**Flower-like ZnO hollow microspheres on ceramic mesh substrate for
photocatalytic reduction of Cr(VI) in tannery wastewater**

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Abstract

Flower-like ZnO hollow microspheres were synthesized on flexible ceramic mesh substrate using a simple and economical hydrothermal technique and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocatalytic reduction of Cr(VI) in leather tannery wastewater by flower-like ZnO hollow microspheres was evaluated under ultraviolet light irradiation for the first time. The addition of different organics and pH value of the reaction solution played important roles in the photocatalytic reduction of Cr(VI). In addition, UV radiation intensity and catalyst content were critical parameters in the photocatalytic reduction process and their effects were also investigated. Under the optimal conditions, ZnO hollow microspheres exhibited excellent removal efficiency of Cr(VI) (~86%) and good photocatalytic stability. Moreover, more than 24% biochemical oxygen demand (BOD₅), 32% chemical oxygen demand (COD) and 30% total organic carbon (TOC) of tannery wastewater were reduced significantly after only 180 min of exposure to the UV lamp. It shows

much promise to be an attractive photocatalyst for photocatalytic application.

Keywords: ZnO, Ceramic mesh substrate, Photocatalytic reduction, Cr(VI), Tannery wastewater

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1. Introduction

The growth in civilization and industrial activities has caused a great number of environmental problems. For decades, large quantities of pollutants have been discharged into the environment irresponsibly^[1-2]. Unlike most organic pollutants, metals are particularly problematic because they are not biodegradable and can accumulate in living tissues. Although at low doses some heavy metals are essential micronutrients for plants and animals, in higher doses they can detrimentally affect the health of most living organisms^[3-4].

Hexavalent chromium (Cr(VI)) is a common heavy metal pollutant in wastewaters, which mainly comes from the irrational release of leather tanning, cooling towers, electroplating wood preservation and steel manufacturing^[5-7]. The most common chromium oxidation states in nature are Cr(III) and Cr(VI). Among them Cr(VI) is carcinogenic and toxic for the environment and human beings, whereas Cr(III) is less toxic and can be readily precipitated^[8-9]. Currently, the methods for the removal of Cr(VI) include adsorption^[10-12], biosorption^[13], electrocoagulation^[14], ion exchange^[15-16], membrane filtration^[17-18] and photocatalytic reduction^[19-21].

Among those methods, photocatalysis has attracted the attention of the scientific community since it is an economical, efficient, and clean technology for Cr(VI) reduction in aqueous media^[22-24]. Briefly, photocatalytic method is based on the reactive properties of an electron-hole pair generated in the semiconductor when irradiated by UV/vis light having energy greater than the band-gap energy of the semiconductor. If the charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with adsorbed species^[25-26]. It has been shown that the Cr(VI), highly toxic species, can be reduced to Cr(III), non-toxic species, with the help of semiconductors and light^[27].

Recently, more efforts have been devoted to exploring efficient photocatalyst for Cr(VI) reduction. Compared to some other semiconductor oxides, Zinc oxide (ZnO) is one of the most popular photocatalysts used in the photodegradation of organic and inorganic compounds, owing to its high activity, low cost and environmental friendliness^[28-30]. A number of investigations into photo-reduction of Cr(VI) have been reported^[31-33]. However, the general effluent in the industry usually consists of wastewater from each batch process and can therefore contain adverse and complex chemical mixture. No doubt that photo-reduction of Cr(VI) in industrial wastewater will greatly increase the difficulty of photocatalytic process. To the best of our knowledge, there are few scientific literatures on the treatment of Cr(VI) photoreduction in leather tannery wastewater. Moreover, most photocatalysts that have been studied previously were mobile-type, and only a few immobilized photocatalysts have been reported although they have clear advantages over

mobile-type catalysts from a practical perspective. For example, immobilized photocatalysts minimize the power required for mixing and can be recycled without an additional process and operated at flow-type reactors^[34].

