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Short Communication

Highly efficient photocatalytic reduction of Cr(VI) by bismuth hollow nanospheres

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Uniform bismuth hollow nanospheres with efficient Cr(VI) adsorption capacities were used to the photodegradation of highly toxic Cr(VI) for the first time, which exhibited outstanding visible-light photocatalytic abilities for the reduction of Cr(VI) to less toxic Cr(III).

1. Introduction

Hexavalent chromium (Cr(VI)) is a frequent highly toxic pollutant in wastewater which commonly arises from industrial process such as paint making, leather, tanning, and metal electroplating, etc. Hence, the elimination of Cr(VI) is of great importance and has stimulated vital development of effective technologies for wastewater treatments. Accordingly, various conventional approaches for Cr(VI) removal including biological treatment, ion exchange, membrane separation, precipitation, and adsorption have been reported [1]. However, these approaches generally suffer from large chemical dosage, high cost, extra organic additives, and secondary pollution, all of which potentially impede their practical applications. Therefore, the development of effective and economical treatment process is highly desirable. Among recently innovative technologies, photocatalysis has been proven to be a quite attractive, efficient and clean strategy to reduce the toxic Cr(VI) species to less harmful Cr(III) species [2]. In parallel, various TiO_2-based semiconductor photocatalysts have been also employed in photocatalytic reduction of Cr(VI) because of their powerful catalytic abilities [3–7]. In these studies, considerable efforts were devoted to extending the spectral response of TiO_2 to visible-light region by doping with different elements or coupling with other semiconductors, allowing more solar energy to be utilized in photocatalysis. Unfortunately, several drawbacks are involved in the utilization of modified TiO_2 photocatalysts, such as long exposure time for complete removal of Cr(VI), complicated synthetic procedure, and extra addition of organic sacrificial agent etc. [6–8]. Consequently, it is still desirable to develop novel visible light-responsive photocatalysts for the photocatalytic reduction of Cr(VI) in aqueous solution [9,10].

Bismuth nanomaterial is well-known for its excellent thermoelectric, tribological, electronic, and optical properties.[11–13] In the past decades, bismuth nanostructures with different morphologies and specific electronic band structures such as nanotubes [14], micro/nanospheres [15–17], nanoparticles [18], nanocubes [19] and nanowires [20] were successfully synthesized. In our previous study, bismuth hollow nanospheres were also successfully synthesized and exhibited high efficient Cr(VI) adsorption characteristics [21]. However, the high toxic Cr(VI) species are merely transformed from water phase to the surface of Bi nanospheres, rather than reduced to non-toxic Cr(III) species. Thus, it is considered that simultaneous adsorption and detoxification of Cr(VI) would be a more economical, effective and ideal method [22]. Therefore, the biggest challenge is whether bismuth could be an effective photocatalyst. Considering its small band gap, high carrier mobility and extremely small carrier effective mass, it is expected that metallic bismuth would be a potential photocatalyst by tailing its morphology, structure and size.

Herein, the photocatalytic activities of metallic bismuth nanospheres for Cr(VI) reduction were evaluated under both UV-light and visible-light irradiation. To better understand the outstanding photocatalytic ability of bismuth hollow nanospheres, the diffuse reflectance spectroscopy (DRS) and X-ray photoelectron spectroscopy (XPS) were carried

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out. To the best of our knowledge, there is no report involving the photocatalytic activities of Bi nanomaterials in wastewater treatment.

2. Experimental section

2.1. Synthesis of bismuth nanospheres

The bismuth nanospheres (**S1**–**S3**) were synthesized by soloventhemal method according to our previous work [21]. In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ (0.182 g, 0.375 mmol) was dissolved in HNO_3 solution (5 mL, 1 M), followed by the addition of 25 mL ethylene glycol (EG). Then the mixture was preformed a solvethermal process in a stainless steel autoclave with Teflon liner at 150 °C for 12 h (**S1**). Other bismuth samples were synthesized in the presence of different amount of polyvinylpyrrolidone (PVP) (**S2**: 0.15 g; **S3**: 0.30 g).

2.2. Characterizations

Powder X-ray diffraction (XRD) was carried out on Bruker axs D8 Discover (Cu Kα = 1.5406 Å). Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectrum were taken on a Hitachi S4800 scanning electron microscope operating at 5.0 kV. Transmission electron microscopy (TEM) was recorded on a Philips Tecnai 20 electron microscope, using an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were recorded on a UV–vis spectrometer (Shimadzu UV-2550) by using $BaSO_4$ as a reference and were converted from reflection to absorbance by the Kubelka–Munk method.

