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Room temperature synthesized BaTiO₃ for Photocatalytic Hydrogen Evolution

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ABSTRACT

As a photocatalyst, barium titanate (BaTiO₃) has shown a great potential in photocatalytic water splitting for hydrogen evolution. In this work, BaTiO₃ nanoparticles were synthesized at room temperature conditions under ambient pressure. The small particle size below 10 nm plays a key role in suppressing the recombination of photo-induced carriers, and thus promoting the photocatalytic activity. The photocatalytic hydrogen evolution rates of BaTiO₃ (BTO-R) synthesized at room temperature are 8 and 2.9 times that of commercial BaTiO₃ (BTO-C) in the presence and absence of triethanolamine (TEOA) as a sacrificial agent, respectively. This work provides a good example on size control, low-cost synthesis and photocatalysts' design.

Keywords

BaTiO₃; Room-temperature synthesis; Photocatalysis; Hydrogen evolution; Nanoparticle.

1 Introduction

Photocatalytic hydrogen evolution has been drawing enormous attention in recent years for its low cost and environmental friendship in solving the energy shortage through facile solar to chemical conversion [1-4]. An ideal photocatalyst must meet the requirements that include wide range optical utilization, effective separation of photo-generated carriers and high-efficient surface redox reaction [5-8]. The photocatalytic efficiency of semiconductors is mainly determined by the coordination and balance of thermodynamics and kinetics [9-11]. Titanium dioxide (TiO₂) as a popular and first reported photocatalyst used in hydrogen evolution, CO₂ reduction and environmental applications has been extensively investigated [12-15]. TiO₂-based photocatalysts supply the merits of low cost, low toxicity, and high physicochemical stability. Various works of advanced TiO2-based semiconductors have been conducted in relation to increasing photo-conversion efficiency [16]. However, by contrast with perovskite-type oxides (ABO₃), the limited diversities in chemical compositions and internal structures hinder the development and application of TiO₂ in environment and energy fields [17]. Therefore, the perovskite oxides are regarded as one of promising materials on photocatalysis and have gained extensive attention in recent years [18]. For example, novel perovskite SrTiO₃-Ba₂FeNbO₆ Solid Solution [19], La/Cr co-doped CaTiO₃ [20], LaCoO₃ co-catalyst for CO₂ reduction [21], PbTiO₃/TiO₂ as ferroelectric oxide heterostructures [22] and so on.

Barium titanate (BaTiO₃), a common perovskite oxides with a band gap energy of about 3.2 eV, has the ability to split water into hydrogen and oxygen for its appropriate conduction- and valence- band position compared with the redox potentials of H^+/H_2 and O_2/H_2O [23, 24]. Electrons with high reduction power in the conduction band (CB) and holes with sufficient oxidation ability in the valence band (VB) are generally required for efficient photocatalytic reactions [25]. Due to its unique physical and chemical properties, a mass of researches have been carried out to overcome the limitations that hamper the enhancement of photocatalytic efficiency [24, 26, 27]. Among the factors that affect the photocatalytic activities of BaTiO₃, a

relatively high recombination rate of photo-excited holes and electrons is the main reason that leads to a poor efficiency of photocatalytic reaction [28]. Thus, some effective approaches have been explored to promote the separation and migration of photo-generated carriers, such as noble metal loading, ion doping, heterogeneous structure and size/morphology control [23, 25, 29-31].

High specific surface area through controlling the morphology or grain size could increase the surface accessibility of photocatalysts, and thus improve the utilization of photo-induced electrons and holes [32-34]. Small size particles or low-dimension materials enable shorter diffusion distance of electrons and holes which could facilitate the surface redox reaction as compared to their bulk counterparts [35, 36]. Various synthetic techniques have been applied in controlling particle size, including solvothermal, sonochemical and wave-assisted hydrothermal methods in recent years [37-39]. It is well-known that most of these methods demand harsh reaction conditions such as good quality equipment, high temperature or high pressure [40, 41]. Therefore, for the purpose of meeting the requirements of industrial application, it is highly competitive to make use of a facile and simple synthetic technology at room temperature under ambient pressure conditions. Our group has demonstrated that BaTiO₃ can be prepared at room temperature [42]. However, the photocatalytic activity of this room temperature synthesized BaTiO₃ nanoparticle has not been discussed.