In this work, flower-like ZnO hollow microspheres photocatalysts were synthesized on flexible ceramic fibers substrate through a facile hydrothermal method. The photocatalytic performances of the as-synthesized photocatalysts on the photocatalytic reduction of Cr(VI)-Cr(III) were investigated in detail and the optimal react conditions were obtained. In addition, ZnO photocatalysts were used to treat the leather tanning wastewater collected from plant under the optimal conditions and the results were also discussed in this work.

2. Experimental

2.1 Chemicals

Ceramic fibers, zinc acetate [$\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$], 99%], zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%], hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$, 99%), trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) of analytical grade were purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. The other chemicals including sodium hydroxide (NaOH, 99%), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 99.8%), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99%), methanol, hydrochloric acid (HCl, 36.0–38.0%), and formic acid were obtained from Tianjin Hongyan Chemical Reagent Co., Ltd.

2.2 Sample synthesis

ZnO hollow microspheres were synthesized on ceramic fibers (CFs) by a simple seed-assisted hydrothermal method. CFs with the area of $2\text{ cm} \times 3\text{ cm}$ were washed

with ethanol and deionized water several times to remove surface impurities. Zero-dimensional ZnO nanoparticles were first deposited as a seeding layer. Synthesis of ZnO nanoparticles was carried out by dipping 4 mM concentrations of zinc acetate dehydrate in ethanol for 10min and drying in oven at 60 °C for 10min (this process was repeated three times). Then the seed modified CFs were immersed into 200mL deionized water in a 250 mL round flask containing 0.596 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.285 g of HMTA and 0.107 g of $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$. After the solution was kept at 80 °C for 1h, the CFs coated with flowerlike ZnO hollow microspheres were taken out of the solution and dried in oven at 70 °C, as shown in Fig. S1. (The whole seeding and growth processes were repeated two times. However, the pH of the mixing solution was adjusted to 10 with 0.2 M NaOH and kept at 80 °C for 4 h in the second growth progress).

Fig. 1. Scheme illustration for synthesis route of flower-like ZnO hollow microspheres.

2.3. Sample characterization

The morphology and composition of the samples were characterized by scanning electron emission (SEM, S4800, operated at 5.0 kV) and transmission electron microscope (TEM, JEM-3010, operated at 50 kV). The crystal structure of the samples was determined by X-ray diffraction (XRD, Rigaku, D/max-2200, Japan)

with Cu Ka irradiation at 30 kV and 30 mV.

2.4. Photocatalysis tests

2.4.1. Treatment of artificial wastewater

Photocatalytic activity was first evaluated with a 250 mg L^{-1} solution of $\text{K}_2\text{Cr}_2\text{O}_7$ prepared in deionized water. The experiment was carried out in a 70 mL quartz cuvette containing photocatalyst sample ($n \times 2.0 \text{ cm} \times 3.0 \text{ cm}$) and 50 mL Cr(VI) aqueous solution. The solution pH was adjusted by 0.1 M HCl and 0.1 M NaOH solutions. The mixture was stirred and the organic compound (methanol and formic acid) was introduced into the suspension. Prior to irradiation, the suspension was ultrasonicated for 30 min and magnetically stirred for 1 h in the dark to ensure adsorption–desorption equilibration. Then the suspensions were irradiated by a 500 W UV lamp. During illumination, 2 mL of suspension was taken out from the reactor for test at a scheduled interval.

2.4.2 Treatment of tannery wastewater

Reaction conditions were first optimized by artificial wastewater, and under these conditions, tannery wastewater was collected at the outlet of tanning system and taken to the laboratory within 2h for same-day processing. The procedure for photocatalytic measurement of wastewater was similar to the degradation of $\text{K}_2\text{Cr}_2\text{O}_7$ as described in artificial wastewater.

2.5 Analytical procedures

The concentration of Cr(VI) was analyzed by the standard diphenylcarbazide colorimetric method at a wavelength of 540 nm using a TU-1900 Double Beam

UV-vis Spectrophotometer. The removal of the metal was estimated as a function of irradiation time.

