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Synthesis of spindle-shaped AgI/TiO_2 nanoparticles with enhanced photocatalytic performance

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ABSTRACT

A novel synthetic route has been developed to prepare silver iodide (AgI) loaded spindle-shaped TiO_2 nanoparticles (NPs). The morphology and crystallinity characterization revealed that small AgI NPs, with an average diameter of 15 nm were dispersed on the surface and interior of nanoporous anatase TiO_2 support. High-resolution transmission electron microscopy (HRTEM), Brunauer-Emmett-Teller (BET) surface area, Raman and X-ray photoelectron spectroscopy (XPS) were used to identify the nanoporous structure of TiO_2 and the existence of AgI NPs. Diffuse reflectance spectra (DRS) showed that AgI/TiO_2 composite exhibited a remarkable enhancement of visible light absorption, which is ascribed to the addition of AgI. For illustrating the superior property of this hybrid as photocatalyst, the degradation experiments were carried out for processing rhodamine B (RhB) solution under visible light irradiation and it was found that the photocatalytic activity was dramatically improved for AgI/TiO_2 compared with nanoporous TiO_2 and commercial P25 TiO_2. The enhanced photocatalytic properties could be attributed to the large surface area of porous TiO_2, good stability of AgI particles, and the effective charge separation due to the synergetic effect between AgI and TiO_2 that can facilitate the separation of electron-hole pairs. Our novel composite based on nanoporous spindle-shaped TiO_2 represents a promising new pathway for the design of high-performance photocatalysts for environmental applications.

1. Introduction

In the past few decades, semiconductors for photo- or electrocatalysis have received much attention because of their potential roles in alleviating environmental and energy challenges [1,2]. As one of the most promising semiconductor materials, titanium dioxide (TiO_2) has been extensively studied in various domains such as solar cells, energy convertors [3–5] due to its flexibility in fabrication and favorable electric properties [6,7]. TiO_2 is also popular for photocatalysis [8,9] because of its high activity, non-toxicity, low price and chemical stability [10,11]. However, the photocatalytic performance of TiO_2 is limited by the large bandgap, which confines its response only to UV light. Consequently, it is of crucial importance to extend the excitation wavelength to the visible light range, which accounts for approximately 44% of solar irradiation compared to 5% for the UV range [12,13]. A second challenge is to reduce the recombination rate for photo-induced electron-hole pairs, which contributes a substantial loss of efficiency in TiO_2 photocatalysts [6,14,15]. To address these issues, various strategies are adopted. The band gap can be narrowed by doping with nonmetallic elements, such as nitrogen, sulfur and carbon atoms [16–18] to increase the light absorption. Coupling TiO_2 with metals or metal oxides to form heterostructures can also enhance the photocatalytic activity because this strategy can induce fast electron transfer to hinder the recombination of electron-hole pairs [19–23].

Silver halides (AgX, X = I, Br, Cl) are well-known as photosensitive materials and are widely used in photographic films [24]. In the photographic process, AgX absorb photons and liberate electron-hole pairs. The electrons will combine with the mobile interstitial silver ions, leading to the formation of silver atoms [25]. Therefore, AgX are unstable under light irradiation. However, the presence of a support (e.g.TiO_2, graphene, carbon nanotube) can stabilize AgX NPs by inhibiting the photographic process [26–28]. As one member of AgX, AgI is a direct-gap semiconductor with a smaller band gap (2.80 eV) than AgCl or AgBr, and it has been reported that AgI is a class of highly efficient visible light sensitizers to modify TiO_2 [29,30]. The combination of AgI and photoactive oxide semi-

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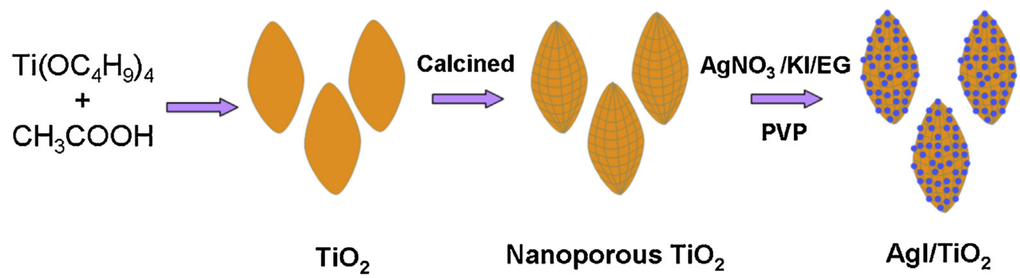

Scheme 1. Schematic illustration the formation of spindle-shaped AgI/TiO_2 NPs.

