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Short Communication

Effect of heating temperature on photocatalytic reduction of CO_2 by N–TiO_2 nanotube catalyst

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ABSTRACT

Nitrogen-doped TiO_2 nanotubes (N-TNTs) have been synthesized via a hydrothermal method using hexamethylene tetramine (HMT) and $TiCl_3$ as precursors. Photocatalytic activity was characterized by XRD, SEM, TEM, BET and UV–vis DRS. N was doped into the TiO_2 lattice, it extended the absorption region of TiO_2 to visible light. Post-heating TNTs at 300–500 °C showed a maximum red-shifted at 500 °C with a band gap energy of 3.09 eV. The visible light activity of N-TNTs was evaluated using CO_2 reduction. The total organic carbon (TOC) yield of N-TNT500 was 14530.0 μmol/g-catal. following 12 h of illumination. The yield is much higher than those of N–TiO_2 and TNTs.

1. Introduction

Increasing carbon dioxide concentration in the atmosphere has become a global environmental issue. Conversion of CO_2 into other materials is an effective way to reduce the greenhouse effect and at the same time to obtain important industrial raw materials. Photocatalytic reduction of CO_2 with photo-catalysts of semiconductor powders has been verified valid for this conversion [1–5]. In Ameta's study [6], as the amount of semiconductor increases, the exposed surface area will also increase, thus causing a corresponding increase in the rate of reaction. According to their research, titania is the most effective photo-catalyst mainly because its conduction band energy is comparable to the reduction potentials of CO_2 which are −0.61v and −0.48v for reduction of CO_2 toward HCOOH and HCHO. In addition to higher specific surface area, higher photon conversion efficiency was more important a key element for such a photo-catalyst reduction reaction. In fact, the primary particle size of the photo-catalyst determines both the specific surface area and the photon conversion efficiency.

Recently, Koci et al. [7] compared the photocatalytic activity of pure TiO_2 and kaolinite/TiO_2 on CO_2 reduction under UV light (254 nm). They found that the yields of CO_2 photocatalytic reduction products methane and methanol were higher over a kaolinite/TiO_2 composite than over commercial TiO_2 (Degussa P25). However, due to the large band-gap energy of TiO_2 particle, they can only be excited under UV light, which occupies less than 5% of the sunlight. To utilize the solar energy efficiently, it is necessary to develop a visible-light photo-catalyst. Currently, various modifications strategy have been used to realize visible light responsiveness [8,9]. For example, TiO_2 was doped with noble metals and cation and/or anion has been proved effective. In 1986, Sato [10] firstly found that TiO_2 doped with N could encouraged by visible-light. In 2001, Asahi [11] reported that nitrogen doped titanium oxide with high visible light photocatalytic activities could be prepared by sputtering TiO_2 in an N_2 (40%)/Ar gas mixture followed by annealing in N_2 gas at 550 °C. Zhang [12] prepared $K_{0.81}Ti_{1.73}Li_{0.27}O_4/TiO_{2-x}N_y$ sandwich-like composite which displayed excellent photocatalytic activity for the decomposition of NOx gas under both visible light and UV light irradiation. Yin [13] believed that nitrogen doping led to narrowing of band gap by mixing the N2p and O2p state and consequently induced the visible-light responsive photocatalytic activity. It was also forecasted that other kind of anions such as C, S and F would result in the similar effect to nitrogen. Such a modification needed higher temperature, expensive precursors and preparation instruments. Moreover, Some researchers have focused on coupling of TiO_2 with other metals or metal oxides to stabilize charge carriers or use metal dopants as electron sinks [14–17].

Guan [18] used a Pt-loaded $K_2Ti_6O_{13}$ photocatalyst combined with a Fe-based catalyst supported on a dealuminated Y-type zeolite to reduce CO_2. Ihara et al. [19] reported that calcaining the hydrolysis product of $Ti(SO_4)_2$ and ammonia liquor produced a visible-light responsive photocatalysis, which was encouraged by 400–500 nm light. Recently, Costa and Prado [20] reported a considerable photocatalytic activity of

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titanate nanotubes towards degradation of indigo carmine dye. With relatively lower activity, the as-prepared titanate nanotubes were easily recovered from the solution in comparison with the traditional TiO_2 catalysts.

In this study, N-doped TiO_2 nanotube was used as the photocatalyst to reduce CO_2. The doping of nitrogen into TiO_2 was an effective method to increase the photocatalytic activity of TiO_2 in the visible light range because its impurity state is near to the valence band edge, and the doping element do not act as charge carriers, so the combination probability of photoinduced electron–hole pairs was minimized [21,22]. Furthermore, the one-dimensional nanotube has big specific surface area and high sedimentation rate, which is beneficial to be separated from reaction system. To the best of our knowledge this is the first report on the photocatalytic reduction of CO_2 using TNTs and N-TNTs. We have found that the reduction of CO_2 was significantly higher using TNTs than TiO_2 particle.

2. Experimental

2.1. TNTs preparation

Degussa P-25 TiO_2 was commercially available, which was a mixture of 80% anatase and 20% rutile. Its BET surface area was about $50\ m^2 \cdot g^{-1}$. Titanium(III) chloride($TiCl_3$, 20% w/w solution in 2 N Hydrochloric acid), hexamethylene tetramine (HMT 99%) were used as starting materials without any further purification. Other chemicals were all reagent grade quality. All aqueous solutions were made up in de-ionized and doubly distilled water.

