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Low temperature fabrication of nanoflower arrays of rutile TiO_2 on mica particles with enhanced photocatalytic activity

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ABSTRACT

In this work, nanoflower arrays of rutile TiO_2 composed of nanorods were directly grown onto mica substrates through hydrolysis of $TiCl_4$ ethanolic solution in water at 70 °C without calcination. SnO_2 as a rutile promoting additive was deposited onto mica prior to TiO_2. The rutile promoting effects of SnO_2 could be ascribed to the structural similarity of rutile and cassiterite. The nanorod crystals grew along the [0 0 1] direction, forming predominantly exposed {1 1 0} side-facets and {0 1 1} top-facets. A reasonable growth mechanism for elucidating the formation of rutile TiO_2 nanoflower arrays was proposed. The obtained nanoflower arrays of rutile TiO_2 coated mica particles show excellent photocatalytic activity towards degradation of rhodamine B (RhB) under UV illumination, which is almost 1.9 times as high as that of Degussa P25. The enhanced photocatalytic activity of rutile TiO_2 superstructures can be ascribed to the combined contribution of high crystallinity, low band gap, and effective separation of electrons and holes by the synergistic effect between the exposed {1 1 0} and {0 1 1} facets of the rutile nanorods. Furthermore, we demonstrated that these rutile TiO_2 coated mica particles can be easily recycled without decrease of the photocatalytic activity, which provide possibility to future industrial applications in environmental pollutants cleaning up.

1. Introduction

In recent years, nanostructured titanium dioxide (TiO_2) materials have attracted increasing attention due to their various applications in solar cells [1–4], biomaterials [5], gas sensors, and lithium ion batteries [6], especially used as photocatalysts to decompose pollutions [7–10]. Both their optoelectronic properties and photocatalytic activity strongly depend on shape, size, and phase composition [11], so exploring novel approaches for the synthesis of nanostructured TiO_2 with the control of particle size and morphology have attracted great interest. Over the past few years, many approaches have been successfully developed to prepare one dimensional (1D) TiO_2 such as nanotubes [12–15], nanowires [16–20], and nanorods [21–26]. What's more, self-assembly of 1D nanostructure into hierarchical 3D architecture has attracted extensive attention because they may exhibit interesting properties because of the large numbers of active sites, unique multidimensional morphology, and the combination of micro-nanoscales.

It is well known that TiO_2 is a polymorphous compound, crystallizing as: rutile, anatase, or brookite. All of these polymorphs have the same fundamental structural octahedral units with different arrangements [27]. In contrast with other two phases, rutile TiO_2 has higher chemical stability [28], higher refractive index, and higher dielectric constant. It is, therefore, found wide application in optical filters, cosmetics, plastics, printed products, ceramic, industrial coatings, and car paints [29]. As a photocatalyst, rutile has been found to show lower photocatalytic activities than anatase in most case [30–33]. However, in some cases rutile was found to be more active for photocatalysis than anatase [34,35].

The synthesis of phase-pure rutile under low temperature is generally believed to be very difficult because most of the techniques adopted for the synthesis of titania produce the kinetically favorable polymorph of anatase [27,36]. Rutile can often be obtained via high-temperature calcination of anatase nanoparticles. However, calcination unavoidably leads to agglomeration and growth of the nanocrystalline particles, leading to the poor photocatalytic performances of rutile. So fabrication of rutile TiO_2 with hierarchical 3D architecture at low temperatures is of great importance.

To our knowledge, few researches have reported low temperature preparation of novel flower-like rutile TiO_2, although the flower-like structures might have high photocatalytic activity [37]. In this paper, a novel method of depositing nanoflower arrays of

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rutile TiO_2 onto mica substrates at 70 °C without calcinations was described. Rutile TiO_2 coated mica particles were synthesized by hydrolysis of $TiCl_4$ ethanolic solution with a prior deposition of SnO_2 as a seed layer. The phase composition, morphology and photocatalytic performance of as obtained nanostructures were investigated.

