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Short Communication

Preparation and characteristics of TiO_2 nanotube catalysts used in hybrid photocatalysis/membrane process

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ABSTRACT

A novel photocatalytic membrane reactor (PMR) system was reported by the usage of TiO_2 nanotube (TNT) photocatalysts and microfiltration (MF) membranes. TNTs were prepared by hydrothermal method and the optimal preparation conditions were determined. Results showed that prepared TNT had good photocatalytic activity which was 2.5 times higher than that of P25 in reactive brilliant blue X-BR degradation. Due to its one-dimensional structure, the membrane flux in TNT separation was also 4–5 times higher than P25 no matter what kind of membrane was applied. Surface morphology analysis predicted less membrane fouling and better recycling in TNT PMR system.

1. Introduction

Photocatalytic membrane reactor (PMR) systems have attracted much attention in recent years because of the wide application potential in water and wastewater treatment [1–3]. It is possible to realize the photocatalysis degradation of contaminants and the recovery of nano-sized photocatalysts simultaneously [4]. One remarkable advantage of the PMR systems is the high photocatalytic activity of photocatalysts suspending in reactors [5]. However, the usage of conventional powder photocatalysts, such as TiO_2 (P25), in PMR systems resulted in membrane fouling due to pore blocking and/or cake formation [6]. To overcome this drawback, efforts were made to alleviate the membrane fouling in the hybrid photocatalysis/membrane process by altering the configuration of photocatlaysts and some valuable results were obtained [7–10]. For example, the F–TiO_2 hollow microsphere photocatalyst was prepared by self-etching method, and applied in PMR system, in which F–TiO_2 hollow microsphere exhibited excellent performances [7]. TiO_2 nanowire photocatalysts was also combined with MF for water treatment [8], and high photocatalystic activity and less membrane fouling was observed compared with P25. Besides hollow microsphere and nanowire, nanotube showed to be another primary configuration of photocatalyst apart from powders [11–13]. Due to its high specific surface area and ion exchange ability [14,15], TNT has attracted much attention since it was first synthesized in a hydrothermal system [16]. Although TNTs were applied in the combination of photocatalysis with membrane distillation (MD) [9] and simple filtration by a filter paper [10], there are still some obstacles for the application of TNT in hybrid photocatalysis/membrane process. This is not only because there are limitations in industrial application for both MD and filter paper compared with pressure driven membrane process such as microfiltration (MF) and ultrafiltration (UF), but also because the TNT prepared for those coupling systems only showed low photocatalytic activities.

Therefore, TNTs with high photocatalytic activities for PMR systems will be obtained by investigating the effect of the hydrothermal time, temperature and heat treatment on their microstructures. After that, the pressure driven MF membranes were applied with prepared TNTs to set up a novel TNT PMR system, in which the performance of TNTs was compared with P25 carefully.

2. Experimental

2.1. Preparation and characterization of TNTs

TNTs were prepared using hydrothermal method as before [16]. TiO_2 nanopowder (P25, Degussa, Germany) was used as starting material. In a typical preparation, 1.5 g P25 was mixed with 140 ml of 10 M NaOH solution, sonicating for 15 min. The mixture was then introduced into a Teflon-lined autoclave. The hydrothermal temperature and time was controlled at 110–150 °C and 24–48 h, respectively. After treatment, the obtained suspension was washed with deionized water and 0.1 M HCl. The deionized water was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC to meet the requirement of $\sigma \leq 0.5$ μS/cm. The precipitate was dried for 8 h at 80 °C, then calcined at temperatures ranging from 400 to 700 °C for 4 h. The nanotubular TiO_2 obtained was denoted as TNT-300, TNT-400, TNT-500, TNT-600 and TNT-700, respectively.

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Powder X-ray diffraction (XRD) patterns were measured by a Rigaku D/Max 2550PC X-ray diffractometer (Cu Kα, 40 kV, 100 mA). Morphologies were analyzed by Hitachi JEM-1200EX transmission electron microscopy (TEM) and TM-1000 scanning electron microscopy (SEM).

2.2. Photocatalytic activity

In order to evaluate photocatalytic activity of TNT, photodegradation experiment was carried out in a 1 L glass cylinder, inside which a 150 W UV lamp was used as light source. The cooling water was piped from bottom of container to maintain the temperature at 20 ± 1 °C. X-BR solution of 50 mg·L^{-1} was used as model pollutant, and the concentration of photocatalysts was 250 mg·L^{-1}. The mixture in the reactor was continuously stirred by a magnetic stirrer. After 30 min of adsorption in the dark, the suspensions were illuminated by UV light. The concentration of X-BR was determined by a Shanghai UV1102 ultraviolet–visible spectrophotometer, and the total organic carbon of solution was measured by a Shimadzu TNM-1 TOC analyzer.

2.3. Membrane filtration

Nylon 6 (N6) and CN-CA microfiltration membranes with pore size of 3 μm and 5 μm were used in the PMR system. A plate and frame membrane unit with effective filtration area of 19.63 cm^2 was applied and the transmembrane pressure (TMP) in the separation was set at 0.06 MPa. The turbidity of solution before and after filtration was measured to observe the rejection during filtration.

