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Simple fabrication of twist-like helix N,S-codoped titania photocatalyst with visible-light response

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Abstract

Visible-light responsible N,S-codoped titania photocatalyst was fabricated by simple hydrolysis of titania tetrachloride using ammonia in the presence of glacial acetic acid and ammonium sulfate. The N,S-codoped titania materials were fabricated by a template-free route and demonstrated twist-like helix morphology. The morphology and microstructure characteristics of N,S-codoped titania photocatalysts were characterized by means of the N_2 adsorption–desorption measurements, thermal gravimetric and differential thermal analysis (TG-DTA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), UV–visible diffuse reflectance spectra (DRS) and X-ray powder diffraction (XRD). The unique morphology of N,S-codoped titania materials and mesoporous microstructure were maintained after a heat treatment at 723 K for 3 h, exhibiting significantly thermal stability. The photocatalytic activity was evaluated by degrading phenol in aqueous suspension under ultraviolet and visible light irradiation. The results obtained with these novel photocatalysts are compared with the behavior of the well-studied and widely used Degussa P25 TiO_2 under the same conditions. The N,S-codoped titania samples were more superior than P25 and the sample calcined under 723 K for 3 h shows the best photocatalytic activity, the higher activity of which could be attributed to its high surface area, large pore volume, well-crystallized anatase, red-shift in adsorption edge and strong absorbance of light with longer wavelength.

Keywords: Titanium dioxide; Titanium tetrachloride; Mesoporous; Visible-light; N,S-codoped; Photocatalyst

1. Introduction

Semiconductor photocatalysis is an efficient method for the chemical utilization of solar energy. TiO_2, among various photocatalysts, is most frequently employed owing to its cheapness, nontoxicity, and structural stability [1–5]. However, the widespread technological use of TiO_2 is impaired by its wide band gap (ca. 3.2 eV for crystalline anatase phase) which requires the use of UV light during the reaction while the solar spectrum usually contains about 4% UV light, thus limiting the possibility of employing solar light in TiO_2 photocatalysis. Besides, the low quantum efficiency of the TiO_2 also limited its application.

Many researchers paid their much attention on anion doped photocatalysts since Sato et al. firstly reported in 1986 that nitrogen doped titanium oxide with high visible-light photocatalytic activities could be prepared by treating anatase TiO_2 powder in the NH_3 atmosphere [6–13]. Modification TiO_2 with various metal and non-metal ions were powerful ways to extend the adsorption light from UV to visible area and to reduce the recombination of photo-generated electrons and vacancies of TiO_2. N, anion-doped TiO_2 photocatalysts having an anatase form that show a relatively high level of activity when irradiated by visible light have been reported, and substitution of the lattice oxygen with nitrogen might narrow the band gap by mixing the N 1s and O 1s states. Other kind of anions such as C, S and F would result in the similar effect to nitrogen [14–19]. However, most methods are high temperature processes, using expensive precursors or preparation instruments. Besides the energy waste, the treatment at such high temperature usually resulted in the low surface area due to the undesirable sintering of nanocrystallites [12,20]. Hence, the seeking of new facile approaches to synthesize doped TiO_2 caught hold of increasingly interesting.

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It is also known that hierarchically ordered mesoporous TiO_2 materials may be promising candidates in the field of photocatalysis owing to their large surface area and convenient mass transfer in mesopores in degrading large pollution molecules. However, these TiO_2 materials are traditionally prepared by using surfactant templating in which supramolecular aggregates are considered to direct inorganic deposition across a range of length scales [21,22]. The organic templates must then be removed by thermal treatment, resulting in high-energy consumption, environmental pollution and most important the agglomeration and collapse of pore structure in many cases [23–25]. So most reported mesoporous titania materials have a low thermal stability. To the best of our knowledge, although there were some researches related with N,S-codoped titania photocatalysts [26,27], no hierarchically ordered mesoporous N,S-codoped titania material with highly thermal stability has been reported yet by using titanium tetrachloride as the titanium precursor under mild conditions.

In the present work, we use a simple template-free approach for the synthesis of N,S-codoped titania photocatalysts with visible-light response via a low-temperature precipitation treatment of $TiCl_4$ by ammonia in the presence of glacial acetic acid and ammonium sulfate. The reaction condition is much milder than that of conventional methods. In addition, it is more interesting to find that the N,S-codoped titania sample shows a unique twist-like helix structure which has never been reported yet.