2.3. Photocatalytic activity measurment

The photocatalytic activities of the Bi nanostructures were evaluated by the degradation of Cr(VI) under UV light (300 W, mercury lamp, BL-GHX-IV, Shanghai Bilon Instruments Co., Ltd.) and visible light (500 W, Xe lamp with a 400 nm cutoff filter, Beijing Changtuo Technology Co., Ltd.) irradiation, respectively. In each experiment, 0.02 g of Bi sample was added into 20 mL Cr(VI) solution (40 mg L^{-1}). Prior to irradiation, the suspensions were stirred in the dark for 1 h to reach adsorption-desorption equilibrium. Then, the solution was exposed to both UV-light and visible-light irradiation under magnetic stirring. At each given time interval, 2 mL suspension was sampled and centrifuged to remove the solid photocatalysts. The concentration of Cr(VI) during the degradation was monitored using a Shimadzu UV2800 spectrophotometer, and the characteristic absorption of Cr(VI) at around 350 nm was used to determine the Cr(VI) concentration. The final reduction product Cr(III) was verified by XPS. The photocatalytic activities of the Bi hollow nanostructures over Congo Red (CR) were also evaluated by the same precedure upon visible light irradiation. In each experiment, 0.01 g as-prepared Bi sample and 20 mL CR solution (50 mg L^{-1}) were used. The dark adsorption-desorption equilibrium time is 2 h.

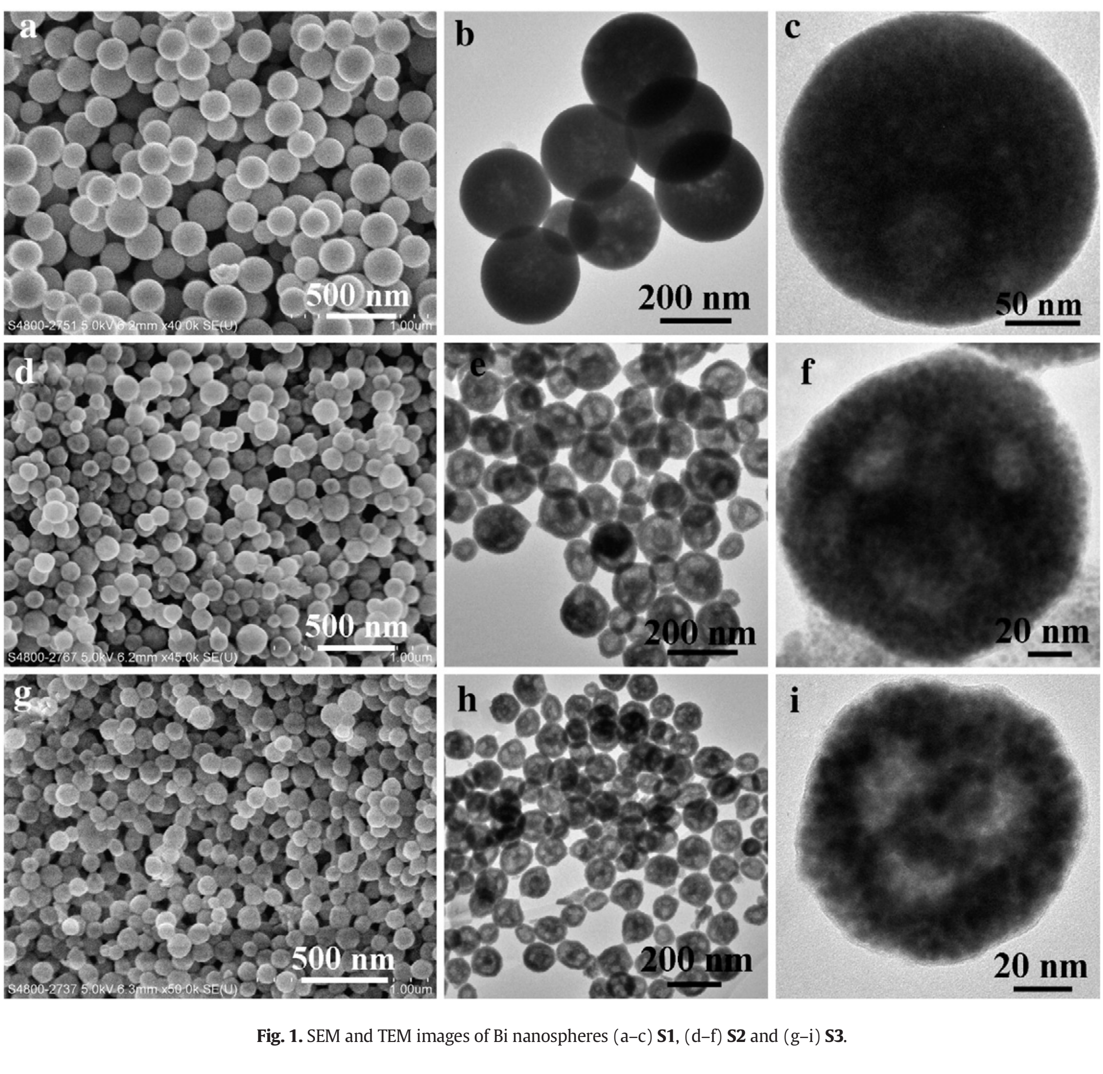

Fig. 1. SEM and TEM images of Bi nanospheres (a–c) **S1**, (d–f) **S2** and (g–i) **S3**.