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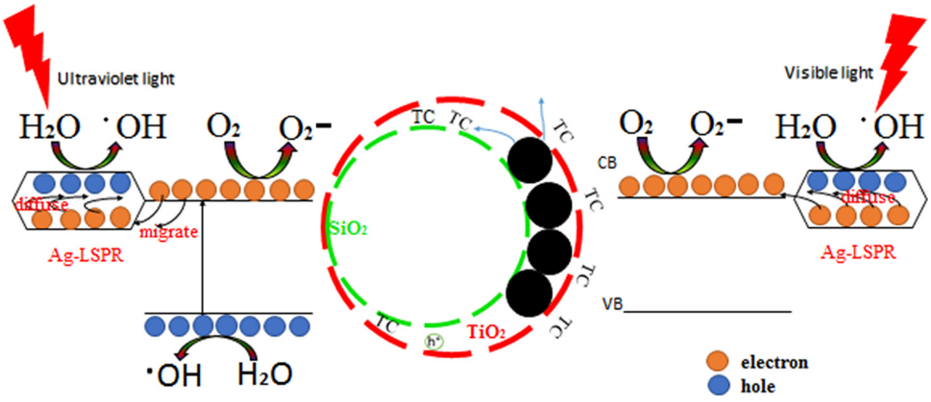
Hierarchically-structured SiO_2-Ag@TiO_2 hollow spheres with excellent photocatalytic activity and recyclability

Ying Zhang[a,c], Juanrong Chen[b,*], Hua Tang[a], Yingguan Xiao[a], Shoufei Qiu[a], Songjun Li[a], Shunsheng Cao[a,c,*]

[a] *Institute of Polymer Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China*
[b] *School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China*
[c] *School of Chemistry and Materials Engineering, Fuyang Normal College, Fuyang 236037, China*

GRAPHICAL ABSTRACT



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ABSTRACT

A new protocol for constructing sandwich-like SiO_2-Ag@TiO_2 hollow spheres (SAT) is introduced, in which SiO_2 acts as an efficient support for the Ag nanoparticles (Ag NPs) immobilization, while TiO_2 maintains its hierarchical structure and prevents the aggregation of Ag NPs during the photocatalytic reaction. As a photocatalytic agent, the inner and outer surfaces of TiO_2 can be fully occupied by pollutants molecules because of its unique structure, which faster boosts the photo-generated electrons to transfer the substrates, leading to an enhanced photocatalytic performance. Compared with Ag NPs deposited on the surface of SiO_2@TiO_2 (STA), the as-synthesized SAT exhibits a markedly enhanced visible-light and UV light activity than STA for degrading tetracycline and traditional dyes. The excellent photocatalytic performances are ascribed to the enhanced transport paths of photo-generated electrons, reduced recombination probability of e^-/h^+ pairs, and decreased threat of oxidation and corrosion. Especially, the SAT still maintains its photocatalytic efficiency after five consecutive runs even though the sample is recovered under visible-light irradiation, far beyond the reusability of STA under the same conditions. Therefore, the outstanding photocatalytic activity and excellent recyclability make SAT more potential to purify aquatic contaminants and to meet the demands of future environmental issues.

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[*] Corresponding authors.
E-mail addresses: chenjuanrong@ujs.edu.cn (J. Chen), sscao@ujs.edu.cn, sscaochem@hotmail.com (S. Cao).

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1. Introduction

Persistent efforts have been focused on practical photocatalysts for environment purification. Among them, TiO_2 has been deemed to be a promising photocatalyst because of its good physical and chemical properties [1–3]. However, the photocatalytic efficiency of pure TiO_2 holds a poor absorption under direct sunlight irradiation due to its intrinsic bandgap, leading to a low quantum yield and poor visible-light photocatalytic activity [1,4].

Various methods have been introduced to improve the photocatalytic performances of TiO_2. One is morphological change by designing its crystalline phase, pore size and shell thickness, the other is chemical modification by introducing external components into the TiO_2 [1,4,5]. The main purpose of the former is to improve the capacity of adsorbed contaminants and the surface area of TiO_2. However, this strategy cannot yet break its drawbacks including UV dependency and agglomeration. By contrast, the latter not only can increase the photocatalytic behaviours of TiO_2, also can shift the UV dependency of TiO_2 to visible-light region by developing supported-photocatalysts; and/or by doping elements [2,4,5]. Therefore, how to exert the synergistic effects of two methods is vital in exploring TiO_2-based photocatalysts with high photocatalytic performances.

