



A new method for the synthesis of monodisperse-porous titania microbeads by using polymethacrylate microbeads as template



Kadriye Özlem Hamaloğlu^a, Bekir Çelebi^a, Ebru Sağ^a, Ali Tuncel^{a, b, *}

^a Hacettepe University, Chemical Engineering Department, Ankara, Turkey

^b Hacettepe University, Division of Nanotechnology and Nanomedicine, Ankara, Turkey

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ABSTRACT

Monodisperse-porous titania microbeads were synthesized by sol–gel templating method by using a new type of polymethacrylate microbeads as template. Monodisperse-porous poly(3-chloro-2-hydroxypropyl methacrylate-co-ethylene dimethacrylate), poly(HPMA-Cl-co-EDMA) microbeads 5.4 μm in size were used as starting material for the preparation of new template. Strong cation exchanger –SO₃Na groups were generated on the selected polymethacrylate template via the reaction between chloropropyl groups of template and sodium bisulfite. –SO₃Na functionalized-polymethacrylate microbeads were treated with the precursor, TiCl₄ in an aqueous medium and subsequently treated with ammonia to obtain titania-polymer composite microbeads. The composite microbeads were then calcined at 450 °C to have monodisperse-porous titania microbeads. Monodisperse-porous titania microbeads in the size range of 3.0–5.0 μm with crater-like or fine porous structures with specific surface areas ranging between 50 and 91 m²/g were obtained by changing the concentration, crosslinking density of the template beads and the calcination temperature. The selection of a polymethacrylate template decomposed at lower temperatures with respect to poly(styrene-co-divinylbenzene) type templates, commonly used for synthesis of porous titania microbeads, allowed to perform the calcination of titania-polymer composite microbeads at lower temperatures. Monodisperse-porous titania microbeads with higher specific surface area and a crystalline structure with higher percent of anatase phase could be obtained by performing calcination at lower temperatures. The photocatalytic activity of monodisperse-porous titania microbeads was investigated using an anionic azo-dye, Remazol Black 5 (RB5) in batch-fashion. Higher photodegradation rates were observed with the monodisperse-porous titania microbeads in the acidic pH region compared to TiO₂ nanoparticles.

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1. Introduction

Porous titania beads with a high porosity have attracted much attention due to its usability in different areas such as hydrogen storage, sensor fields, dye-sensitized solar cells and photocatalysis [1–5]. Two of the most important factors affecting on the photocatalytic activity of titania beads are its specific surface area and crystallinity [6,7]. The higher surface areas can be obtained with titania nanoparticles, however the removal of the nanoparticles from solutions is a serious problem after the catalytic reaction. From the viewpoint of practical applications, in addition to high

surface area, controllable shape and size is also important for developing convenient porous titania beads.

Using polymeric templates, which controls the morphological property such as pore size, outer shape and size, has a great importance for the synthesis of monosized porous titania beads [8]. The sol–gel templating is a suitable method for the preparation of titania beads with controlled morphology and structure. This method involves sol–gel chemistry of pure metal alkoxides within porous polymeric template. The template is removed from the composite structure. By using this method, Caruso and co-workers demonstrated the use of porous polystyrene–divinylbenzene, poly(S-co-DVB) microbeads as template and titanium chloride (TiCl₄) as precursor in the production of titania microbeads [9,10]. Meyer et al. used non-functionalized and hydroxyl/amine functionalized poly(S-co-DVB) microbeads as template and titanium isopropoxide (TIP) as precursor for the preparation of titania

* Corresponding author. Hacettepe University, Chemical Engineering Department, Ankara, Turkey. Fax: +90 312 299 21 24.

E-mail address: atuncel@hacettepe.edu.tr (A. Tuncel).

microbeads [11]. Wang and co-workers also used the same particles but in larger size to synthesize titania macrobeads by using $\text{Ti}(\text{SO}_4)_2$ as precursor [12]. Qi and co-workers prepared hollow microbeads of titania, with commercial porous polymer beads (Sephadex G-100 beads) as template and TiCl_4 as precursor [13]. The calcination temperature for the titania/poly(S-co-DVB) composite microbeads was 550 °C in the related articles [9–12].

The effects of calcination temperature on the surface area and crystalline structure of the ultrafine (<10 nm) titania powders synthesized by sol–gel method were studied by Guo and co-workers [14]. Qi and co-workers changed the calcination temperature and showed its effect on the surface area of hollow microbeads of titania [13]. However, the effects of calcination temperature on the structural properties of titania microbeads synthesized by using sol–gel templating method were not studied yet.

In this work, we report a new protocol for the preparation of monodisperse-porous titania microbeads by using monodisperse polymethacrylate microbeads with $-\text{SO}_3\text{Na}$ groups as template and TiCl_4 as precursor. First, the hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) nanoparticles, formed by hydrolysis reaction of the precursor, were adsorbed onto the polymeric template. Upon treatment with ammonia, titania-polymer composite microbeads were formed by the precipitation of hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) nanoparticles within the pores of $-\text{SO}_3\text{Na}$ attached-polymeric template. After repeating the hydrolysis and precipitation steps, the removal of polymer template was achieved by calcination. By using a polymethacrylate template with low degradation temperature, the calcination of titania-polymer microbeads were performed at lower temperatures. This allowed the synthesis of monodisperse-porous titania microbeads with higher anatase content and higher specific surface area. The synthesis protocol proposed is suitable for the production of monodisperse-porous titania microbeads with prescribed particle size, crystallinity and specific surface area. The photocatalytic activity of monodisperse-porous titania microbeads was studied using an anionic azo-dye in batch-fashion.

