $R_2$ value (0.99) suggesting that the Cr(VI) adsorption on the Zn doped $Fe_3O_4$ can be well followed Langmuir-Hinshelwood model. The monolayer adsorption potential (Qm) was 3.47 mg/g in the equilibrium at pH 3.0.

#### *The photo-reduction of Cr(VI)*

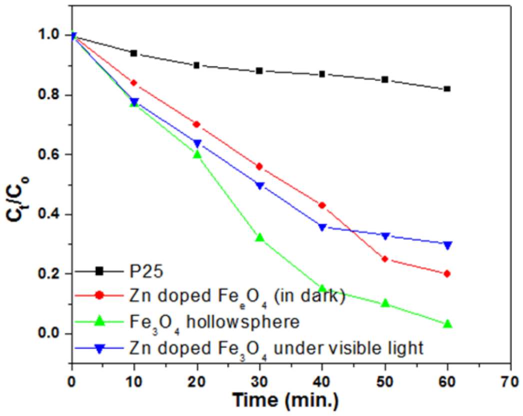

Figure 4: The photo-reduction for Cr(VI) with different photocatalysts

In the presence of Zn doped $Fe_3O_4$ hollowsphere under visible light irradiation, Cr(VI) can be reduced to Cr(III) by the exicited electrons. The overall parthway of Cr(VI) photo-reduction could be expressed as the following reactions [11]:

$Photocatalyst+h_y \rightarrow Catalyst(e_{cb},h_{vb})$ (1)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (2)

$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ (3)

To further demonstrate the excellent photocatalytic activity in the removal Cr(VI) under visible light, P25 and pure $Fe_3O_4$ hollowsphere are also employed in this experiment. The photo-reduction of Cr(VI) with different catalysts and conditions are shown in the Fig.4. It can see that Cr(VI) removal efficiency reached 97% with Zn doped $Fe_3O_4$ hollowsphere under visible light, while only reached at 78% in dark. The results also indicated that Zn doped $Fe_3O_4$ exhibited the highest photo-removal Cr(VI) compared to $Fe_3O_4$ hollowsphere and P25. The enhanced photo-reduction of Cr(VI) activity of Zn-doped $Fe_3O_4$ hollowsphere could be ascribed to unique hollow structure as well as metal doping effect of the as-prepared sample. The unique hollow structure will improve visible-light photoresponses [12]. Furthermore, the improvement of the photo-removal of Cr(VI) in the present of Zn-doped Fe$_3$O$_4$ could be attributed to that metal doping can make the electron transfer process amore accelerated[13,14].

*Effect of pH*

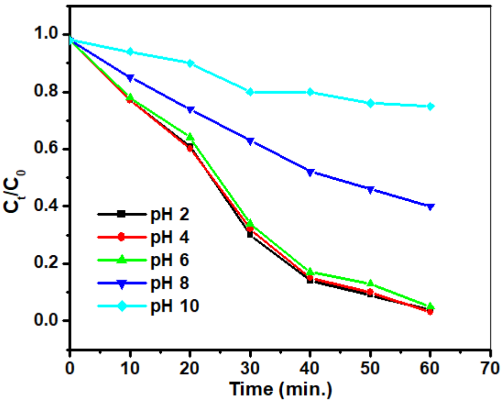

Figure 5: Effect of pH on the photo-reduction Cr(VI).

The pH of initial solution usually plays an important role in controlling the performance of contaminant removal. Therefore, the effect of initial pH on the efficiency of the photocatalytic degradation Cr(VI) also was studied. The reaction was carried out by varying pH from 2 to 10, whereas other parameters are constant. The Figure 5 illustrates the variation of the degradation of Cr(VI) at different pH. The results show clearly that the pH distinctly influence on the reaction rate whereas get higher rates in the region 2.5±6. It can see that at pH4, the reaction rate is highest. This was due to the fact that the removal of Cr(VI) both strongly dependent on the solution pH and favorable at lower pH3. The Cr(VI) exist in solution as HCrO$^{-4}$ and Cr$_2$O$_7^{2-}$, at acidic pH the HCrO$^{-4}$ is the dominant specie. Moreover, higher pH also can leads to the precipitation of Cr and Fe in the form of Cr(OH)$_3$ and Fe(OH)$_3$, which may cover surface active sites and resulting in decreased photocatalytic activity [15].

