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Influence of ammonia on the morphologies and enhanced photocatalytic activity of TiO_2 micro/nanospheres

Li Cong-Ju[a,b,*], Xu Guo-Rong[a]

[a] College of Material Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, PR China
[b] Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing 100029, PR China

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ABSTRACT

TiO_2 micro/nanospheres were synthesized by a combination process contains hydrolysis of titanium tetra-n-butyl in mixed solution of anhydrous ethanol/ammonia and the subsequent calcination under 550 °C for 7 h. The pH values of the mixed solution were tuned to be 10.4, 11.0 and 11.6, respectively, by adding different amounts of ammonia. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize the morphologies and the crystallinity. X-ray diffraction (XRD) patterns indicated that pH value of the precursors has an important effect on the crystal phase composition. UV–vis diffuse reflectance spectrum was applied to characterize the optical properties of samples. Degradation of methylene blue under the irradiation of 300 W Hg lamp confirmed the enhanced photocatalytic activity of TiO_2 micro/nanospheres. In addition, the formation mechanism was proposed.

1. Introduction

TiO_2 has attracted enormous research as the catalyst since Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light in 1972 [1]. Till now, the mechanism of the photocatalytic reactions has been generally confirmed. When TiO_2 was irradiated by the light with energy equal to or higher than its bandgap (3.2 ev for anatase and 3.0 ev for rutile), the absorption of photons leads to a charge separation due to the promotion of the electrons (e−) from the valence band to the conduction band, with the simultaneous generation of a hole (h+) in the valence band. The photogenerated electrons and holes combine with the adsorbed chemical groups to form some radicals with strong oxidative activity, such as hydroxyl radicals (•OH), superoxides(O_2•−) and hydroperoxyl radicals(HO_2•−) [2]. So most organic compounds can be oxidized completely in the photocatalytic process [3]. However, the recombination of photogenerated electron–hole pairs and the limited light source have blocked the development of the photocatalysts. Therefore, to prevent the recombination of photogenerated electron–hole pairs was the main effort that has been done in recent decades. Metal-semiconductor system [4], composite semiconductor [5] and transition metal doping [6] have been used to inhibit the recombination by increasing the charge separation and therefore the efficiency of the photocatalytic process.

Besides the modifications mentioned above, another method to improve the photocatalytic activity was to enlarge the surface area. It has been well known that the photodegradation is a surface reaction. So the properties of the surface have crucial effect on the degradation efficiency. Large surface areas could facilitate the reaction/interaction between the photocatalyst and the interacting molecules, thus increasing the degradation efficiency. Surface area has a crucial correlation with surface morphologies. In addition, the surface morphologies could influence the electron–hole recombination. So many photocatalysts with unique morphologies, such as spherical morphologies, have been investigated [7,8].

Many synthesis routes have been applied to fabricate TiO_2 spherical materials [9,10]. The most common used one was template method [11]. It was reported that spherical morphologies could be obtained by adding ammonia into agglomerates of titanium hydroxide after the hydrolysis of titanium tetra-n-butoxide in anhydrous ethanol [12]. In the current experiment, titanium tetra-n-butoxide was hydrolyzed directly in mixed solution of anhydrous ethanol and ammonia. The subsequent calcination results in the formation of TiO_2 micro/nanospheres. The mechanism was proposed. Degradation of methylene blue under irradiation of 300 W Hg lamp indicated that TiO_2 micro/nanospherical structures showed enhanced photocatalytic activity.

* Corresponding author at: College of Material Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, PR China. Tel.: +86 010 6428 8192; fax: +86 010 6428 8192.
E-mail address: congjuli@gmail.com (C.-J. Li).

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2. Experimental

2.1. Materials and preparation of TiO_2 micro/nanospheres

Titanium tetra-n-butoxide ($Ti(OBu)_4$) was purchased from Beijing Xingjin Fine Chemicals. LTD. Anhydrous ethanol (CH_3CH_2OH) and ammonia solution (25%) were purchased from Beijing Tongguang Fine Chemicals. LTD. All the materials were used as received without any purification.

1 ml $Ti(OBu)_4$ was dropped into 20 ml mixed solution of anhydrous ethanol and ammonia. The pH values of the solution were tuned by adding different amounts of ammonia. Wait a few minutes for the hydrolyzation and put the precipitation under 60 °C for 24 h, finally anneal the precipitations under 550 °C for 7 h to obtain the samples.

2.2. Characterization and measurements

The morphologies of samples were examined by scanning electron microscopy (SEM: JSM-6360LV, JAPAN). The deep investigation of the obtained samples was examined by transmission electron microscopy (TEM: Tecnai G^2 20S-TWIN). X-ray diffraction (XRD) patterns were collected on a Rigaku-D/max 40,000 V X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm) at a step width of 5°/min. The UV–vis absorption spectrum were measured on a TU-1901 UV–vis spectrophotometer in the wavelength range of 190–800 nm.