2. Experimental

2.1. Materials

For the synthesis of monodisperse-porous poly(3-chloro-2-hydroxypropyl methacrylate-co- ethylene glycol dimethacrylate) [poly(HPMA-Cl-co-EDMA)] and poly(styrene-co-divinylbenzene) [poly(S-co-DVB)] microbeads; the monomers, glycidyl methacrylate (GMA), 3-chloro-2-hydroxypropyl methacrylate (HPMA-Cl), styrene (S), the crosslinking agents, ethylene dimethacrylate (EDMA), divinylbenzene (DVB), and the diluents, ethylbenzene (EB), dibutyl phthalate (DBP) were supplied from Aldrich Chem. Corp., USA. The initiator, benzoyl peroxide (BPO), the stabilizer, polyvinyl alcohol (PVA, 87–89 % hydrolyzed, $M_w = 85,000\text{--}1,46,000$) and polyvinylpyrrolidone (PVP K-30, Sigma, average molecular weight: 40,000 Da), the emulsifier, sodium dodecyl sulfate (SDS) were supplied from Aldrich. The initiator, BPO was dried under vacuum at 30 °C before use. 2,2-azobisisobutyronitrile (AIBN) supplied from Across Organics, USA were recrystallized from methanol before use. Ethanol (EtOH, HPLC grade, Merck A.G., Darmstadt, Germany), 2-methoxy-ethanol (HPLC grade, Aldrich) and tetrahydrofuran (THF, HPLC grade, Aldrich) were used as the solvents. For the synthesis of polymethacrylate microbeads with $-\text{SO}_3\text{Na}$ groups, sodium bisulfite (NaHSO_3 , Sigma Chemical Co., St. Louis, MO, USA) was used. Titanium chloride (TiCl_4) as precursor, ammonium hydroxide solution (NH_4OH , 26% w/w) and hexadecyltrimethylammonium bromide (CTAB) were also purchased from Sigma. Titanium (IV) dioxide nanoparticles

(Degussa P25) and the dye used in the photocatalytic activity runs, Remazol Black 5 (RB5) were 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 polymer microbeads by multistep microsuspension polymerization

Two types of polymeric microbeads were used as template. The new sol–gel templating method was constructed by using poly(HPMA-Cl-co-EDMA) beads as template. The typical multistage microsuspension protocol utilized for the synthesis of poly(HPMA-Cl-co-EDMA) beads is given below:

First, monodisperse poly(GMA) seed latex particles 2.5 μm in size were synthesized by dispersion polymerization performed in a sealed glass polymerization reactor placed in a temperature-controlled shaking water bath kept at 70 °C for 24 h [15].

Monodisperse porous poly(HPMA-Cl-co-EDMA) microbeads, were synthesized by a multi-step microsuspension polymerization using poly(GMA) particles as the seed latex [16]. In the first stage, the seed particles were swollen by an organic diluent in an aqueous emulsion medium by preserving the monodispersity of the seed latex. For this purpose, SDS (0.125 g) was dissolved in distilled water (50 mL); and the diluent (EB, 2.5 mL) was added into this solution. The resulting medium was sonicated for 8 min for dispersion of EB in the form of micron-size droplets in the aqueous medium. After emulsification, the aqueous dispersion of poly(GMA) seed particles (0.3 g) was added to the emulsion and sonicated for 4 min. Then the medium was stirred at room temperature for 24 h for complete absorption of EB by the seed particles. In the second stage, the diluent swollen seed particles were reswollen by the monomer phase, containing HPMA-Cl (3.5 mL) and EDMA (1.5 mL) and the initiator, BPO (0.3 g). For this purpose, the monomer phase was emulsified in water (50 mL) containing SDS (0.125 g) by sonication for 12 min. After sonication, the emulsion was added to the aqueous dispersion of diluent-swollen seed latex prepared in the first step. The resulting dispersion was stirred at room temperature for 24 h for complete absorption of monomer phase by the seed particles. Then, the stabilizer PVA (0.8 g in 10 mL DDI water) was added to the resulting dispersion. In the last stage, the monomer phase was polymerized within the swollen seed particles. For this purpose, the temperature was increased to 80 °C and the polymerization was performed in a temperature-controlled shaking water bath kept at this temperature with a shaking rate of 120 rpm for 24 h.

The monodisperse-porous poly(HPMA-Cl-co-EDMA) microbeads were isolated by centrifugation and then washed with EtOH for several times and extracted with THF. The polymer microbeads were then extensively washed with EtOH and DDI water and finally dispersed in DDI water.

In order to obtain monosized-porous titania microbeads with different size and porous properties, poly(HPMA-Cl-co-EDMA) microbeads prepared with different crosslinking agent feed concentrations (*i.e.* also with different reactive chloropropyl contents) were used in the sol–gel templating synthesis. For this purpose, the feed concentration of EDMA in the monomer phase (*i.e.* HPMA-Cl + EDMA) was changed between 15 and 100 % v/v by keeping the total volume of monomer phase constant in the multistage microsuspension polymerization.

On the other hand, monodisperse-porous poly(S-co-DVB) microbeads with different functional groups were also tried as template by different research groups. By considering this situation, monodisperse-porous poly(S-co-DVB) microbeads were also produced by utilizing a similar multistage micro-suspension polymerization of corresponding monomers. For this purpose,

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