Herein, in this work, BaTiO₃ nanoparticles have been facilely synthesized at room temperature conditions under ambient pressure using ethanediamine (EDA) as solvent. The small particle size below 10 nm plays a key role in suppressing the recombination of photo-induced carriers, and thus promoting the photocatalytic activity compared with commercial BaTiO₃. The photocatalytic hydrogen evolution rates of room-temperature synthesized BaTiO₃ (BTO-R) are 8 and 2.9 times that of commercial BaTiO₃ (BTO-C) in the presence and absence of triethanolamine (TEOA) as a sacrificial agent, respectively. The specific characterizations and photocatalytic mechanisms have been discussed. This work provides a better reference for other works on the size control, crystal growth and design of photocatalysts.

2 Experimental section

2.1 Preparation

BaTiO₃ nanoparticles synthesized temperature were at room using enthylenediamine (EDA) as solvent. All reagents were analytical stage without further purification. Typically, 50 mmol of tetrabutyl titanate (C₁₆H₃₆O₄Ti) was firstly dissolved in 100 mL ethylene glycol monomethyl ether (HOCH₂CH₂OCH₃), followed by the addition of ammonium hydroxide (NH₃·H₂O) to obtain titanium hydroxide. The titanium hydroxide precipitate was filtered and washed with distilled water several times for subsequent use. At the same time, Ba(CH₃COO)₂ aqueous solution (20 mL 2.5 M) was dispersed in a 300 mL of EDA stirring for 4 h. Then Ba(CH₃COO)₂/EDA solution and KOH (20 mL 2.5 M) were put into the titanium hydroxide precipitate in sequence under stirring. After stirring for 48 h at room temperature under ambient pressure, the resultant product was washed with distilled water several times, and then dried at 80°C for 12 h, namely BTO-R. The Commercial BaTiO₃ (BTO-C) bought from SIGMA-ALDRICH Corporation was used as a comparison sample.

2.2 Characterization

The crystalline phase of as-obtained BaTiO₃ nanoparticles was examined by X-Ray powder diffraction (XRD) on a PANalytical X'Pert PRO X-ray powder diffractometer with monochromatic Cu K α radiation in the range of 10-90°. The field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with an energy dispersive X-ray spectrometer (EDX) for elemental analysis were performed on Hitachi SU-70 and Tecnai G² F20, respectively. UV-vis diffuse reflectance spectra were collected with a spectrophotometer (Persee TU-1900) using BaSO₄ as the reflectance standard. Photoluminescence (PL) spectra were recorded by fluorescence spectrometer (Edinburgh instruments FLS920) with an excitation wavelength of 325 nm. The specific surface area was determined by the the Brunauer-Emmett-Teller (BET) method from N₂ adsorption isotherms (Quantachrome AUTOSORB-IQ2-MP). X-Ray photoelectron spectra (XPS) were recorded on an Escalab 250Xi for the surface electronic states.

2.3 Photocatalytic reaction

Photocatalytic reaction was carried out in a closed circulation system mainly consisting of vacuum system, cooling water, and gas analysis device (Labsolar-IIIAG photocatalytic system, Beijing Perfectlight Technology Co. Ltd). The samples (0.05 g) were dispersed in a quartz reaction cell filled with 100 mL of aqueous solution. Prior to irradiation, the reaction system was evacuated and then flowed with Ar gas to remove the dissolved oxygen. The reaction was proceeded under the illumination of a UV Xe lamp (200-400 nm). The produced hydrogen was analyzed through an on-line gas chromatograph with a TCD detector (GC9790, FULI). The Pt loading on the photocatalysts was prepared by chemical reduction method using H₂PtCI₆·6H₂O and NaBH₄ as precursor and reducing agent, respectively. After continuous ultrasonic oscillation for 30 min, the samples were washed by water and ethanol several times and dried at 80 °C in the oven for overnight.

3 Results and discussion

Fig. 1 shows the XRD patterns of BaTiO₃ samples. The diffraction peaks of BTO-C and BTO-R can be well indexed to the perovskite phase (JCPSD No. 74-1967) with the space group of Pm-3m. The BTO-R exhibits broad diffraction peaks compared with BTO-C, indicating the formation of small size nanoparticles. For BTO-R prepared at room temperature, the lower diffraction peak intensity can be ascribed to low crystalline degree compared with BTO-C, which is common in materials with small crystal sizes. The average crystallite size was about 7 nm calculated by the Debye-Scherrer formula. Furthermore, it could be observed that the diffraction peaks of BTO-R shift toward lower angles, which is related to their synthesis process and the corresponding different crystal parameters.