2. Experimental

2.1. Materials

The mica used as the substrate in this study was fluorophlogopite (synthetic mica). All chemicals used in this study were analytical reagent without further purification. Distilled water was used in all experiments. The starting material in this study to deposit TiO_2 layer on mica was $TiCl_4$ ethanolic solution. In order to prevent the sudden reaction between concentrated $TiCl_4$ and water at room temperature, $TiCl_4$ was added dropwise into absolute ethanol to obtain the precursor. The main components of the precursor are $TiCl_x(OCH_2CH_3)_{4-x}$ complex species [38].

2.2. Preparation method

2.2.1. Preparation of anatase TiO_2 thin film on mica

The preparation of anatase TiO_2 thin film on mica was carried out in the following way [39]. 10 g mica was suspended in distilled water and was heated to 70 °C. The pH value of solution was adjusted to 1.0 with diluted hydrochloric acid. Next, 0.12 L precursor was introduced into the agitated slurry at a rate of 0.5 mL/min. The pH value of the slurry was kept constant by simultaneous addition of NaOH solution. After the addition was completed, the slurry was aged for 1 h and then allowed to settle and cool to room temperature. The particles were separated, washed with distilled water, and dried at 70 °C for 24 h. This sample was labeled as mica@A-TiO_2.

2.2.2. Preparation of nanoflower arrays of rutile TiO_2 on mica

The introduction of SnO_2 in order to obtain rutile phase of TiO_2 onto mica substrate was achieved using $SnCl_4$ solution. First, mica was suspended in distilled water and heated to 70 °C, and the pH value of the slurry was adjusted to 2.0 using hydrochloric acid. Then, $SnCl_4$ aqueous solution (15 g/L) was added dropwise while the pH value was held constant by simultaneous addition of NaOH solution for 1 h. Weight rations of SnO_2 to mica were 0.32%, 0.64%, and 0.96% respectively. Then, the pH value was adjusted to 1.0, and the TiO_2 coating was deposited on mica by addition of precursor the same way as described in Section 2.2.1. The final samples were labeled as mica–x% SnO_2–TiO_2 (x = 0.32, 0.64, or 0.96).

2.3. Characterization

X-ray powder diffraction (XRD) analysis was performed using a PANalytical X'Pert Pro diffractometer using Cu Kα radiation at 40 kV and 40 mA for the crystal structure determination of TiO_2 on mica. XRD patterns were recorded in the 2θ range from 20° to 60° with a step size of 0.01° and a scan step time of 0.3 s at the incident angle of 2°. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were recorded on a Nova NanoSEM 430 equipped with an Oxford Inca X-Act. The operation voltage was 10 kV. The size and crystalline structure of TiO_2 coatings were investigated by transmission electron microscopy (TEM, JEM-2010HR, accelerating voltage: 200 kV). Atomic force microscope (AFM) investigations were conducted using MFP-3D (Asylum Research), in the tapping mode. The weight ratio of TiO_2 in catalysts was determined by X-ray fluorescence spectrometry using a model PANalytical Axios. Raman spectroscopy was done on a LabRAM Aramis (HORIBA Jobin Yvon) with spectral resolution of 1 cm^{-1}. The laser line of the exciting source was at 532 nm. UV–Vis diffuse reflectance spectra were collected using a UV–Vis near-infrared spectrometer (Lambda950, PerkinElmer, United States). The specific surface area of products was estimated by the Brunauer–Emmet–Teller (BET) method based on nitrogen adsorption (Nova 4200e, Quantachrome, United States).

2.4. Photocatalytic test

The photocatalytic activities of the samples were evaluated by the degradation of rhodamine B (RhB) in an aqueous solution. Each sample containing 150 mg of catalyst was suspended in a 150 mL of aqueous solution of 20 mg/L RhB. The solution was continuously stirred for about 1 h to ensure the establishment of absorption–desorption equilibrium among catalyst, RhB, and water before irradiation. Then the solution was illuminated by a 160 W high pressure mercury lamp with a strongest emission at 365 nm (Philips) in a black box. The distance between light source and the top of the solution was about 10 cm. The concentration of RhB solution was monitored by using a Cary 60 UV–Vis spectrophotometer (Agilent Ltd.).

