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Short Communication

Influence of TiO_2 hollow sphere size on its photo-reduction activity for toxic Cr(VI) removal

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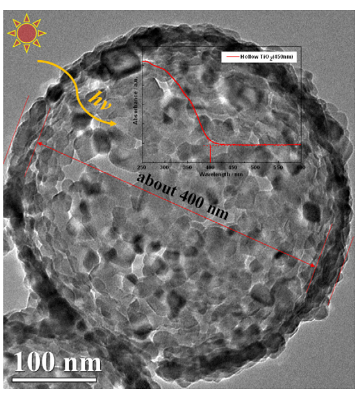
GRAPHICAL ABSTRACT



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ABSTRACT

After polystyrene@titanium dioxide (PS@TiO_2) composite with different size was calcined at designated temperature, TiO_2 hollow sphere with controllable size was obtained for high efficient photo-reduction of Cr(VI). The feature of the TiO_2 hollow sphere was investigated by SEM, TEM, XRD, UV–Vis, and photoluminescence. The photo-reduction of Cr(VI) were measured for the performance assessment of the TiO_2 hollow sphere, Cr(VI) was used as an electron acceptor. After irradiation for 2 h, the photo-reduction rate of Cr(VI) (pH = 2.82) for TiO_2(450 nm) was 96%, which exhibited an increase of 5% and 8% compared with TiO_2(370 nm) and TiO_2(600 nm). The absorption edges of TiO_2 hollow sphere (450 nm) was largest with the increasing of hollow sphere size from 370 to 600 nm. The optimal hollow sphere size of TiO_2 was 450 nm for the photo-reduction of Cr(VI), because the light-harvesting efficiency (the best of absorption edge) and photo-generated electron-hole separation rate (the best of photo-reduction rate) of TiO_2 hollow sphere were controlled by its hollow sphere size. In addition, we find that the behavior of the hydrogen production was inhibited by the coexistence Cr(VI) solution. This study can improve our understanding of the mechanism for the activity enhancement by the optimal hollow sphere size of TiO_2.

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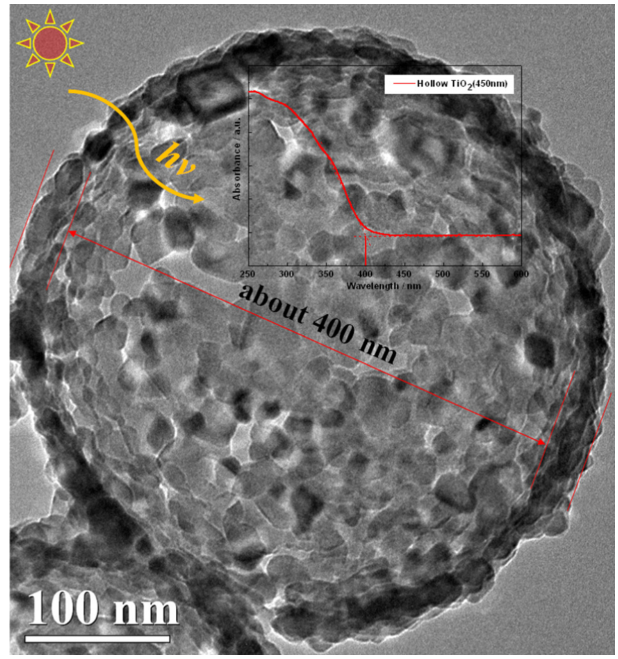
1. Introduction

As we all know, hexavalent chromium (Cr(VI)) is one of the forms of chromium that poses a health risk to humans because of its high acute toxicity and carcinogenic activity [1–3]. Industrial processes, such as electroplating, paint making, leather tanning, and others, have made Cr(VI) to be a widespread pollutant in wastewaters [4–6]. Its treatment is performed generally by transforming Cr(VI) to the less noxious Cr(III), which is considered non-toxic and an essential trace metal in human nutrition. After Cr(VI) photo-reduction, Cr(III) can be precipitated and removed as a solid waste [7,8].

Among various reductive methods, photocatalytic reduction using the semiconductor photocatalyst TiO_2 were proposed as an economical and simple method for the removal of Cr(VI) in recent times [9–11]. Structural architectures of the TiO_2 photocatalyst was demonstrated to be an effective way to improve its photocatalytic activity. Among different TiO_2 structures (including nanoparticles [12,13], microspheres [14], nanorods [15], and nanosheets [16,17]), the TiO_2 hollow sphere structure has received considerable attention due to its low density, large surface area, good surface permeability, and greater light-harvesting capacity [18–20]. The cavity sizes in the hollow sphere play a crucial role in determining the photocatalytic reactivity and efficiency. The photocatalytic activity of TiO_2 was deeply influenced by the actual features of the oxide particles, with respect to both structural and morphological characteristics [21]. Therefore, the TiO_2 hollow sphere with controllable size was proposed by this paper.