Fig.1 XRD patterns of (a) all samples, (b) room temperature synthesized $BaTiO_3$ (BTO-R) (the blue lines represent the positions of standard diffraction patterns of the $BaTiO_3$ (JCPSD NO. 74-1967)).

The difference in crystalline size for the sample BTO-C and BTO-R could also be seen in SEM images obviously (Fig. 2a and Fig. S1). The BTO-C sample consists of large-size crystalline particles (around 500 nm) with irregular morphology (Fig. S1). It is obvious that the crystal size of BTO-R was smaller than that of BTO-C as shown in Fig. 2a. TEM was employed to further study the microstructure of BTO-R. A low-magnification TEM image was shown in Fig. 2b, from which we can see that room temperature synthesized BaTiO₃ (BTO-R) was composed of mutually aggregated nanoparticles with the size of 5-10 nm. This result is consistent with XRD analysis. According to our precious study, the high activity of the titanium hydrous gel and the high basicity of the solvent play a significantly important role in room temperature synthesis. The organic solvent of EDA adsorbed on the surface of particles was able to confine the crystal growth. Meanwhile, the ambient temperature results in a low diffuse coefficient compared with high temperature reaction, thus leading to the BaTiO₃ particle with small size.[42] The particle size plays a key role in promoting photocatalytic activities which can be seen in the following section. The high-resolution TEM (HRTEM) reveals the lattice fringes of about 0.297 nm

corresponding to the (110) plane of cubic $BaTiO_3$ (Fig. 2c). The interplanar crystal spacing of BTO-R is larger than that of PDF card (0.287 nm), which is in consistent with XRD results according to Bragg equation. The indexed selected area electron diffraction pattern (SAED) reveals that the room temperature synthesized nanoparticles are well crystallized with the cubic perovskite phase, which is aslo confirmed by HRTEM result. The contrast on crystal size are also reflected in the surface area (Fig. S2). The specific surface area of BTO-R sample is 120.98 cm²/g, cm^2/g). which is larger than the BTO-C sample (2.11)



Fig. 2 the electron microscopy images of room temperature synthesized BaTiO₃ (BTO-R): (a) SEM, (b) low-magnification TEM, (c) high-resolution TEM and (d) selected area electron

diffraction (SAED).

In order to evaluate the surface state of $BaTiO_3$ samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out and the corresponding results are displayed in **Fig. 3**. The peaks of Ba, Ti and O are presented in the survey spectrum which can be seen in **Fig. 3a**. Two band peaks located at 793.9 eV and 779.6 eV can

be assigned to Ba $3d_{3/2}$ and Ba $3d_{5/2}$ signals, respectively (**Fig. 3b**) [43]. In addition, the spectrum of Ti 2p is mainly made up of two characteristic peaks, Ti $2p_{1/2}$ at 463.8 eV and Ti $2p_{3/2}$ at 458.0 eV, indicating the chemical valence of Ti⁴⁺ in the as-obtained room temperature synthesized BaTiO₃ samples (**Fig. 3c**) [44]. The O 1s signal displays three components corresponding to oxygen in BaTiO₃, CO₃²⁻ and hydroxyls (**Fig. 3d**) [45]. Based on the above analysis, the results of the XPS spectra demonstrate the formation of well-crystalline BaTiO₃ in the room temperature condition.



Fig. 3 XPS spectra of samples: a) survey, (b) Ba 3d, (c) Ti 2p and (d) O 1s.

The optical properties of the obtained BaTiO₃ samples were characterized by UV-vis diffuse reflectance spectra at room temperature. As shown in **Fig. 4a**, the absorption edges of BTO-C and BTO-R locate at about 394 nm and 384 nm, respectively. It is interesting that BTO-R shows a lower optical absorption range compared with BTO-C because of the size effect of nanomaterials. Meanwhile, the band gaps of samples are estimated from the Tauc plot of $(\alpha h\nu)^{1/2}$ versus hv

