



Hydrothermal-assisted synthesis of the multi-element-doped TiO₂ micro/nanostructures and their photocatalytic reactivity for the degradation of tetracycline hydrochloride under the visible light irradiation

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ABSTRACT

The TiO₂ and copper-containing TiO₂ (Cu-TiO₂) micro/nanostructures are synthesized using a multi-element-doping route, and their visible-light-induced photocatalytic degradation of tetracycline hydrochloride (TC) is evaluated. Using metallic Ti powders with impurities as raw material, these two cauliflower-like micro/nanostructures can be hydrothermally synthesized through a dissolution and hydrolysis process in the NH₄HF₂ solution and NH₄HF₂ + CuSO₄ solution, respectively. Then, after a calcining treatment at 600 °C for 2 h, their phase compositions can be transformed from anatase to mixed anatase-rutile, the optical absorption edges are decreased from 452 and 439 nm to 569 and 581 nm, respectively. The apparent reaction rate constants for the photodegradation reaction of TC over the calcined TiO₂ and Cu-TiO₂ samples, which can be described by pseudo-first-order kinetics model, are increased from 0.00313 min⁻¹ and 0.00407 min⁻¹ to 0.00468 min⁻¹ and 0.00978 min⁻¹, respectively. The enhanced photocatalytic degradation abilities of these TiO₂ and Cu-TiO₂ are attributed to their unique mixed phase composition and optical properties, and the trace doped Fe, Cu, F and N elements in their structure.

1. Introduction

How to remove the organic pollutants in the wastewaters is an important concern of the environmental protection in recent years, especially for those chemicals that are hard to be treated by the traditional methods such as physical adsorption, chemical oxidation, and biological degradation [1–3]. As an alternative removal method, the photocatalytic techniques using catalysts have been demonstrated their potentiality featuring with high efficiency, high mineralization rate, simplicity of operation, and low cost [4,5]. Among the well-known photocatalysts, TiO₂ nanomaterials are obviously the promising candidates because of their unique physical and chemical properties. However, the pure TiO₂ is restricted by their large band gap (~3.2 eV), which is effective only under the ultraviolet irradiation ($\lambda < 380$ nm) and subsequently hinders the practical application under solar light or indoor usage. What's more, the complicated post-filtration procedures to separate photocatalysts and the gradual inactivity of photocatalysts during the continuous operation also limit the application of nanorange TiO₂ photocatalysts. Thus, it is essential to investigate the facile synthesis of TiO₂-based photocatalysts with strong absorbance of broad ranged visible lights, high efficiency, and relatively large size for easily

reuse [4–8].

TiO₂ materials have rutile, anatase, and brookite crystalline polymorphs, their anatase phase and mixed anatase/rutile phase are generally assumed better photocatalytic properties [9]. The TiO₂ nanostructures such as nanorod, nanowire, nanotube, and nanoparticle display large percentage of reactive facets and a relatively shorter conduction path of the photogenerated electrons-holes although larger particles are in favor of the recycling treatment. By now, the titanium precursors, medium acidity and temperature, and reaction time are considered as the key parameters for the formation of crystal phases and nanostructures. Based on the requirement to adjust the energy bands of TiO₂ photocatalysts, it has demonstrated that the modification with doping elements such as noble-metal (Au, Pt, Pd and Ag), non-metal elements (N, B, S, F, and I) doping, iron-group metal (Fe, Co and Ni) grafting, as well as with the coexisted semiconductors such as Bi₂O₃, CdS, Cu₂O, and BiOX (X = Cl, Br, and I) can reduce the recombination of photo-generated electrons-holes and extend the light absorption into the visible light region [7,10]. Thus, large numbers of works relating with the crystal phase, exposed facet, particle size and morphology, doped elements, and/or coexisted semiconductors of TiO₂-based photocatalysts have been extensively carried out in the past decades.

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However, only one or two of these mentioned measures have generally been utilized to prepare a special TiO₂-based photocatalyst with visible-light activity or higher reactivity under the UV irradiation due to the restriction of preparing conditions or the requirement of a complicated, rigorous and time-consuming process. And some properties can't be materialized in the TiO₂-based products, and subsequently affect their using in different application fields. For example, a pure TiO₂ can't be used under the visible-light irradiation even if it has nanostructures and with exposed active facets. Therefore, it remains a great challenge to develop feasible methods for the synthesis of TiO₂-based photocatalysts, especially with visible-light response and enhanced photocatalytic activity.

As a unique reactant, the inimitable effects of fluoride anions (F⁻) on the synthesis and properties of TiO₂ have been used to construct TiO₂-based photocatalysts [11,12]. The theoretical and experimental studies found that the {001} facets of anatase TiO₂, which could be preferentially formed in the solution containing F⁻ ions, in the equilibrium state have much higher chemical activities than other facets. Lu et al. [13] synthesized the anatase TiO₂ microcrystals with exposed {001} facets using TiF₄ as the raw material. By using metallic Ti as precursor to react with HF solutions, the flower-like TiO₂ nanostructures with exposed {001} facets and enhanced photocatalysis could be synthesized, and anatase TiO₂ single crystals with exposed {001} and {110} facets were also obtained with a H₂O₂-HF mixed solution [14]. Compared to the volatile HF, ammonium bifluoride (NH₄HF₂) is safer and easier to handle in treatment with Ti precursors, Yu and co-authors [15] prepared the mesoporous surface fluorinated TiO₂ powders with anatase phase and high photocatalytic activity in a NH₄HF₂-containing solution. These results give some guiding clues on the modulation of the morphology, microstructure, and properties of TiO₂ via F⁻ ions and additives in the precursor solutions to adjust the surface energy of exposed facets or the hydrolysis velocity of the titanium precursors.