On the other hand, the application of photocatalytic water-splitting technique to hydrogen production from water is a well-known process [22,23]. However, vast majority of reported works have investigated the photocatalytic reduction removal of Cr(VI) or photocatalytic water-splitting technique to hydrogen production from water alone [24,25], while little attention is paid to collectively treat the samples containing both Cr(VI) and water splitting. In fact, Cr(VI) often affect on the performance of hydrogen production in many water-splitting techniques [26–28]. Therefore,



Scheme 1. Schematic illustration of UV–vis of TiO_2 hollow spheres (450 nm).

the study of their mutual interactions in photocatalytic conversion processes is of important for the practical use of photocatalysis.

Here, we used polystyrene spheres (PS) with different sizes as sacrificial templates, the nanoparticles of TiO_2 was coated successively onto PS, the resulted PS@TiO_2 nanocomposites are calcined at elevated temperature to removal of PS, and then TiO_2 hollow sphere with different sizes are obtained. The photo-reduction performance of TiO_2 hollow sphere was assessed by toxic Cr(VI) removal. Our objective is to increase the light-harvesting efficiency and photo-generated electron-hole separation rate through

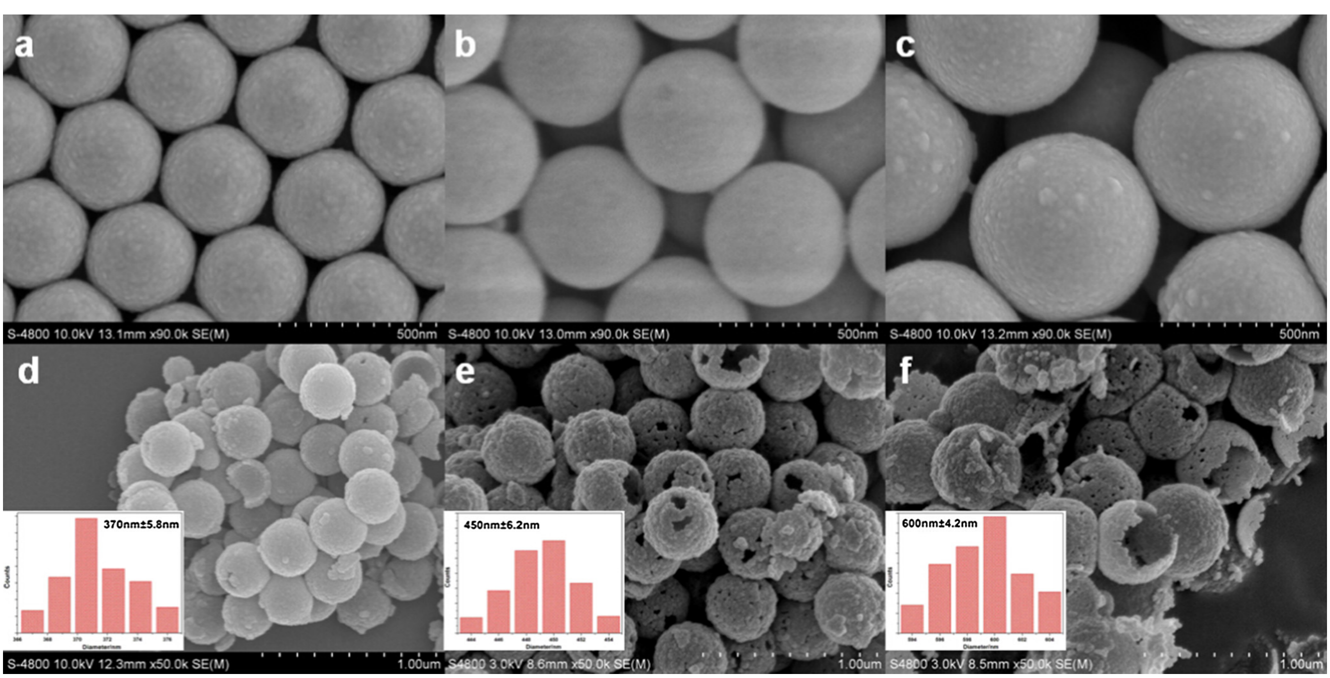


Fig. 1. (a–c) The SEM image of PS with diverse sizes, (d–f) the SEM image and the size distribution histogram with diverse sizes of single-shelled TiO_2 hollow spheres (370 nm, 450 nm, 600 nm).