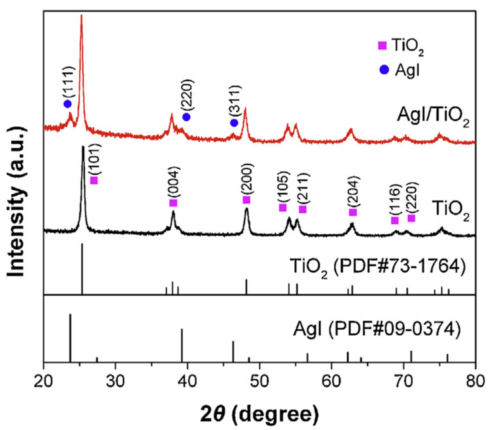

Fig. 1. XRD patterns of nanoporous TiO_2 mesocrystals and spindle-shaped AgI/TiO_2 NPs.

conductors with a high surface area or special morphology has been an effective strategy to obtain hybrid photocatalysts with high activity. AgI-loaded TiO_2 had shown high efficiency for the photocatalytic degradation of non-biodegradable azodyes, crystal violet, 4-chlorophenol and disinfection of pathogenic bacteria under visible light irradiation [31–33]. Thus, incorporating visible light-active Ag or its compounds is an appealing strategy to design efficient visible light-driven photocatalysts. The composite of AgI/TiO_2 is a promising photocatalyst because the light response of TiO_2 is extended into the visible region, and the photo-stability for AgI is increased simultaneously [34–36].

Recently, porous anatase structures of TiO_2 with spindle shapes were reported; they exhibited remarkable crystalline-phase stability and proved to be excellent candidates for lithium ion battery applications [37]. It is indicated that the obtained nanoporous TiO_2 is polycrystalline and composed of small crystals with anatase phase, which is with tunable architectures that is promising candidate as a support. To the best of our knowledge, previous studies on AgI/TiO_2 were all performed using solid TiO_2, such as P25, anatase TiO_2 [29] and amorphous TiO_2 [30], little attention was paid to nanoporous TiO_2. Since nanoporous TiO_2 is an excellent electron reservoir with high specific surface area, acting as electron mediators, the utilization of nanoporous TiO_2 instead of amorphous or the other ones as support for AgI also facilitates electron transportation and stabilizes AgI, thus induces efficient separation of photogenerated electron-hole pairs, which eventually leads to enhanced photocatalytic activity.

Inspired by these works, we demonstrated a facile and practical approach to synthesize spindle-shaped nanoporous anatase TiO_2 particles, composed of many tiny nano-crystals, which were used as a suitable support to fabricate the AgI/TiO_2 composite. Spindle shaped TiO_2 materials, acting as a photoactive supporting material, can help AgI to remain its stability and prevent agglomeration. Visible light-active AgI expands the light absorption range for this hybrid. It was shown that the combination of nanoporous TiO_2 and AgI improved the efficiency for photocatalysis, showing highly active photocatalytic performance by photodegradation of organic pollutant RhB under visible light irradiation compared with TiO_2 and P25 NPs. Our study emphasizes the novelty and superiority of using spindle shaped nanoporous TiO_2 as support, and electron mediator for preservation the stability and high activity of AgI under visible light irradiation. It sheds light on the new sights in the preparation of multiple shape TiO_2-based hybrids with visible-light absorbing capability for potential environmental applications.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$) was purchased from Shanghai Shenbo Chemical Co., Ltd. Polyvinylpyrrolidone (PVP) K-30 ($M_W \approx 58000$) was purchased from Amresco. Tetrabutyl titanate (TBOT) and

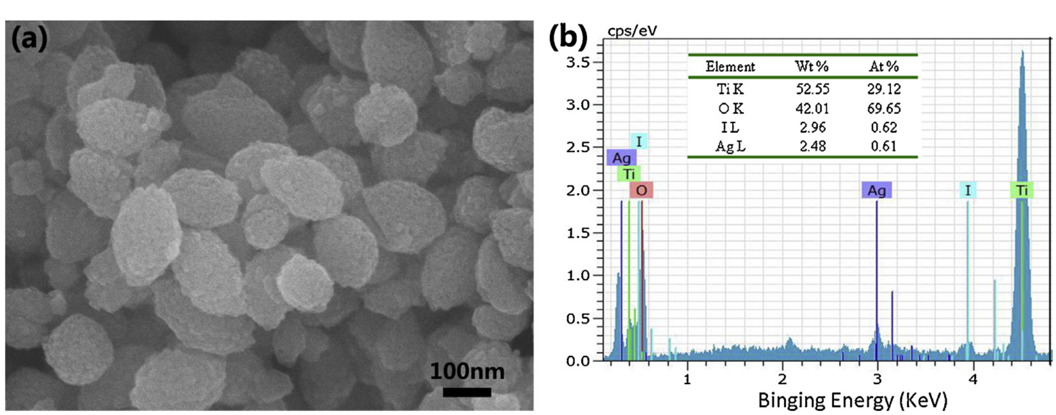

Fig. 2. SEM image (a) and EDS spectra (b) of spindle-shaped AgI/TiO_2 NPs; Inset in (b) is elemental composition.