*Effect of catalyst dosage*

Catalyst content introduced in the photo-reduction Cr(VI) reaction is considered as one of the important parameters. The influence of catalyst dosage on the heterogeneous photo-degradation of Cr(VI) by Zn doped Fe$_3$O$_4$ is shown in Figure 6. Catalyst dosage of 0.05, 0.1, 0.2 and 0.4 mg/L was studied while keeping other parameters constant. The results reveal that the photo-degradation of Cr(VI) increased with added Zn doped Fe$_3$O$_4$ concentration from 0g/L to 0.2 mg/L.

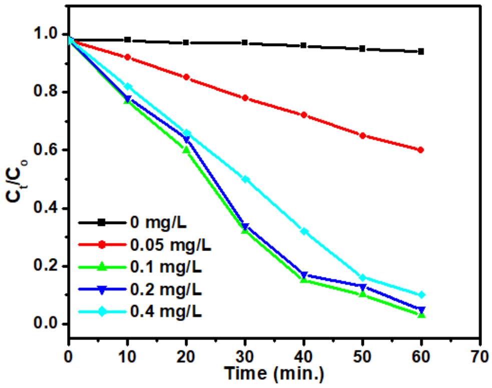

Figure 6: Effect of catalyst contents on the photo-reduction reaction of Cr(VI)

However, when the catalyst dosage was beyond 0.2 mg/L the rate of reaction decreased. The similar trend of this effect has studied by other authors[16]. At Zn doped Fe$_3$O$_4$ concentration increasing from 0 to 0.2 mg/L leaded to increase in the rate of degradation, which can be attributed to more active sites and the free reactive radical generation. The rate of reaction reduced at the higher dosage of catalyst can be assigned to the enhanced muddiness of solution, resulting in the light harvesting reduced[17].

*The stability and reusability*

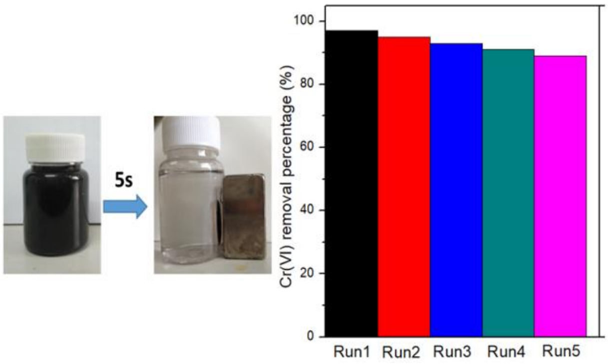

Figure 7: The recovery of the as-prepared products under an external magnetic field

In addition, the stability and reusability of Zn doped Fe$_3$O$_4$ hollowsphere in the Cr (VI) photo-reduction process were also investigated. After the experiment, the photocatalyst was collected and then it was transferred into 50 mL aqueous solution with deionized water, 0.1 M NaCl, 0.1 M HNO$_3$ and 0.1 M HCl, respectively. The mixtures were shaken at room temperature overnight, and the filtrates were analyzed to determine the concentration of Cr(VI) after desorption, the same experiment was repeated for five times. The results show that the catalyst was easily separated by an external magnetic field (Figure 7) and their photo-reduction efficiency for Cr(VI) degradation has no significant change even after the five successive cycles (losing only 3%), indicating high stability of the catalyst. These properties will play a very important role in application for water treatment at industry scale.

## Conclusion

Uniform and magnetic recyclable Zn doped $Fe_3O_4$ hollow were fabricated via a facile solvothermal process in EG solvent. The as-prepared products are uniform hollowsphere with high porosity and ferromagnetic behavior. The Zn-doped $Fe_3O_4$ hollowsphere exhibited high photocatalytic efficiency for degradation of Cr(VI) in water under visible light irradiation. The hollowsphere catalyst has high stability and is easily separated and recycled by external magnetic field and could be promising photo-reduction catalysts for the degradation of Cr(VI) in water and wastewater.

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