SiO_2 matrix is effective in enhancing the efficiency of TiO_2 due to its transparency in the UV region [6,7]. However, the hybrid SiO_2/TiO_2 photocatalyst is not able to drive the ultra-violet of TiO_2 to visible-light range because SiO_2 cannot absorb any visible light [8–10]. Clearly, coupling with doping technique is required to develop SiO_2/TiO_2 visible-light photocatalyst. Although non-metallic doping can generate energy levels just above the top of the valence band of TiO_2, and thus narrowing the bandgap, this narrowing is not enough up to the mark to take full of visible light due to low concentration mono-doping [11]. At higher content of anions doping, it has been experimentally confirmed that the impurity levels serve as recombination centres of photo-generated e^-/h^+ pairs, decreasing the photocatalytic efficiency of TiO_2 [12]. While metal decorating is especially pursued to prolong the lifetime of e^-/h^+ pairs because of its unique surface plasmon resonance [13], in which the metal NPs serve as reservoirs/mediators in shuttling and storing e^- from TiO_2 to pollutant molecules [14]. For example, Theil et al. [15] prepared functionalized Au-SiO_2@TiO_2 nanoassemblies with enhanced visible-light activity for degrading methylene blue. Soylak et al. [16] synthesized Fe_3O_4@SiO_2@TiO_2 for photocatalytic decomposition of organic pollutants. E. S. Baeissa [10] developed cobalt metal decorated on TiO_2–SiO_2 photocatalyst with a higher visible-light activity for cyanide degradation; recently, Pinho et al. [17] reported the preparation of Ag–SiO_2–TiO_2 with enhanced visible-light photoactivity for self-cleaning application. However, the above-mentioned methods to prepare the SiO_2/TiO_2 visible-light photocatalyst both used low-surface area nonporous SiO_2 as matrix via sol-gel method [10,15,17], severely impairing their photocatalytic efficiency. Besides, most of the previous works were focused on the investigation of metal deposited SiO_2/TiO_2 hybrid materials [10,15,17], making metal NPs to be subjected to the threat of corrosion, aggregation, and oxidation during photocatalytic process. Therefore, optimal design and construction such as the geometry and position of metal NPs is crucial to explore high photocatalytic activity of metal modified SiO_2/TiO_2 photocatalysts.

To the best of our knowledge, this is the first attempt to devise hierarchically-structured SiO_2-Ag@TiO_2 (SAT) hollow spheres endowed with an excellent catalytic activity and recyclability, in which inner shell of SiO_2 serves as an efficient backbone to support Ag NPs and outer wall of TiO_2 acts as membrane-like shell for Ag NPs protection and prevents Ag NPs aggregation. The as-synthesized SAT can promote the diffusion of reactants by decreasing diffusion resistance and enhancing accessibility because of its high surface area and hollow structure, leading to an enhanced photocatalytic activity. Moreover, SAT photocatalyst can effectively overcome the many disadvantages including oxidation, corrosion and dissolution produced by directly immobilizing metal NPs on the surface of TiO_2. Especially, the as-synthesized SAT holds excellent photocatalytic activity and recyclability for degrading tetracycline (TC) and dyes than the Ag NPs immobilized on the surface of SiO_2@TiO_2 (STA) due to confined effect and hierarchically structure, providing a new insight for the construction of other metal NPs confined in TiO_2-based photocatalysts with efficient photocatalytic performances.

2. Experimental

2.1. Materials

Most of chemicals and reagents including initiators ($K_2S_2O_8$ and AIBN), tetraethylorthosilicate (TEOS), allyltrimethoxysilane (ATS) and titaniumtetrabutoxide (TBT) were purchased from J&K Chemical Technology and were used without any further purification. Styrene (St), silver nitrate, and pollutants (tetracycline (TC), rhodamine B (RhB), methylene blue (MB), and methyl violet (MV)) were available from Sinopharm Chemical Reagent Co., LtdS, while styrene monomer should be purified by using NaOH solution (5 wt.%) to remove inhibitor before use. Besides, methacryloxyethyltrimethyl ammonium chloride (DMC) was available from Sigma Aldrich Company Ltd.

2.2. Synthesis of CPS@SiO_2

The hybrid CPS@SiO_2 spheres were prepared via several steps: firstly, emulsifier-free polymerization was used to prepare cationic polystyrene spheres (CPS) according to our previous works [18–20]. Secondly, absolute ethanol (40 ml) was used to disperse CPS templates (3.5 g), and then TEOS and ammonia were added quickly and the mixture was reacted at 50°C for about 6 h with constant stirring (~350 rpm) in the presence of ATS monomer, achieving CPS@SiO_2 composites.

2.3. Silver ions loading

Silver ions were deposited on the surface of CPS@SiO_2 composites by using the impregnation method. Typically, CPS@SiO_2 spheres (2 g) were dispersed into 20 mL ethanol containing $AgNO_3$ aqueous solution (5 mg/mL), and then strongly stirred at 50°C for 8 h, evaporated and dried under overnight, obtaining CPS@SiO_2-Ag^+ spheres.

2.4. The synthesis of hierarchical SiO_2-Ag@ TiO_2 hollow spheres

The as-synthesized CPS@SiO_2-Ag^+ (1 g) was used as the template and further surrounded by using TBT (2 g) under $NH_3 \cdot H_2O$ (3 ml) to generate TiO_2 layer, and then SiO_2-Ag@TiO_2 (SAT) could be obtained by pyrolysis of CPS (450°C) and followed by reduction of Ag^+ ($NaBH_4$). Besides, the direct deposition of Ag NPs onto the surface of hierarchical SiO_2@TiO_2 (STA) was synthesized as a reference photocatalyst in this work.

2.5. Characterization of SiO_2-Ag@ TiO_2 photocatalyst

The morphology, surface area and pore size of the as-synthesized SAT photocatalyst were measured using a transmission electron microscope (TEM), a scanning electron microscope (SEM) and a nitrogen surface area analyzer (TriStar II 3020). In addition, X-ray diffraction (XRD), UV–vis spectroscopy, and X-ray photoelectron spectroscopy (XPS) were employed to investigate crystal structure, absorbance spectra and bonding energy of SAT photocatalyst.

2.6. Photocatalytic activity measurement

The photocatalytic activities were evaluated by the degradation of