(1) The N–TiO_2 powder was prepared by mixing 2 g HMT, 5 ml of 20 wt.% $TiCl_3$ solution and 5 ml of distilled water. The mixture was placed into a Teflon® autoclave of internal volume of $60\ cm^3$. The autoclave was heated to start hydrothermal reaction at 230 °C for 10–30 min. The powder products was separated by centrifugation, washed with distilled water and acetone three times, respectively, then vacuum dried at 60 °C for 20 h. The products was marked N–TiO_2.

(2) The N-TNTs were prepared by N–TiO_2 powder. N–TiO_2 powders were ultrasonic suspended in 40 ml of 10 mol/L NaOH solution for 20 min and transferred to a Teflon® autoclave. The autoclave was closed tightly and kepted at 155 °C for 28.5 h. Then the precipitates were collected by centrifugation, washed with 0.1 mol/L HCl until pH reached ca 2.5, and washed with stirring for 2 h at room temperature. The precipitate was washed with distilled water until pH reached ca 7. The products were dried at 90 °C, followed by the calcination at 300 °C, 400 °C, 500 °C in air for 2 h, respectively. The samples obtained were labeled as N-TNT300, N-TNT400 and N-TNT500.

(3) The TNT was prepared by Degussa P25. 0.5 g P25 and 40 ml of 10 mol/L NaOH solution were ultrasonic mixed for 20 min, then hydrothermal treated at 155 °C for 49 h. After the same dry and calcination process as above, the TNT was successfully prepared and labeled as TNT300, TNT400 and TNT500, respectively.

2.2. Characterization of TNT catalysts

The phase compositions of the samples were determined by X-ray diffraction analysis (XRD. Shimadzu XD-1) using graphite-monochromized CuKα radiate ion (30 kV, 30 mA). The size and shape of the nanoparticles were observed by scanning electron microscope (SEM. Hitachi S-4100) and transmission electron microscope (TEM. JEOLJEM-2010). A diffusive reflective UV–vis spectrophotometer (DRS) was employed to measure the UV–vis absorption and estimate the bandgap of the catalysts. The specific surface area and pore structure of the prepared catalysts were measured by adsorption/desorption of nitrogen using a Thermo Electron Corporation Sorptomatic 1990 and evaluated by the BET and BJH methods, respectively.

2.3. Photocatalytic reduction of CO_2

Photocatalytic reaction was carried out in a quartz reactor. Catalyst nanotube (150 mg) was suspended in 100 ml of 0.1 N NaOH aqueous solution. Illumination was performed with a visible-light of 500 W tungsten–halogen lamp for 12 h. The reactor was tightly closed during reaction and stirred continuously by a magnetic stirring bar to prevent sedimentation of catalyst, then CO_2 was bubbled through the reactor for at least 45 min to purge air and saturate the solution. The yields for the formation of methanol, formaldehyde and formic acid were determined with UV–vis spectrophotometer or gas chromatograph equipped with FID detector and the HP5 column for methanol and ethanol analysis. Helium was used as a carrier gas.

Blank reaction was conducted to ensure that hydrocarbon was the product of photo-reduction of CO_2 and eliminated surrounding interference. The following conditions were employed for three bland tests, respectively. (1) vis-illumination, no catalyst, CO_2; (2) dark, catalyst, CO_2; and (3) vis-illumination, catalyst, N_2. No product was detected in the above three blank tests.

3. Results and discussion

3.1. Characterization of TNT and N-TNT

Fig. 1 presents XRD patterns of the N–TiO_2, TNT and N-TNT. Fig. 1(a) shows the XRD images of N–TiO_2 powder, in which rutile and anatase-type TiO_2 powders coexist. The peaks at 2θ of 25.3°, 36.7° and 53.9° are corresponded to anatase (101), (004)and (106) (JCPDS 21–1272). Peaks at 2θ of 27.4° and 40.9° are corresponded to rutile. In N–TiO_2 powder, rutile and anatase-type crystal grains with diameter of about 10 nm coexist. The diffraction peaks of N–TiO_2 powder and N-TNT are different, implying the preparation of nano-tube. Fig. 1(b,c,d) shows that rutile is disappeared. N–TiO_2 powder is a mixture of anatase(49%) and rutile(51%), as the TNTs are completely anatase. It means that it is the post-heat treatments that convert the rutile to anatase via the formation of titanate. For the titanate structures, there should be peaks around 2θ of 10° corresponding to the d-spacing of the layered structure [23,24]. Three characteristic peaks positioned at 2θ of 24°, 28° and 48° in the diffraction patterns of nanotubes, have been assigned to the diffraction of titanates. Fig. 1 N-TNTs peaks at 2θ of 12°, 24.5° and 48.5° are corresponded to (200), (110)

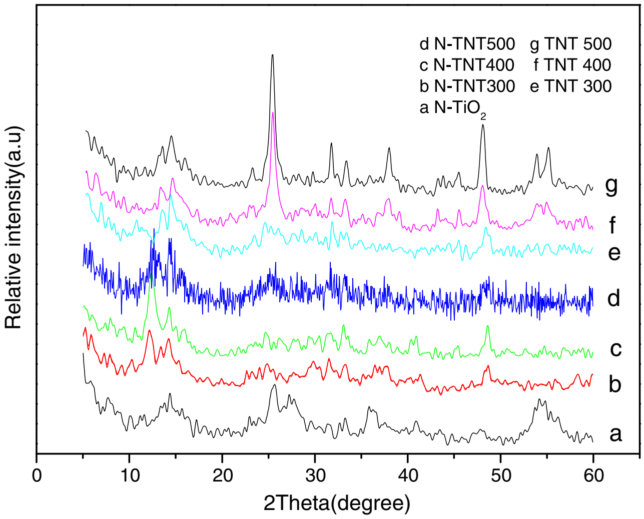

Fig. 1. XRD patterns of N-TNTs and TNTs.