Total organic carbon (TOC) was measured using a Liqui TOC II instrument. Colorimetric method 5220D^[35] of Standard Methods procedures was followed by use of a spectrophotometer (Hach Lange DR 1010), employing Pyrex-glass vials, after 2 h of extreme catalytic oxidation conditions at 150 °C to analyze the chemical oxygen demand (COD).

Biochemical oxygen demand (BOD₅) determinations were carried out according to the Standard Methods (HJ 505-2009)^[36] by using a BOD Trak II Apparatus (HACH, America). The value reported here is the average of three experiments.

3. Results and discussion

3.1 Morphology and crystal structure

Figure 1(a) presents a typical low-magnification image of flower-like ZnO hollow microspheres on ceramic fibers. Because solution-based methods were employed for both ZnO seed deposition and ZnO hollow microspheres growth, ZnO hollow microspheres were uniformly fabricated on the ceramic fibers substrate, which was webbed with round-shaped wires. The enlarged SEM images shown in Fig. 1(b) and (c) suggested that the spheres were actually hollow spheres consisting of numerous nanosheets, which exhibited rather uniform spheres ranging from 1 μm to 2 μm in diameter. Figure 1(d) shows the TEM image of a typical microsphere, confirming that it is a hollow sphere and the related electron diffraction (ED) pattern shows clear rings characteristic of wurtzite ZnO. The HRTEM image shown in Fig. 1(e) exhibited clear

lattice fringes with a d spacing of 0.26 nm, which can be indexed to the (002) plane of the wurtzite ZnO crystal. The XRD pattern of the obtained hollow spheres was shown in Fig. 1(f), which revealed that all the diffraction peaks could be ascribed to ZnO in the hexagonal wurtzite phase, indicating a pure crystal phase of wurtzite ZnO.

Fig. 2. SEM (a)–(c), TEM (d) and HRTEM (e) images and XRD pattern (f) of ZnO hollow microspheres. Inset shows the related ED pattern.

3.2 Effects of process parameters on the photocatalytic reduction of Cr(VI)

Control experiments were carried out to obtain the optimum photocatalytic

reaction condition. The photocatalytic activity of flower-like ZnO hollow microspheres was evaluated based on the reduction of Cr(VI) in the aqueous solution. The major parameters that influence the rate and conversion of Cr(VI) to Cr(III) are species of organics, UV radiation intensity, pH and number of ZnO samples. The effects of the parameters were studied over reasonable ranges of their values.

3.2.1 Effect of the different organics on the photocatalytic reduction process

The presence of organic matters is inevitable in wastewater containing Cr(VI). Therefore, it is necessary to investigate how the organic pollutants influence the photocatalytic reduction of Cr(VI)^[37].

As shown in Fig. 3a, the addition of the organics (formic acid and methanol) increased the photocatalytic activity of flower-like ZnO hollow microspheres for the reduction of Cr(VI). Compared to formic acid, methanol was found as the more efficient organics for the reduction of Cr(VI) over flower-like ZnO hollow microspheres. It was observed that the flower-like ZnO hollow microspheres and methanol system exhibited the highest reduction ratio (82%), which was about 1.35 and 1.30 times higher than that of no hole scavenger (63%) and formic acid (66%), respectively. The result was also in agreement with the gradual color change of the solution from yellow to laurel-green with irradiation time (inset in Fig. 3a).

This phenomenon was ascribed to holes (h^+) captured at the photocatalyst surface, and holes were able to react with the organic pollutants. This way would suppress electron-hole recombination. Thus, more electrons would escape from the pair recombination and were available to reduce Cr(VI). These results implied that the

efficiency of photocatalytic reduction of Cr(VI) was promoted when the organics such as formic acid and methanol were present in the reaction system. The existence of some organics was beneficial for practical application. As shown in Eq. (1), (2), (3), the facilitated redox process could be outlined. From Fig. 3b, the reduction ratio of Cr(VI) increased with increasing methanol concentration up to 0.2 mol/L while beyond it the value decreased. This was possibly due to an increase intermediates adsorbed onto ZnO microspheres with the increase of methanol concentration. The active sites would be occupied and the reduction rate was decreased.