according to

$$(\alpha h\nu)^n = A(h\nu - E_q)$$

where α , h, v, A, and E_g represent the absorption coefficient, Plank constant, light frequency, proportionality and band gap, respectively [46]. The factor *n* is related to the optical transition of a semiconductor where *n*=1/2 for direct transition and *n*=2 for indirect transition. The value of *n*=2 is corresponding to our samples because cubic BaTiO₃ is an indirect semiconductor confirmed by previous report [47]. Herein, the band gaps of BTO-C and BTO-R are estimated to be 3.27 eV and 3.38 eV, respectively (**Fig. 4b**). PL spectra were provided to investigate the migration and separation efficiency of photo-induced holes and electrons. In **Fig 4c**, the broad emission band centeres at around 438 nm for both BaTiO₃ samples with an excitation wavelength of 325 nm. The as-prepared BTO-R sample exhibits a lower PL intensity compared with BTO-C sample, implying that the recombination rate of photo-excited carriers is efficiently restrained. For these nanoparticles with smaller size, more photo-generated carriers are easy to migrate from inner part of particles and take part in surface redox reaction, further promoting the photocatalytic performance.



Fig. 4 optical properties of samples: (a) diffuse reflectance spectra, (b) the optical transition type determination and (c) photoluminescence spectra (Pt loaded samples).

The photocatalytic hydrogen evolution of BaTiO₃ samples were studied under UV light (200-400 nm) illumination (**Fig. 5a**). With the assistance of TEOA as a sacrificial reagent, the H₂ production rate of BTO-R sample is 789.7 umol/g/h, which is about 8 times that of commercial BaTiO₃ (BTO-C, 98.5 umol/g/h). Meanwhile, BTO-R sample exhibits a better photocatalytic hydrogen production from pure water

without any sacrificial agent as shown in Fig. 5b. Furthermore, BTO-R sample performs a better photocatalytic H₂ evolution after 4 cycles under UV light irradiation compared with BTO-C sample (Fig. 5c). By comparing the XRD patterns and TEM images before and after UV irradiation (Fig. S3), it can be found that the BTO-R sample keeps a good crystal structural integrity after long time illumination. The peak of $BaCO_3$ may result from the reaction of Ba^{2+} and CO_2 . It is well known that the optical response range and the recombination rate have a significant impact on the final photocatalytic efficiency. Because of the size effect, in comparison with BTO-C sample, the BTO-R shows a lower optical absorption ability which is negative to the photocatalytic performance. Usually, materials with low crystallinity always have a lot of defects that influence the final photocatalytic activity [48]. If we normalize the specific surface area, it can be found that the photocatalytic hydrogen generation rate per S_{BET} of BTO-R (6.5 umol/g/h/S_{BET}) is far lower than BTO-C (46.7 umol/g/h/S_{BET}). So the defects in the BTO-R act as charge carrier recombination center and suppress the photocatalytic performance to some extent [49]. Based on the above analysis, for the BTO-R sample, its light absorption range and structure defects have adverse effect on photocatalytic performance. Therefore, the small particle size and large specific surface area play a key role in enhancing its hydrogen evolution rate by promoting the separation of photo-induced carriers and providing more reactive sites. As a matter of fact, in the previous reports the BaTiO₃ photocatalyst was mainly studied for the uses in dye degradation [25, 28, 29, 50]. So this work provides an important example for BaTiO₃ as a photocatalyst for splitting water into H₂ with low-cost synthesis.



Fig. 5 photocatalytic hydrogen evolution of samples (catalyst: 50 mg, 0.38 wt.% Pt as co-catalyst): (a) in the presence of TEOA (10 vol.%), (b) without TEOA, and (c) cycle

experiments

4 Conclusions

In summary, $BaTiO_3$ nanoparticles (~7 nm) have been synthesized at room temperature conditions under ambient pressure. Because the particle size is lower than that of commercial $BaTiO_3$, there are more photo-induced carriers migrating from inner part of particles to participate in the surface photocatalytic reduction reaction. Under UV light irradiation, the room temperature synthesized $BaTiO_3$ (BTO-R) shows a better photocatalytic hydrogen evolution ability, which is 8 and 2.9 times that of commercial $BaTiO_3$ in the presence and absence of TEOA as a sacrificial agent, respectively. This work provides a good example on size control, low-cost synthesis and photocatalysts' design.

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- BaTiO₃ nanoparticles have been facilely synthesized at room temperature under ambient pressure.
- The particle size below 10 nm plays a key role in promoting the photocatalytic performance.
- This work provides a better reference for other works on the size control, crystal growth of photocatalysts.

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