In this paper, we report a facile route for one-pot synthesis of novel TiO₂ and copper-containing TiO₂ (Cu-TiO₂) micro/nanostructures with cauliflower-like appearance by a hydrothermal reaction of metal Ti powders and NH₄HF₂-containing solution. Especially, the Ti precursor contained multi-element impurities such as Fe, Si, Cl, C, and N, and the copper oxides can also be introduced into the TiO₂ micro/nanostructures by adding Cu²⁺ in the NH₄HF₂ solution. These hierarchical micro/nanostructures can expose large reactive area, which is favor to the contact with the pollutant molecules and the subsequent photocatalytic reaction [16–18]. The enhanced photocatalytic activity of the as-synthesized TiO₂ micro/nanostructures is evaluated by using tetracycline hydrochloride (C₂₂H₂₄O₈N₂·HCl, TC) wastewater as the target pollutant. As the second most common antibiotics, tetracyclines have been widely used in human and animal cure against infectious diseases, and can induce the development of antibiotic-resistant pathogens and cause serious problems for human health when their residues are left in the aquatic environment [1,8,19]. The as-synthesized TiO₂ and Cu-TiO₂ photocatalysts have been demonstrated their photocatalytic degradation reactivity to TC under the visible-light irradiation.

2. Experimental

2.1. Materials and methods

The metal Ti powders (400 mesh, with impurities of 0.18% Fe, 0.08% Si, 0.15% Cl, 0.10% C, 0.10% N, 0.60% O, and 0.04% H) were purchased from Beijing Yitianhui Metal Institute. TC was purchased from Aladdin Reagent Co. Ltd. All other chemicals were used as received without further purification. Distilled water was used to prepare the TC solution in the experiments.

In a typical synthesis of the cauliflower-like TiO₂, 0.2 g metal Ti powders, 40 mL NH₄HF₂ solution (0.14 mol L⁻¹), and a magnetic stirring rod were added into a Teflon-lined stainless steel autoclave

(50 mL). After completion of the reaction under magnetic stirring for 0.5 h, the autoclave was sealed and kept in the oven at 130 °C for 15 h, and the intermittent stirring, i.e. 2 min in every 3 h, was performed during the hydrothermal process. Afterwards, the products were collected by centrifugation and thoroughly washed with high-purity water until pH = 7.0 was reached, and then dried in the vacuum at 80 °C and subsequently calcined at 600 °C for 2 h in the air atmosphere. The Cu-TiO₂ was synthesized by a similar process only adding CuSO₄ (0.004 mol L⁻¹) into the NH₄HF₂ solution during the hydrothermal reaction.

2.2. Characterization and photocatalytic measurements

The crystal structures of metallic Ti powders and the as-synthesized TiO₂ and Cu-TiO₂ samples were characterized by X-ray diffractometer (XRD, D/Max-III A, Rigaku, Japan) using Cu K α radiation (λ = 0.154 nm), at 30 kV and 30 mA. The morphology and microstructure of the samples were observed by field-emission scanning electron microscopy (FE-SEM; ZEISS Ultra 55, Germany) operated at 5 kV, and the element composition was analyzed via the energy dispersive X-ray detector (EDX; ZEISS Ultra 55, Germany). The UV–vis diffuse reflection spectroscopy (DRS) and photoluminescence (PL) spectra were used to characterize the optical properties of the samples. The UV–vis diffuse reflection spectra (DRS) were recorded on a UV–vis spectrophotometer (UV-3010, Hitachi, Japan) using BaSO₄ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method. The band gap energy (E_g) was evaluated using the following equation (Eq. 1) [20]:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (1)$$

where α , ν , E_g and A are the absorption coefficient, light frequency, band gap energy, and a constant, respectively; n is determined by the type of optical transition of the semiconductor. The PL spectra were measured on a F-2500 fluorescence spectrophotometer (Hitachi, Japan) with an exciting light of 251 nm.

The photocatalytic degradation experiments were carried out in a photochemical reactor (XPA-VII, XuJiang, China), equipped with a 1000 W Xe lamp combined with a 420 nm cut-off filter as light source. All photocatalytic reactions were performed in quartz tubes. Before the experiments, TC solution (50 mL) and photocatalyst were added into each tube, the initial concentration of TC was 20 mg L⁻¹, the catalyst dosage was 20 mg L⁻¹, and the constant magnetic stirring rate in the TC solution was 800 rpm. Throughout the reaction, 2.5 mL solution was timely taken out and the catalyst powders were removed from the solution using 0.45 m cellulose acetate syringe membrane filter. The TC content in the filtration solution was measured on a high performance liquid chromatography (HPLC, LC-20AT, Shimadzu, Japan) using a C18 reverse phase column (5 μ m, 4.6 \times 250 mm) with Ultra-violet detector (λ = 357 nm).

3. Results and discussion

3.1. Morphology and structure composition

Fig. 1 shows the SEM images of the metal Ti raw material and the hydrothermally synthesized samples in the NH₄HF₂ solution. It can be seen that the metal Ti powders (Fig. 1A) have broad particle size distribution, irregular morphology, and polished surface layer, while the as-synthesized samples exhibit a rough surface and a largely morphologic similarity as the metal Ti particles, showing the formation of the resultants is generally encircled the metal Ti particles. Especially, from the high-magnification SEM image (Fig. 1B), mass cauliflower-like micro/nanospheres, which stick together to form three dimensional (3D) particles or exist as individual particles, can be observed. Compared to the morphology of other samples that were synthesized under

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