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Glass capillaries with TiO_2 supported on inner wall as microchannel reactors

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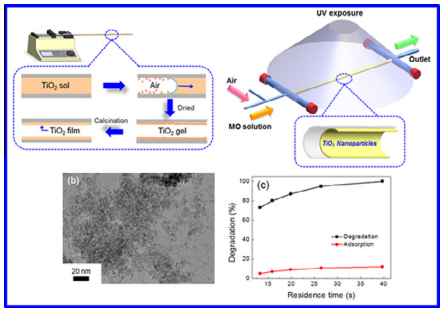
HIGHLIGHTS

- TiO_2 nanoparticles were immobilized on the inner surface of glass capillaries.
- The catalytic system was used for ODS of DBT and discoloration of MO.
- TiO_2 nanoparticles showed good crystallization with a mean size of 6.8 nm.
- 100% conversions of DBT and MO were obtained after 2.8 min and 40 s, respectively.

GRAPHICAL ABSTRACT

We have successfully immobilized TiO_2 nanoparticles with small particle size (6.8 nm) and narrow size distribution on the inner surface of glass capillaries. By integrating the beneficial properties of nano-sized TiO_2 particles with microreactors, the highly efficient catalytic system showed good performance in oxidation of dibenzothiophene (DBT) and photocatalytic discoloration of methyl orange (MO). DBT was converted completely within 2.8 min with an initial concentration of 20 ppm, and 100% discoloration of MO was obtained after 40 s.



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ABSTRACT

In this work, we have successfully immobilized TiO_2 nanoparticles with small particle size and narrow size distribution on the inner surface of glass capillaries. By integrating the beneficial properties of nano-sized TiO_2 particles with microreactors, the highly efficient catalytic system showed good performance in oxidation of dibenzothiophene (DBT) and photocatalytic discoloration of methyl orange (MO). The mean particle size and loading amount (Ti content: 0.21–2.81 wt.%) are both controllable via the simple manufacturing procedure. The diameter varied from 6.8 to 20.8 nm with the pH increased from 1.59 to 6.48 using ethanol as the solvent. Particles prepared by methanol showed the largest size (18.2 nm) and broadest size distribution compared with those synthesized with ethanol and isopropanol. DBT was converted completely within 2.8 min with an initial concentration of 20 ppm, and 100% discoloration of MO was obtained after 40 s. The highly efficient microreactor is easy to be integrated on a large scale, thus providing a highly promising alternative for a broad range of catalytic applications.

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1. Introduction

TiO_2-based catalysts have been recognized as the most promising catalyst for photo-catalytic synthesis, photo-degradation of contaminated water and even photo-oxidation of organosulfur compounds in fuels, owning to their excellent properties such as high light-conversion efficiency, chemical stability, nontoxic nature and low cost [1–10]. Commercial TiO_2 catalysts are typically available in suspension mode (for example, Degussa P25 powder) or immobilized on a substrate. Uses of TiO_2 powder are usually avoided in practical engineering applications because of three reasons: first, because of the small particle size and solubility in aqueous medium, the separation and recovery of the catalysts from reaction systems can be problematic; second, small particles of TiO_2 tend to agglomerate into large particles, militating against the catalytic activity; third, the penetration depth of the UV light is decreasing fast due to the strong adsorption by the suspended TiO_2 particles. Therefore, immobilized TiO_2 particles seem more attractive. However, systems with immobilized TiO_2 suffer from the limited amount of exposed catalytic surface area leading to mass transfer limitations [11–13].

Microreactors have proved to be highly effective for catalytic reactions due to its large surface to volume ratio, precise temperature and time control, and high production rate [12,14,15].

Many researchers have devoted great efforts into possibilities of immobilizing TiO_2 in microreactors, and the prepared microreactors have proved to be efficient [16–40]. A photo-catalytic flow reactor was developed in the work of Montero-Ocampo [26]. In situ discoloration of indigo carmine dye was studied on TiO_2 films prepared by PVD magnetron sputtering technique. A discoloration of 80% was obtained with the irradiation time of 50 min. As reported by Ahsan [28], a microfluidic platform immobilized with Pt-TiO_2 was used to study photo-catalytic water-splitting. And they demonstrated that such platform has the potential to enhance the reaction rates by proving mass transport. Increasing the flow rates yielded at least 2-fold improvements in reaction rates. A microfluidic-based photo-catalytic microreactor using TiO_2 (the mean particle size is 132 nm) as the catalyst was fabricated in Meng's work [29]. The microreactor gave a 38% degradation of methylene blue after 53 s. Obviously, despite the progress in combining a microreactor with immobilized TiO_2, the approach still faces great challenges because of the complicated producing process, high preparation cost, addition of novel metal elements, unmentioned stability and big particle size of the catalysts. And it is well known that the catalytic activity of TiO_2 is greatly influenced by the crystallinity, particle size and morphology. Problems need to be solved in order to improve the catalytic activity in these microreactors. Therefore, there is great need to fabricate microreactors with supported TiO_2 catalysts offering high active surface area and highly dispersed properties in a controllable and green way.