2. Experimental

2.1. Preparation of mesoporous N,S-codoped titania samples

Titanium tetrachloride ($TiCl_4$, analytical reagent grade) was used as titanium precursor. Commercially available reagents were obtained from Aldrich and used without further purification. The mesoporous N,S-codoped titania samples were prepared by hydrolysis $TiCl_4$ with ammonia in water solution in the presence of glacial acetic acid and ammonium sulfate ($(NH_4)_2SO_4$). In a typical procedure, 25 mL of dilute aqueous solution of $TiCl_4$ (3.0 mol L^{-1}) was carefully added into 150 mL deionized water with gentle stirring in ice-water bath to avoid a drastic hydrolysis of $TiCl_4$ in water at room temperature. Subsequently, 4.5 mL of glacial acetic acid and 10 g ammonium sulfate was added into the solution, then the solution was heated to 323 K. After that, a 35% (w/w) solution of ammonia was added dropwise with vigorous stirring until pH 8, then the mixed solution was quickly cooled down to ambient temperature (about 298 K) by rinsed with running water. After aging in the mother liquor for a few days, the resultant slurry was suction-filtered and washed with distilled water until pH 7 and then washed carefully with absolute ethanol for three times. The N,S-codoped titania samples were finally obtained after the as-prepared filter residue being vacuum-dried at 353 K for 12 h, followed by calcination at certain temperatures for 3 h with the rate of 10 K min^{-1}.

Six new samples, including the as-prepared precipitate and five calcined samples denoted as N,S-TiO_2-AS, N,S-TiO_2-623, N,S-TiO_2-723, N,S-TiO_2-823, N,S-TiO_2-923 and N,S-TiO_2-1023 were obtained (see Table 1).

2.2. Characterizations

XRD patterns of N,S-TiO_2 samples (2θ ranges from 20° to 70°) were recorded at room temperature with scanning speed of 2° min^{-1} using Cu Kα radiation ($\lambda = 0.154$ nm) from a 40 kV X-ray source (Bruker D8 Advance) and diffracted beam monochromator, operated at 40 mA. The Scherrer equation was applied to estimate the average crystallite sizes of TiO_2 samples: $d = 0.89\lambda/B(2\theta)\cos\theta$, where $B(2\theta)$ is the width of the XRD peak at half peak-height in radian, λ the wavelength of the X-ray in nanometer, θ the angle between the incident and diffracted beams in degree, and d is the average crystallite size of the powder sample in nanometer. The content of anatase in TiO_2 powder was calculated as follows [28]: $X_A\ (\%) = I_A/(I_A + 1.265 I_R) \times 100$, where X_A is the content of the anatase phase, I_A and I_R are peak intensities of anatase (1 0 1) and rutile (1 1 0), obtained from X-ray diffraction patterns, respectively.

The textural structures were measured by N_2 adsorption at 77 K in a Micromeritics TriStar ASAP 3000 system, and specific surface areas of N,S-TiO_2 samples were measured using Brunauer–Emmett–Teller (BET) method. The pore size distributions (average pore diameter and mean pore volume) were measured from the N_2 desorption isotherm using the

Table 1
Textural and structural properties of N,S-TiO_2 samples annealed at different temperatures

Sample	Calcination temperature (K)	Surface area ($m^2\ g^{-1}$)[a]	Pore volume ($cm^3\ g^{-1}$)[a]	Average pore diameter (nm)	Crystallite phase (%)[b]	Crystallite size (nm)[c]
N,S-TiO_2-AS	R.T.	411	0.25	3.5	A-100	A-4.1
N,S-TiO_2-623	623	146	0.19	4.0	A-100	A-7.0
N,S-TiO_2-723	723	82	0.15	4.6	A-100	A-9.9
N,S-TiO_2-823	823	43	0.09	5.1	A-100	A-20
N,S-TiO_2-923	923	4	0.03	8.5	A-100	A-32
N,S-TiO_2-1023	1023	1	0.01	14.1	A-98	A-42
Degussa P25	–	51	0.16	16	A-77/R-23	A-21/R-24

[a] BET surface area, average pore volume of the N,S-TiO_2 samples estimated from nitrogen adsorption.
[b] Ratio of phase of titania based on XRD data, where A and R represent the anatase and rutile phases, respectively.
[c] Average size of titania crystallites estimated from Scherrer equation.