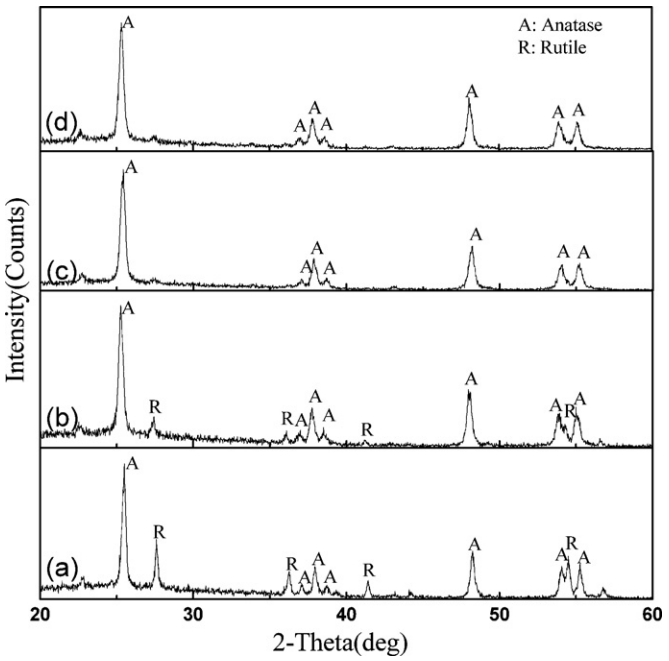

Fig. 1. XRD spectra of samples: (a) without adding ammonia, tuning pH to (b) 10.4, (c) 11.0 and (d) 11.6 by adding ammonia during hydrolysis of Titanium tetra-n-butyl in mixed anhydrous ethanol/ammonia solution.

2.3. Photocatalytic experiments

The photodegradation of methylene blue in water was used to evaluate the photoactivity of the samples as prepared, which is considered as one of the most standard method for the evaluation of photo-oxidation activity. In our experiment, a consistent dosage of 150 mg samples were suspended in 400 ml methylene blue (MB) solutions with the initial concentration of 20 mg/L. The photodegradation experiment was carried out in the photochemical reactor (BL-GHX-II, Shanghai Bilon Instrument Co. LTD). Before the irradiation, the solutions were agitated for 3 h to establish the adsorption/degradation equilibrium. The concentration of methylene blue in solutions was monitored and analyzed by measuring the absorbance at 663 nm wavelength using TU-1901 UV–vis spectrometer (Beijing Purkinje General Instrument Co. LTD) at given irradiation time intervals.

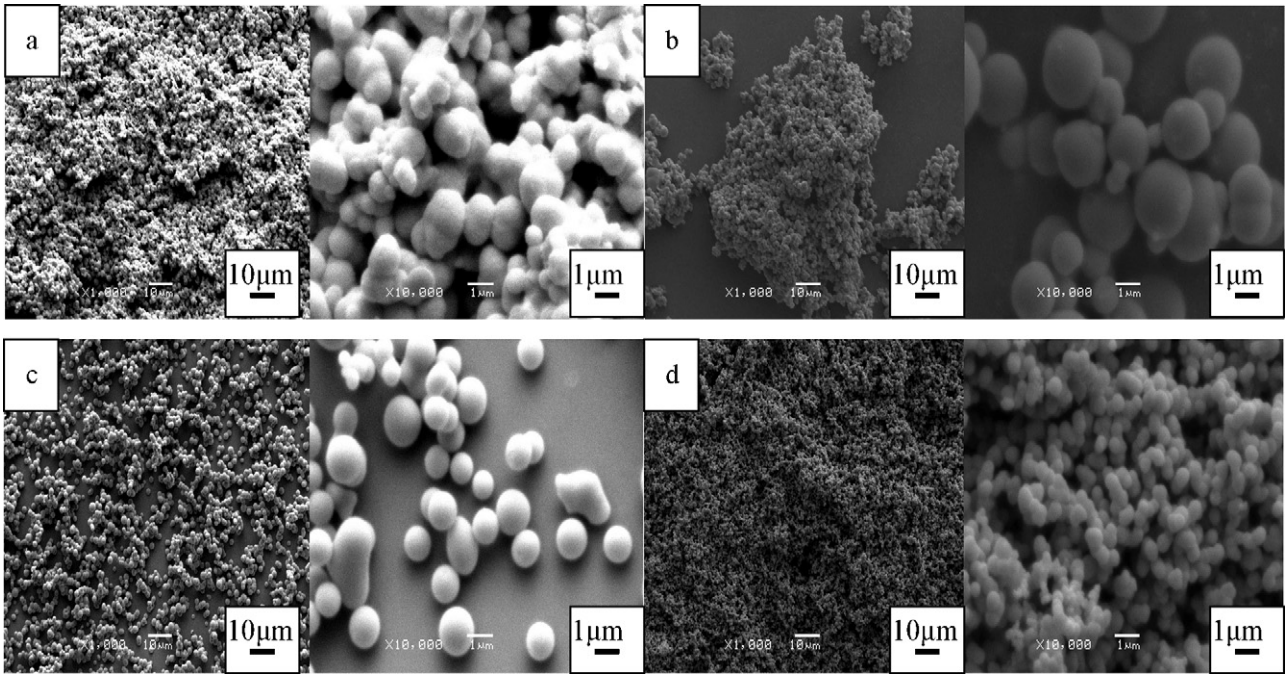

Fig. 2. Low and high magnified SEM images of TiO_2 micro/nano materials after the calcination of the precursors: (a) without adding ammonia, (b) pH = 10.4, (c) pH = 11.0 and (d) pH = 11.6.