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A facile strategy to fabricate hollow cadmium sulfide nanospheres with nanoparticles-textured surface for hexavalent chromium reduction and bacterial inactivation

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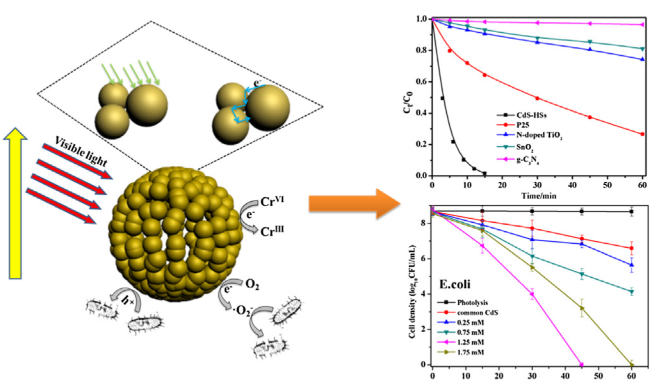
GRAPHICAL ABSTRACT

The hollow CdS nanospheres with nanoparticles-textured surface were successfully fabricated via a simple template self-removal strategy for the applications on Cr(VI) reduction and bacterial inactivation.



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ABSTRACT

Exploring morphology and surface structure of semiconductor photocatalyst is crucial for researching their photocatalytic performance. In this paper, hollow CdS nanospheres (CdS-HSs) were successfully fabricated via simple template self-removal strategy. The prepared CdS-HSs were characterized by XRD, SEM, HR-TEM, UV–vis diffuse reflectance spectra (DRS), XPS, photocurrent response (I-T), photoluminescence (PL) and electrochemistry impedance spectroscopy (EIS). It was found that the prepared CdS-HSs have nanoparticles-textured surface composed of ultra-small CdS nanoparticles (~20 nm) and large surface areas. DRS result demonstrated that the CdS-HSs exhibit strong visible light absorption capacity. The results of photocurrent response, photoluminescence and EIS revealed that hollow structure and nanoparticles-textured surface can effectively increase light reflection effect and decrease recombination rate of electrons and holes. Compared to the traditional CdS, the hollow CdS nanospheres exhibit higher photocatalytic activity on Cr(VI) reduction under visible light irradiation, which are primarily attributed

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to its rapid separation of electron-hole pairs and improved visible light absorption. Moreover, CdS-HSs was also demonstrated as an effective and potential material on photocatalytic disinfection. The result of mechanism experiments proved that h^+, e^- and $O_2^{\cdot -}$ play important roles on the bacteria inactivation.

1. Introduction

Increasingly serious water pollution caused by hexavalent chromium (Cr(VI)) is a risk for humanity health because of its strong toxicity, high solubility and easy accumulation [1–3]. In the past years, various technologies have been developed to remove Cr (VI) from wastewater, such as physical absorption, chemical reduction, ion exchange and so on [4–6]. However, the high cost, long treatment time and secondary pollutions are not favorable for their wide application. Currently, photocatalysis with the advantages of fast reaction rate, environmental friendliness and good reusability is considered as an effective and promising technology for Cr(VI) reduction [7–10]. Generally, Cr(VI) is transformed into Cr(III) with the assistance of photo-generated electrons in the process of photocatalytic reduction, while Cr(III) is environmentally friendly and vital to human life [11,12].

Cadmium sulfide (CdS), as a visible-light-driven (VLD) photocatalysts, has attracted increasing interests on photocatalytic reduction, solar cells and hydrogen evolution [13–16]. However, the high recombination rate of photoelectrons and holes of CdS lead to relatively low quantum conversion efficiency in photocatalytic reaction and poor photocatalytic performance [17,18]. Therefore, fabricating desired CdS photocatalysts with strong visible light absorption and efficient light conversion is important to enhance its application prospects and research value. Over the years, structure design, especially hollow spherical structure, is demonstrated as an effective strategy to improve intrinsic physical and chemical properties of semiconductor nanomaterial [19–22]. For example, Archer and co-workers demonstrated that SnO_2 nanospheres with hollow structure exhibit higher lithium storage capacity than ordinary SnO_2 [23]. And, Niu et al. successfully fabricated hollow $CuO@SiO_2$ spheres which showed excellent catalytic performances for the CO oxidation [24]. So, we have reasons to believe hollow spherical structure can greatly improve the photcatalytic activity of photocatalyts. For the reason that hollow spherical structure with both outer and inner surfaces can provide large surface areas for visible light absorption and more active sites for photocatalytic reaction. In addition, multi-reflection effect of visible light within interior hollow structure can improve the light-harvesting efficiency [17]. Further, hollow structure will shorten the path of electronic transport, resulting in rapid separation of electron and hole [23]. According to the analysis above, it is highly desirable to obtain CdS with hollow spherical structure.

