



High efficient photocatalyst of spherical TiO₂ particles synthesized by a sol–gel method modified with glycol



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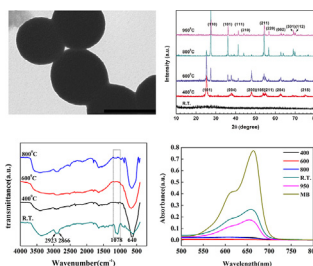
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HIGHLIGHTS

- TiO₂ spherical colloids are synthesized by sol–gel method modified with glycol.
- The size of titania colloids range from 250 to 550 nm by varying the water amount.
- The rate of hydrolysis is depressed with the increase of EO unit in glycol.
- The calcinated TiO₂ at 600 °C shows the highest photocatalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Monodisperse spherical TiO₂ particles were prepared by a sol–gel method modified with different glycols at room temperature and were calcined at different temperatures between 400 and 950 °C. The synthesized and calcined TiO₂ powders were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and thermogravimetric analysis (TG). The TEM images showed particles with sizes ranging from 250 to 550 nm. XRD revealed the phase transition from anatase to rutile was around 600 °C for TiO₂ particles. The photocatalytic activity of the prepared TiO₂ particles was determined by degradation of methylene blue (MB) in aqueous solution under UV irradiation and the results showed that the photocatalytic activity of TiO₂ particles strongly depended on the calcination temperature. Especially, the TiO₂ powder calcined at 600 °C showed the highest photocatalytic activity benefiting from the mixture of anatase and rutile of TiO₂.

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1. Introduction

In recent years, nanosized TiO₂ has been proven to be the most popular photocatalyst for the elimination of environmental pollutants [1], along with other applications, including anodes for batteries [2], hydrogen production [3] and self-cleaning films [4]. In particular, designing TiO₂ nanostructure with large surface area, high crystallinity and controlled shape and pore structure is a crucial subject for realization of these applications. Many studies on TiO₂ have focused on the synthesis of uniform spheres with control of their particle sizes at the nanometric scale using

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conventional methods, such as the hydrothermal method [5–8], templating method [9], sol–gel method [10–12], and micelle and inverse micelle methods [13].

The sub-micrometer titania particles became attractive due to its large surface area, easily separation [14] and controlled crystalline phase by calcination. Therefore, a larger number of chemical methods have been developed for generating TiO₂ colloidal particles. Usually, TiO₂ particles were synthesized by controlling the hydrolysis and condensation of an appropriate precursor. For example, Chen [15] has developed a procedure by combining sol–gel and solvothermal process to prepare grain diameter anatase TiO₂ beads (diameters in ranges 320–1150 nm). Tanaka [16] has synthesized TiO₂ spheres (diameters in ranges 380–960 nm) by using ammonia or amine as catalysts in methanol/acetonitrile system.

It has been suspected [17] that the conventional sol–gel methods could not be used to prepare monodisperse spherical TiO₂ particles because the hydrolysis rates of the precursors were too fast, and thus the nucleation and growth were never separated into two steps. Moreover, the concentration of titania monomer was always higher than the critical value, nucleation events could continuously occur in the entire sol–gel process and lead to the formation of polydispersed particles. To solve this problem and obtain monodisperse TiO₂ spheres, an effective route was slowing the hydrolysis rate of precursors. If a slow and controllable nucleation can be driven to occur in a separated step, spherical TiO₂ particles with narrower distributions in sized could be obtained. A few works have been reported by using the co-effect of metal–ligand coordination and a long hydrophobic chain to slow down the hydrolysis and condensation rate of the precursor [18]. Sugimoto [17,19] has discussed the effects of catalyst, water, temperature and solvent in details. Few works have been reported by using glycolates precursor to generate TiO₂ spheres [20,21]. Different from titanium alkoxides that are highly susceptible to moisture, the glycolated precursors are more resistant to hydrolysis [17]. However, the effect of glycol types on the morphology of TiO₂ particles has scarcely ever been reported in literatures.