3. Results and discussion

3.1. Low temperature synthesis of rutile TiO_2 thin film

The XRD patterns of mica@TiO_2 particles prepared with different amounts of SnO_2 are shown in Fig. 1. The XRD peaks appearing at 2θ = 25.1° corresponds to (1 0 1) plane of anatase TiO_2 (JCPDS 21-1272),while the XRD peaks with 2θ values of 27.1°, 35.9°,40.9°, 54.0°, 56.2° correspond to (1 1 0), (1 0 1), (1 1 1), (2 1 1), (2 2 0) planes of rutile TiO_2 (JCPDS 21-1276). It is found that when the sample is not treated with any additives, only anatase appears (Fig. 1a). However, the peaks of rutile phase appear when mica particles are deposited with SnO_2. Then the intensity of rutile increases and the peaks of rutile sharpen with increasing loadings of SnO_2 while the intensity of anatase decreases. When the loading of SnO_2 is increased to 0.96%, the TiO_2 in mica@TiO_2 particles is in the rutile phase. More interestingly, for the rutile TiO_2 thin film, the intensity ratio of (1 0 1) plane and (1 1 0) plane diffraction peaks is about 0.82, which is about 1.6 times as high as that of JCPDS 21-1276 (0.5), probably reflecting that the {1 1 0} and {1 0 1} facets are preferentially exposed on the surfaces of rutile crystals.

The percentages of anatase and rutile in TiO_2 layer were quantitatively calculated using a well-known equation [40]:

$$X_R = \frac{1}{1 + 0.79(I_A/I_R)} \times 100\% \quad (1)$$

where X_R is the mass fraction of rutile in the powders, while I_A and I_R are the intensities of anatase (1 0 1) reflection and rutile (1 1 0) refection, respectively.

Fig. 2 shows the graphical illustration of the change of mass fraction of rutile phase with varying SnO_2 loadings. It is clear that the mass fraction of rutile phase goes up gradually with increasing SnO_2 loadings, which finally reaches 100%.

In order to further confirm the surface coating of mica–0.96%SnO_2–TiO_2 is in rutile phase, Raman spectroscopy was used. The anatase and rutile phase of TiO_2 can be sensitively identified by Raman spectroscopy based on their Raman spectra. The typical Raman bands of rutile phase appear at 143, 235, 447, 612 cm^{-1}, which can be ascribed to the B_{1g}, two-photo scattering, E_g, and A_{1g} modes, respectively [41,42]. The major Raman bands of anatase phase are at 144, 197, 399, 515, and 639 cm^{-1}.These bands can be attributed to the five Raman-active modes of anatase phase with the symmetries of E_g, E_g (low-frequency), B_{1g}, A_{1g}, and E_g (high-frequency), respectively [43,44]. As can be seen from Fig. 3, the peaks appearing at 253, 437, and 609 cm^{-1} are typical rutile bands, and

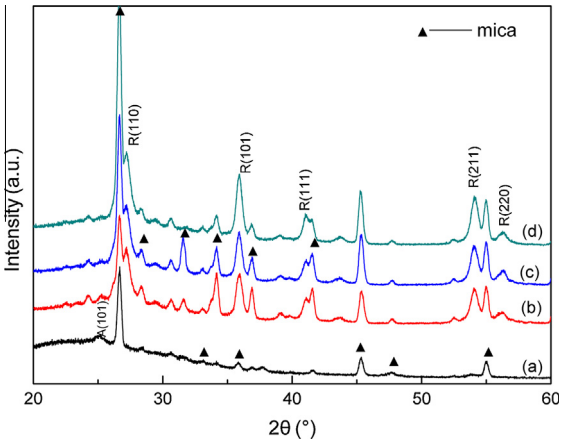

Fig. 1. XRD patterns of mica@TiO_2 particles with different amounts of SnO_2: (a) mica@A–TiO_2, (b) mica–0.32% SnO_2–TiO_2, (c) mica–0.64% SnO_2–TiO_2, (d) mica–0.96% SnO_2–TiO_2.