Hard-template method is considered as the most versatile strategy to synthesize hollow nanostructure with high uniformity and dispersibility [25,26]. Recently, various morphology and scale of hollow nanostructure are successfully fabricated by using different template. Owing to the chemical stability, porous structure and modifiable surface, SiO_2 particles were frequently used as template for the preparation of hollow structure. For instance, Yang first reported a simple strategy for the synthesis of metal oxide mesoporous with varying morphologies, size and phases by silica nanoreactor [27]. And Li et al. used SiO_2 as template to prepare monodisperse metal oxide hollow spheres with sandwich hererostructured shells [28]. However, the harsh template removal conditions, including strong acid or high temperature calcination, are not favorable for the synthesis of metal sulfide (CdS, SnS_2, NiS, MnS) hollow nanostructure. As far as we know, metal sulfide has unique superiority in the field of photocatalytic reduction, hydrogen production and energy storage [14,29,30]. Undoubtedly, it is a meaningful theme to explore a novel strategy for the synthesis of metal sulfide hollow structure without intricate template removal procedures.

In this paper, a simple template self-removal strategy was proposed to fabricate CdS hollow spheres (CdS-HSs) by using SiO_2. Different from traditional SiO_2 template method, the formation of hollow shell structure is based on the chemical dissolution property of SiO_2 rather than its porous and modifiable surface feature, which is beneficial for the generation of regular surface. It was found that the obtained CdS-HSs have large surface areas and nanoparticles-textured surface, which could greatly increase visible light absorption and enlarge transport channel space of electrons. A detailed formation route of CdS-HSs was proposed and the probable influence factors on the formation of hollow structure were also discussed. The photocatalytic activity of CdS-HSs was evaluated by Cr(VI) reduction. UV–vis diffuse reflectance spectrum (DRS), electrochemical impedance spectroscopy (EIS) and photoluminescence spectrum (PL) were conducted to investigate the effects of hollow spherical structure and nanoparticles-textured surface on the light absorption and photoelectrons transfer of CdS-HSs. Meanwhile, the CdS-HSs were demonstrated as a promising material on bacterial inactivation. And the mechanism of photocatalytic sterilization was also studied. Our work can not only provide a new idea for the synthesis of metal sulfide with hollow spherical architecture, but also offer us with better understanding for the relationship between surface structure and photocatalytic behavior of photocatalysts.

2. Experimental section

The detailed experiments and characterization were provided in Supporting Information.

3. Results and discussion

The CdS-HSs are prepared via a simple template self-removal strategy assisted by NH_4Cl. A possible formation route is schematically illustrated in Scheme 1. Firstly, the silicon-oxygen bonds of SiO_2 are break by hydroxide ions came from ammonium hydroxide at high temperature [31,32], and the negatively charged silicate ions are produced and released to react with free cadmium ion. Therefore, a large-scale cadmium silicate seeds will be formed on the surface of corroded SiO_2, which guarantees the growth of CdS shell. Second, cadmium silicate shell is formed with the progress of reaction. And, the cadmium silicate hollow spheres are obtained accompanied by the erosion of silica core. Finally, hollow spherical structure composed of CdS nanoparticles is synthesized in situ around cadmium silicate surface with the addition of sulfur ion. The release of negatively charged silicate ions is beneficial for Cd^{2+} adsorption and allows for the generation of cadmium silicate shell. Thus the well-defined CdS-HSs were obtained. The results of FTIR spectroscopy characterization (Fig. S1, Supporting Information), XPS (Fig. S2, Supporting Information) and zeta-potential measurement (Fig. S3, Supporting Information) confirmed the chemical bond change and electronegativity of SiO_2 surface.