



Invited feature article

Bare, gold and silver nanoparticle decorated, monodisperse-porous titania microbeads for photocatalytic dye degradation in a newly constructed microfluidic, photocatalytic packed-bed reactor

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ABSTRACT

Monodisperse porous titania microbeads were synthesized by a sol-gel templating protocol. Gold nanoparticles (AuNPs) synthesized by Turkevich and Martin methods 16 and 5 nm in size, respectively and silver nanoparticles (AgNPs) 12 nm in size were decorated onto the primary amine attached titania microbeads. Both size and porous properties of bare or AuNP/AgNP decorated monodisperse-porous titania microbeads were suitable for using them as a photocatalyst in a “**Microfluidic, Photocatalytic Packed Bed Reactor (MPPBR)**” with reasonable pressure drops in the microflow rate range. Then, a MPPBR system for “**continuous photocatalytic dye degradation**” was first constructed by slurry packing of bare or AuNP/AgNP decorated titania microbeads into a fused silica capillary 320 μm in diameter. The photocatalytic activities of bare and AuNP/AgNP decorated titania microbeads were determined in MPPBR using a textile dye, Remazol Black 5 (RB5). The complete removal of RB5 was achieved in continuous mode and an appreciable enhancement in the photoremoval rate of RB5 was observed with the MPPBR containing Martin AuNP decorated titania microbeads. The system constructed can be evaluated as a promising tool for both pre-column and post-column applications involving the removal of coloured contaminants in the assays conducted in micro-liquid chromatography systems.

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1. Introduction

Wastewaters generated by textile industries contain large amounts of toxic aromatic compounds, especially azo dyes. Various combinations of conventional methods like biological, physical and chemical processes have been used to deal with textile wastewaters [1,2]. Due to the limitations of these processes, investigations have been focused on the treatment of wastewater using heterogeneous photocatalysis (UV/TiO₂) [1,3]. This process, in which semiconductor metal oxides are used, is based on the formation of hydroxyl radicals and reaction of these hydroxyl radicals with organic contaminants. Due to high activity, low cost and non-toxicity, TiO₂ is one of the most suitable semiconductors that have been used for photocatalysis [4,5–7]. Among the other

noble metal nanoparticles, gold nanoparticles (AuNPs) have received great attention due to their effectiveness in the enhancement of the photocatalytic activity of TiO₂. Referring to literature, there has been an increasing research on using AuNPs for the modification of TiO₂ and the results showed that the band gap energy of TiO₂ was decreased by AuNPs which resulted in a better photocatalytic activity [8–13]. By considering this, we planned to apply Au nanoparticle decoration onto the monodisperse-porous titania microbeads synthesized in our recent studies for obtaining a high performance new photocatalyst.

Most of reported studies on using heterogeneous photocatalysis were carried out in batch reactors [14–21]. However, several studies were reported in which the decolorization of azo dyes was performed in continuous processes. Merzouk et al. [22] used continuous electro-coagulation for decolorization of a synthetic textile wastewater by aluminum electrodes. In another study, Li and Jia [23] designed a packed-bed bioreactor for continuous decolorization of synthetic dyes using rice hull *Schizophyllum* sp. F17. Rahimi et al. designed a continuous Y-shaped microreactor in

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which the Fenton degradation of an azo dye was taken place [24]. Sun et al. proposed a microporous tube-in-tube microchannel reactor for the decolorization of azo dye Acid Red 14 [25].

In most of the photocatalytic processes, titania nanoparticles were used in batch reactors since both their size and porous properties are not suitable to work in continuous reactors by forming packed beds within the tubular systems. In this work, we synthesized bare and AuNP/AgNP decorated forms of monodisperse porous titania microbeads with size and porous properties extremely suitable for the construction of packed-beds in a tubular reactor with reasonable column-permeabilities. Then, a **"Microfluidic, Photocatalytic Packed Bed Reactor"**, MPPBR system was first constructed by slurry-packing of bare and AuNP/AgNP decorated, monodisperse-porous titania microbeads into fused silica capillary tubing. By using the microfluidic system, the complete removal of a textile dye, Remazol Black 5 (RB5) was achieved under UV-irradiation in continuous mode with different flow mobile phase rates and dye feed concentrations.

2. Experimental

2.1. Materials

All the chemicals used for the preparation of sodium sulfonate attached-poly(3-chloro-2-hydroxypropyl methacrylate-co-ethylene glycol dimethacrylate) ($-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA)) microbeads were purchased from Sigma Chemical Co., St. Louis, MO, USA, as reported in earlier studies [26]. Titanium chloride (TiCl_4) as precursor, ammonium hydroxide solution (NH_4OH , 26%w/w) and hexadecyltrimethylammonium bromide (CTAB) were also purchased from Sigma. For the derivatization of monodisperse-porous titania microbeads with amine groups aminopropyltriethoxysilane (APTES) and triethylamine (TEA) were purchased from Sigma Chemical Co., St. Louis, MO, USA with groups. For the synthesis of gold nanoparticles (AuNPs), chloroauric acid-trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma Chemical Co., St. Louis, MO, USA), trisodium citrate (TSS, Sigma Chemical Co., St. Louis, MO, USA), sodium borohydride (NaBH_4 , Sigma Chemical Co., St. Louis, MO, USA) were used. Sodium hydroxide (NaOH , Sigma Chemical Co., St. Louis, MO, USA) and hydrochloric acid (HCl , 37%w/w, Sigma Chemical Co., St. Louis, MO, USA) were used for the preparation of NaBH_4 and HAuCl_4 solutions, respectively. For the synthesis of silver nanoparticles (AgNPs), silver nitrate (AgNO_3 , Sigma Chemical Co., St. Louis, MO, USA) was used. The dye used in the photocatalytic activity runs, Remazol Black 5 (RB5) was purchased from Aldrich. Distilled deionized (DDI) water (Direct-Q 3 UV (Type 1), Millipore, USA) with a resistivity of $18 \text{ M}\Omega \text{ cm}$ was used during all synthesis runs.