In this work, we explored the feasibility of integrating the beneficial properties of nano-sized TiO_2 particles with microreactors to produce highly efficient catalytic system and the possibility of their application in the oxidation desulfurization (ODS) of DBT and photocatalytic discoloration of MO. A novel kind of capillary-based microchannel reactor containing TiO_2-coated on the inner walls was constructed by flowing TiO_2 sol into capillaries. There are four possible advantages for choosing glass capillary as the support: first, surface modification of glass capillary is extremely viable. It is well known that the interaction and combination between the support and the synthetic sol are critical to inducing an oriented crystal growth. Changes in the surface chemistry of the chosen support may directly impact the interaction and combination between the two phases, and impact the morphology and catalytic activity of TiO_2 nanoparticles as well; second, the glass capillary is light-transmitted resulting in large surface area explored to UV light and prevention of serious loss of light intensity for photo-catalytic reactions; third, the thin glass wall facilitates quick and exact temperature control of the reactor; fourth, it is cheap and environmentally friendly, offering a more efficient alternative to other inorganic supports.

The as-prepared microchannel reactor was characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM), X-ray diffraction (XRD), inductively coupled plasma atomic emission spectrometer (ICP, IRIS Intrepid II XSP from ThermoFisher Corp., America), X-ray photoelectron spectroscopy (XPS), and ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy. The catalytic activity was investigated by the oxidation of DBT and discoloration of MO.

2. Experimental

2.1. Materials and chemicals

Glass capillary (I. D. 0.5 mm) with a length of 10 cm was purchased from Instruments Plant of West China University of Medical Sciences. Tetrabutyl titanate ($Ti(OBu)_4$) and cumene hydroperoxide (CHP) were purchased from J&K Chemical Ltd. Octane, concentrated hydrochloric acid, methanol, ethanol and isopropanol in the analytical grade were purchased from Fuchen Chemical Plant in Tianjin, China. DBT was purchased from Acros Organics. All chemicals were used as received without further treatment.

2.2. Surface modification of microchannel reactor

In the work of Yeung [41], mesoporous silica MCM-41 has been successfully prepared in a microreactor and the particles showed more uniform size and shape by sol–gel process. Inspired by this work, we developed a method to immobilize TiO_2 nanoparticles with small particle size and narrow size distribution on the inner surface of glass capillaries. The transparent capillary was treated with alkaline solution (10 wt.% NaOH aqueous solution) at 413 K for 5 h before coating, and then washed several times with deionized water before further use. In a typical run, 12.5 mL of $Ti(OBu)_4$ was added to 33.3 mL of ethanol and the solution was stirred for 10 min. Then a certain amount of concentrated hydrochloric acid was added and stirred for another 30 min. The mixture of 16.7 mL of ethanol and 1.5 mL of deionized water was added dropwise afterwards. The resulting sol was injected into the capillary through a Teflon tube using a syringe so that wetting of the channels was guaranteed and excess liquid was removed by air leaving

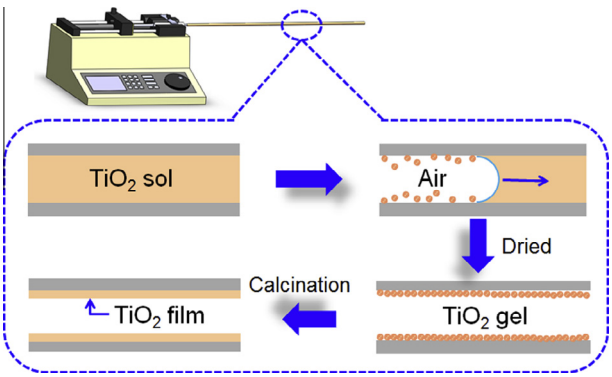

Fig. 1. Experimental set up.

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