Fig. 3. Photocatalytic reduction of aqueous Cr(VI) in presence of (a)various organic species and (b)methanol at different concentrations.

3.2.2 Effect of UV radiation intensity on the photocatalytic reduction process

The photocatalytic activity of ZnO hollow microspheres is greatly influenced by the different UV lights and UV radiation intensity. ZnO is a semiconductor with a band-gap energy (≈ 3.37 eV, 370nm). The high spectral selectivity of the light wavelength less than 370 nm suggests that it is indeed ‘visible-blind’ and highly

UV-sensitive^[38]. The higher photocatalytic activity was claimed by Wu et al. with ZnO under illumination of 350 nm UV light^[39]. Also high pressure Hg lamp as UV light source has been used in most of the previous work. Therefore, the present investigation deals with the Cr(VI) removal from water system using a 365 nm high pressure Hg lamp. However, few researches reported the effect of UV radiation intensity on the photocatalytic activities.

The effect of UV radiation intensity on photocatalytic reduction of Cr(VI) was mainly investigated in this work and the obtained results were presented in Fig. 4. The power of the UV lamp could be varied from 200 to 500 W. As shown in the curves, the reduction efficiency of Cr(VI) were 80%, 82% and 86% at 200 W, 300 W, and 400 W, respectively. These observations indicated that the UV radiation intensity has no significant influence on the photocatalytic reduction of Cr(VI). It appeared that the conversion reached a maximum of about 86% at 400 W but decreased with increasing radiation intensity. The slight decrease of the conversion might be attributed to the photo-corrosion due to higher UV radiation intensity on the photocatalysts.

Fig. 4. Effect of UV radiation intensity on photocatalytic reduction of aqueous Cr(VI).

3.2.3 Effect of pH value on the photocatalytic reduction process

The pH of the solution is an important parameter in photocatalytic processes. A few experiments for 180 min at different pH values were conducted. The corresponding fractional reduction of Cr(VI) was presented in Fig. 5. It appears that the conversion reaches a maximum of about 90% at a pH 5 but decreases rapidly with increasing pH. The range of pH for the photocatalytic reduction of Cr(VI) using ZnO is rather limited. The catalyst dissolves at a low pH; a high pH is detrimental to both the catalyst and the oxidizing species. The Nernst equation of the over reaction in this system can be expressed as the following [40-41]:

$$\varphi = \varphi^{\theta} + \frac{0.059}{24} \lg \frac{[\text{Cr}_2\text{O}_7^{2-}]_4 \cdot [\text{C}_6\text{H}_5\text{O}_7^{3-}] \cdot [\text{H}^+]^{41}}{[\text{Cr}^{3+}]^8 \cdot [\text{CO}_2]^6 \cdot [\text{H}_2\text{O}]^{23}} \quad (4)$$

The φ value increases with the increasing concentration of H^+ according to Eq. (4). The equilibrium-reaction would move toward right at increased φ value, meaning that the reduction rate of Cr(VI) would be improved in solution with higher acidity. It is apparent that the acid medium facilitates the photocatalytic reduction of Cr(VI) because of the existence of abundant H^+ .

Fig. 5. Photocatalytic reduction efficiencies of aqueous Cr(VI) under different pH values.

3.2.4 Effect of number of samples on the photocatalytic reduction process

ZnO sample was varied ranging from monolayer ($1 \times 2 \text{ cm} \times 3 \text{ cm}$) to penta-layer ($5 \times 2 \text{ cm} \times 3 \text{ cm}$) while other parameters kept constant in the experiment to investigate the effect of photocatalyst dosage on the photocatalytic reduction of Cr(VI). As can be seen from Fig. 6, with the increasing photocatalyst dosage from monolayer to trilayer, the photocatalytic reduction of Cr(VI) was increased from 89.8% to 92.6%, respectively, while a further increase in ZnO samples (from trilayer to tetra-layer) was not found to be much beneficial for the photocatalytic reduction of Cr(VI). When the ZnO samples were increased to penta-layer, the reduction rate was decreased. As the other parameters, such as exposure to a constant UV radiation intensity, Cr(VI) concentration, pH value, and irradiation time, etc. were kept constant, further increasing the number of samples beyond optimum dosage failed to contribute significantly to the reduction process. When the dosage of the ZnO samples was very high, after traversing a certain optical path, ZnO particles impeded further penetration of UV light in the reactor (incidence of the combined phenomena of particle masking and scattering), lowering the efficiency of the catalytic process.