2.2. Synthesis of monodisperse porous bare and AuNP/AgNP decorated titania microbeads

The titania microbeads were synthesized by sol-gel templating method using $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads as template, according to the methods reported in our earlier research [26]. Monodisperse porous $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads were synthesized by a multi-step microsuspension polymerization [26]. The synthesis of titania microbeads consists of hydrolysis and condensation steps. In the hydrolysis step, $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads (0.4 g) were dispersed within the precursor solution (TiCl_4 solution, 60 mL, 0.1 M) and stirred at 250 rpm at room temperature for 24 h for the adsorption of hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) nanoparticles into the polymeric template. In the condensation step, microbeads were treated with ammonia solution (60 mL, 1 M) containing CTAB (0.3 g) and the solution was

stirred at 250 rpm at room temperature for 6 h. In order to obtain integrated titania microbeads, the hydrolysis and ammonia precipitation steps were repeated twice. The polymeric templates were removed from the titania-polymer composite microbeads by calcination at 450°C for 4 h with a heating ramp of $2^\circ\text{C}/\text{min}$, under air atmosphere.

The amine attachment on titania microbeads was obtained by the derivatization with APTES. Briefly, the monodisperse-porous titania microbeads (0.4 g) degassed at 250°C for 6 h before reaction with APTES were dispersed within Iso-PrOH (20 mL), to which APTES (3 mL) and TEA (0.3 mL) were added by ultrasonication, in a sealed glass reactor. Then, the reactor was kept in a temperature-controlled shaking water bath at 80°C for 24 h. After derivatization, to remove the excess APTES the amine attached titania microbeads were washed with Iso-PrOH by centrifugation (5000 rpm, for 3 min) and decantation for several times. Turkevich AuNPs, Martin AuNPs and AgNPs were synthesized and then the decoration of AuNPs/AgNPs on amine attached titania microbeads with an Au/Ag loading percent of 5.0%w/w was carried out according to the methods given in Supplementary material.

2.3. Photocatalytic degradation of RB5 in a microfluidic, photocatalytic packed-bed reactor (MPPBR)

The photocatalytic degradation of RB5 dye was performed in a microfluidic, photocatalytic packed-bed reactor (MPPBR) operated in continuous mode. The microfluidic packed-bed reactor was constructed by slurry-packing of bare titania, Turkevich AuNP or Martin AuNP decorated titania and AgNP decorated titania microbeads into a polyimide coated fused silica capillary (12 cm, ID: $320 \mu\text{m}$, OD: $432 \mu\text{m}$, Polymicro Technologies, U.S.A.) with a UV transparent window, 6 cm in length. Bare titania, Turkevich or Martin AuNP decorated titania and AgNP decorated titania microbeads were slurry packed into the polyimide coated fused silica capillary under high pressure by using a packing system containing a stainless steel column (ID: 4.6 mm, Length: 100 mm) filled with the slurry of microbeads and an HPLC pump (Schimadzu, LC-10AD, Japan). By means of HPLC column, DDI water was pumped into the HPLC column containing the slurry of the microbeads and the slurry was transferred from the column into the fused silica capillary containing a stainless steel frit (diameter: 0.5 mm, pore size: $2 \mu\text{m}$) on one end. The formation of packed-bed by the entrapment of the microbeads within the fused silica capillary was monitored by optical microscope. The packing operation was continued under high pressure (70 bar) till a stable bed formation was obtained.

The microfluid photodegradation system consists of an HPLC pump (Schimadzu, LC-10AD, Japan), a polyimide column (ID: 4.0 mm, Length: 250 mm) filled with the RB5 feed solution and the microfluidic packed bed reactor (MPPBR) connected to the polyimide column. By means of the HPLC pump, DDI water was pumped at a prescribed flow rate ($1\text{--}10 \mu\text{L}/\text{min}$), into the polyimide column completely filled with the RB5 feed solution and the RB5 feed solution within the column was simultaneously transferred into the MPPBR with the same flow rate. The photograph of the continuous MPPBR system is given in Fig. 1. As seen from Fig. 1, silica capillary columns packed with bare and AuNP/AgNP decorated titania microbeads were irradiated 30 cm away from the top of the UV transparent window with a UV light-source (Osram, Ultra-vitalux lamp, 300 W) at 25°C within a closed metal box equipped with a temperature-control system. During the photocatalytic degradation the samples were collected at certain times from the porous frit located at the end of the silica capillary. RB5 dye concentration at any time was determined by measuring the absorption of sample in visible-region at 598 nm using Nanodrop 1000 (Thermo Scientific, ND1000, USA).

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