3. Results and discussion

3.1. Effect of hydrothermal conditions on physico-chemical properities of TNT

TEM images of titanate nanotubes prepared at different hydrothermal temperature and time were presented in Fig. 1. It was noticed that treatment time and temperatures played a crucial role in controlling the morphology of nanotubes. When hydrothermal temperature was kept at 110 °C, the nanopowder treated for 24 h transformed to one-dimensional tube-like structure with a length of several hundred nanometers and diameter of 5–10 nm. With treatment time increasing, the tube-like structure ruptured and became abnormity. According to literature [17], the length of nanotubes increased with hydrothermal treatment time but no significant growth was found in the length when it was longer than 24 h. By comparing Fig. 1 (a) with (d) and (e), it can be concluded that the length of nanotubes decreased with hydrothermal temperature, which was similar to that observed elsewhere [18]. These results indicated that the better tube-like structure can be obtained at 110 °C and hydrothermal treatment for 24 h.

3.2. Effect of calcination temperature on the microstructures and XRD patterns

Generally, calcination temperature has significant effect on phase morphology, photocatalytic activity and other properties of samples. Fig. 2 shows TEM images of samples treated at 110 °C for 24 h and annealed between 300–700 °C. It was obvious that nanotube morphology was affected by calcination temperature. The nanotubes with length of several hundred nanometers can be obtained when heated at 300 °C. Then the tube-like structure ruptured after temperature increased. The samples calcined at 600 °C suffered a microstructure transformation from tube-like to ball-shaped. When temperature reached 700 °C, the nanotubes became aggregated particles. As noticed elsewhere [19], high temperature can cause the dehydration of layered OH group which led to contraction and breaking of the tube structures, therefore the tube-like structure converted back to particles again.

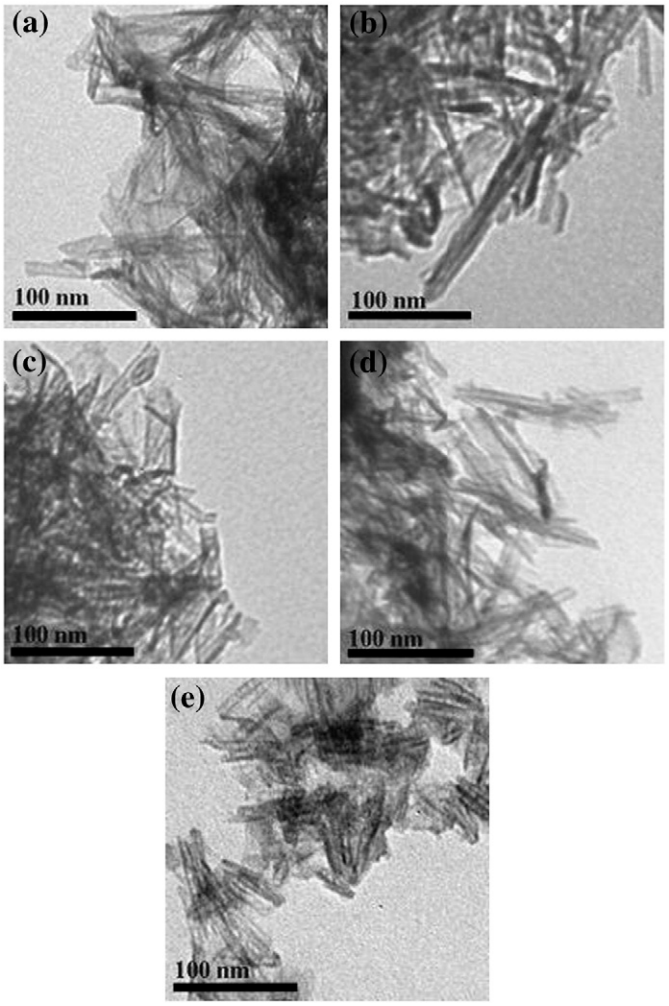

Fig. 1. TEM images of titanate nanotubes prepared under different hydrothermal temperature and treating time: (a) 110 °C, 24 h; (b) 110 °C, 36 h; (c) 110 °C, 48 h; (d) 130 °C, 24 h; (e) 150 °C,24 h.

XRD studies demonstrated that with temperature increasing from 300 to 600 °C, the peak intensity of anatase increased and width of the peak became narrow, implying improvement of the crystallinity of anatase phase (at 2θ = 25, 38, 48). Further, a minority of rutile phase was detected when samples calcined at 700 °C(Fig. 1S. supporting information). The crystallite size was determined by the Scherrer's equation:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where K is Scherrer constant ($K = 0.89$), λ is wavelength of X-ray radiation (λ = 0.15418 nm), θ (rad) is characteristic X-ray diffraction peak and β (rad) is the line width at half-maximum height.

The calculation results listed in Table 1 revealed that crystallite size increased from 7 nm to 38 nm when temperature increased from 300 to 700 °C. The increase of crystallite size with calcination temperature was mainly due to the phase transformation and sintering of the samples.

3.3. Photocatalytic degradation of X-BR using prepared TNT

Prepared TNT under different calcination temperature was used to degrade anthraquinone dye X-BR and compared with P25. TNT annealed between 300 to 600 °C exhibited a higher photodegradation than P25 (Fig. 3 (a)). When samples calcined at 400 or 500 °C, decoloration rate