Fig. 6. Effect of different layer of sample on the photocatalytic reduction of Cr(VI).

3.3 Treatment of real tannery wastewater

The photocatalyst samples ($3 \times 2 \text{ cm} \times 3 \text{ cm}$) were used to study the reduction of Cr(VI) of tannery wastewater under 400 W UV lamp. The procedure for photocatalytic reduction measurement of wastewater was similar to reduction of artificial wastewater as described in section 2.4.1; but the measured pH was changed to 5 and the amount of added methanol was 2.0 mol/L. As displayed in Table 1, about 85% reduction of Cr(VI) could be achieved before and after UV photocatalytic treatment using ZnO catalyst. For practical application, researchers were widely concerned about the durability properties of the photocatalysts. Thus the renewable photocatalytic activity was investigated in this study. The experiments were conducted for 3h with the same set of photocatalysts but wastewater was replenished every time. The result was presented in the same manner as shown in Fig. 7, from which we can see that after 4 photocatalytic cycles, more than 79% of Cr(VI) was reduced within 180 min, indicating the relative stable photocatalytic activity of the flower-like ZnO hollow microspheres. The photocorrosion of ZnO might be one of the factors which led to the degradation of photocatalytic activity.^[42-44] Furthermore, the reason leading to the decline of photocatalytic activity also can be attributed to the adsorption of Cr(VI) onto ZnO microspheres surface for blocking the adsorption of methanol, since Cr(VI) showed a stronger affinity to ZnO.

Fig. 7. Cyclic photoreduction rate constants for Cr(VI) on ZnO samples

BOD₅, COD and TOC are some main parameters in assessing the quality of tannery wastewater. All of these may influence the quality of the wastewater. Table 1 also shows the normalized BOD₅, COD and TOC removal during the photocatalytic treatment with the optimal conditions of catalysts. It can be observed that more than 24% BOD₅, 32% COD and 30% TOC of wastewater can be reduced significantly after only 180 min of exposure to the UV lamp. Thus, flower-like ZnO hollow microspheres can be ideal supported photocatalysts for photocatalytic application.

Table 1

Related parameters of tannery wastewater before and after treatment				
Tannery wastewater	Cr(VI)	BOD ₅	COD _{Cr}	TOC
Before treatment (mg L ⁻¹)	246	290	1716	1277
After treatment (mg L ⁻¹)	42	220	1161	905
Removal (%)	83	24	32	30

Average value of three experiments.

Conclusion

In summary, the application of flower-like ZnO hollow microspheres on flexible

ceramic mesh substrate was considered for the photocatalytic reduction of Cr(VI) in leather tannery wastewater. The results indicated high efficiency of flower-like ZnO hollow microspheres for the photocatalytic reduction of Cr(VI) (86%) under UV light irradiation. The addition of methanol facilitated the photocatalytic Cr(VI) reduction due to its ability to adsorb on the catalyst surface and easy mineralization. Low pH value of the aqueous solution was also crucial to the reduction of Cr(VI) due to the Cr(VI) species and the protonated degree of the photocatalyst surface. Moreover, the rather higher dosage of photocatalysts was detrimental improving the efficiency of photocatalytic because it impeded the further penetration of UV light. Furthermore, the samples possess good photocatalytic stability, which is advantageous to practical applications. This work demonstrates that the flower-like ZnO hollow microspheres on flexible ceramic mesh substrate are effective materials for photocatalytic reduction of Cr(VI), which may also have potential applications in photocatalytic removal of other pollutants.

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