In this paper, monodisperse sub-micrometer spherical TiO₂ particles were prepared by a sol–gel method modified with different glycols (ethylene glycol, diethylene glycol, and triethylene glycol). The effect of glycol species and water content was discussed in details. The morphology and structure of the samples were investigated using transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR). The transition of TiO₂ particles from anatase to rutile by annealing was demonstrated by X-ray diffraction (XRD). And we focus on the photocatalytic activity of sub-micrometer TiO₂ particles. The photocatalytic activity was evaluated in the decomposition of methylene blue (MB).

2. Experimental

2.1. Materials

Tetra butoxy titanium (TBOT) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), methylene blue (MB), acetone, ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis of spherical TiO₂ particles

The standard recipes for preparation of TiO₂ particles by a modified sol–gel process with glycol are listed in Table 1. In a

Table 1
Recipes for the preparation of TiO₂ by a modified sol–gel process.

| Run | Glycol ^a | TBOT (g) | Acetone (mL) | Water (mL) | Time ^b |
|-----|---------------------|----------|--------------|------------|-------------------|
| R-1 | EG | 0.50 | 98 | 2 | ~3 min |
| R-2 | DEG | 0.50 | 98 | 2 | ~4 min |
| R-3 | TEG | 0.50 | 98 | 2 | ~24 h |
| R-4 | DEG | 0.50 | 99.5 | 0.5 | ~3 h |
| R-5 | DEG | 0.50 | 99 | 1 | ~50 min |
| R-6 | DEG | 0.50 | 95 | 5 | ~40 s |

^a Glycol is 50 mL in all the recipes.

^b Time of the mixture of glycol and TBOT from transparent to white or yellow turbidity after adding acetone/water.

typical synthesis, 0.5 g TBOT was added to 50 mL glycol. The solution was magnetically stirred for 24 h at room temperature. Then 98 mL acetone and 2 mL water was immediately poured into the mixed solution with vigorous stirring at 25 °C, and the mixture was allowed to react for 4 h or 24 h. White precipitate was harvested by centrifugation, then washing with ethanol three times to remove glycol. The crystallization from as-made sample was achieved by calcination at 400–950 °C for 2 h.

2.3. Degradation of methylene blue (MB)

In all experiments, the photocatalytic activity of R-2 sample was evaluated by the degradation of MB which was carried out at 298 K by dispersed 10 mg catalyst and 50 mL MB aqueous solution (4 ppm, pH 7). Prior to irradiation, the suspension of photocatalyst was stirred in the dark for 30 min to achieve adsorption/desorption equilibrium. After reaching adsorption equilibrium, the photocatalytic reaction was initiated by irradiating the system with 300 W xenon lamps (PLS-SXE300, Beijing Perfectlight Technology Co. Ltd) placed 20 cm away from the reaction solution. Each run of reactions was lasted for preset time, and the aqueous solution was taken out, centrifuged and UV–vis absorption spectrum of the clear solution was recorded on Shimadzu UV-1800 spectrophotometer at 664 nm. The degradation ratio was calculated using the following two equations:

$$\text{Degradation ratio(\%)} = (C_0 - C)/C_0 \times 100 \quad (1)$$

where C_0 is the initial concentration of MB in water solution, C is concentration of MB after photocatalytic reaction using TiO₂ particles. Concentration of MB is calculated from the standard curve equation ($A = 0.1998C - 0.00457$). Where A is the absorbance value at 664 nm and C is the MB concentration [22].

$$\text{Degradation ratio(\%)} = (S_0 - S)/S_0 \times 100 \quad (2)$$

where S_0 is the initial integration area of MB absorption bands in the ranges of 500–750 nm in water solution, S is integration area of absorption bands MB after photocatalytic reaction using TiO₂ particles.

2.4. Characterizations

The morphology of TiO₂ particles was observed by TEM (Hitachi H-7650) and the diameters of TiO₂ particles were measured from the TEM images (at least 50 particles). FT-IR spectra were recorded on a VECTOR22 FT-IR spectrometer with a resolution of 2 cm⁻¹ using KBr method. Thermogravimetric analysis (TGA) curves of TiO₂ particles were record on Germany Netzsch STA449F3 analyzer with 10 °C min⁻¹ under air. Powder XRD patterns were recorded on X-ray diffractometer (XD-3, Beijing Purkinje General Instrument Co., Ltd.) equipped with Cu-K α radiation over the ranges from 20° to 80° (2θ) and the scan rate is 4°/min.

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