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Shape-controlled fabrication of TiO_2 hollow shells toward photocatalytic application

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ABSTRACT

This paper introduces a droplet-based microfluidic approach, followed by several post-treatments, for the fabrication of TiO_2 hollow shells with novel morphology and perfectly uniform size distribution, which were further decorated with platinum nanostructures to improve their photocatalytic activity and their ability to remove organic pollutants. In particular, a single-emulsion technique was used to emulsify an oil phase containing a titanium dioxide precursor, titanium *n*-butoxide (TBT), and a UV-curable polymer resin, trimethylolpropane triacrylate (ETPTA), into an aqueous phase. These emulsion droplets then readily underwent phase separation and sol-gel reaction at the emulsion interface, forming a TiO_2 shell that would eventually rupture, release the ETPTA core, and form an anatase TiO_2 hollow shell after UV, isopropanol, and thermal post-treatments. Compared with TiO_2 hollow spheres reported in the literature, the TiO_2 hollow shells produced here have a well-defined inner cavity that significantly improves their photocatalytic activity and allows for the selective introduction of advanced functions by the addition of metal co-catalysts like platinum. This new approach, by offering the ability to uniformly control the shape of the TiO_2 photocatalyst and the ability to selectively introduce co-catalysts, offers an alternative platform for the design and fabrication of high-performance photocatalysts for efficient water purification.

1. Introduction

The ability to harness the sun's energy has such wide-ranging implications that different ways to efficiently do so are continually being pursued worldwide. Semiconductor-based photocatalysis is one efficient approach in chemically harnessing the sun's free, abundant energy [1,2]. Unfortunately, inefficient light-harvesting design and the recombination of photo-generated charge carriers limit the performance of these photocatalysts [3]. Thus, the development of functional photo-responsive materials that provide both efficient light-harvesting capabilities and charge carrier separation is the main challenge to be overcome in current photocatalyst design.

TiO_2 photocatalysts with a hollow structure, in particular, have received considerable attention in recent years owing to their unique properties [4–7]. First, the thin shell of these hollow materials provides shorter charge carrier lengths, decreasing the probability that electron-hole recombination reactions occur before active charges reach the surface of the material where actual catalytic turnovers take place. Second, hollow structures have high porosity within their walls, which reduces the diffusion length and increases their accessibility to reactants because of a higher number of active sites. Third, in hollow structures with a wall thickness smaller than the light penetration depth, the voluminous void space improves radiation absorption efficiency through "light trapping" effects. Plain structure, non-hollow, spherical particles can absorb only a small fraction of incident light because the rest is reflected. But in the case of hollow materials, multiple scattering events could occur within the interior cavity of a single particle, which are expected to improve the overall absorption efficiency, thereby contributing to enhanced light-harvesting abilities [8–12].

Aiming to improve photocatalytic activity in this way, a few studies have recently been published detailing the fabrication of TiO_2 hollow shells with a well-defined hollow cavity. Enhanced photocatalytic activity and improved diffusion of the reactant molecules onto the active surface were demonstrated using these hollow shell structures. Typically, these TiO_2 hollow shells were fabricated via templating or ripening processes [13–17]. The high reactivity of titanium precursors towards hydrolysis-condensation reactions, however, makes it challenging to fabricate these TiO_2 hollow structures in a controlled manner. Thus, the fabrication of TiO_2 hollow shells with a well-defined shape for efficient photocatalysis remains an important yet unmet need. One promising strategy to potentially resolve this issue is the use of

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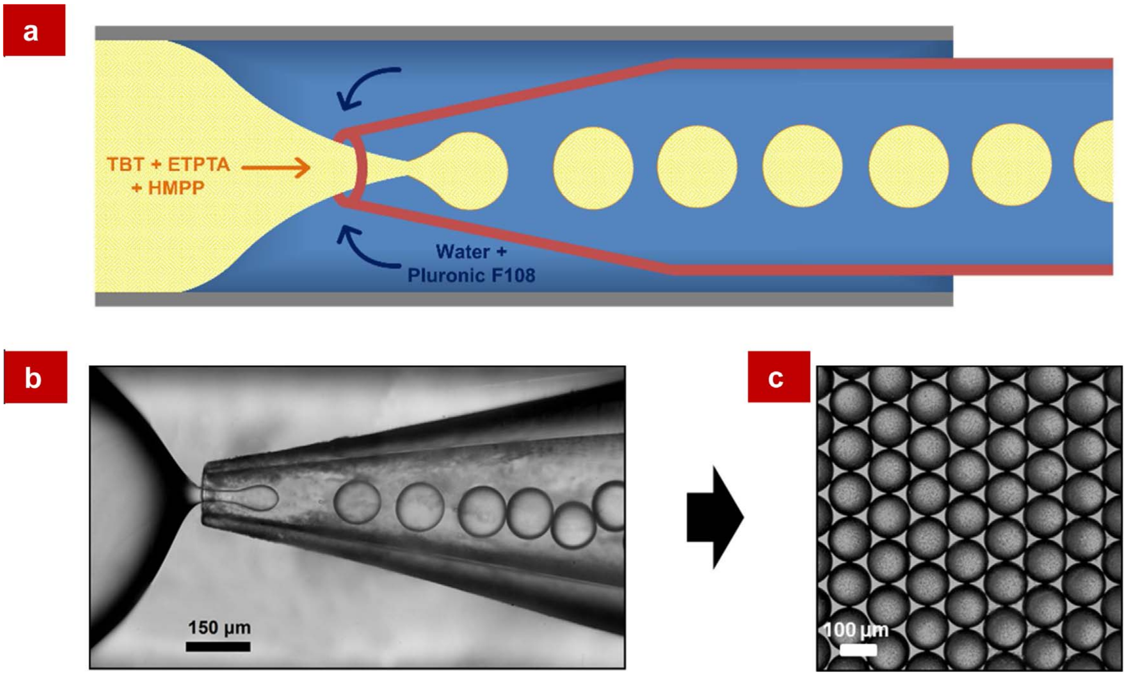

Fig. 1. (a) Schematic illustration of the microfluidic device composed of an outer square capillary for the injection of both oil and aqueous phases and an inner tapered, circular capillary for droplet collection. (b) Optical microscope image showing droplet generation in dripping mode. (c) Optical microscope image of resultant droplets.

high-throughput microfluidic devices. In the past, capillary microfluidic devices have been shown to produce highly monodisperse emulsion droplets, uniform-sized spherical colloidal nanomaterials, polymer microcapsules, hydrophobic porous particles, and monodisperse hollow spheres [18–25]. While this microfluidic approach has not yet been used to fabricate TiO_2 hollow shells, the precise control over particle shape and size that this approach offers could potentially give many advantages over previous approaches.

In this paper, we introduce a TiO_2 catalyst with a new morphology that offers several advantages for photocatalytic application owing to its special configuration. We use a droplet-based microfluidic approach, followed by UV-exposure and other post treatments, to fabricate TiO_2 hollow shells with well-defined shape. These fabricated hollow shell structures could then serve as host for functional co-catalysts such as metal nanostructures, which could further improve photocatalytic activity. Recent reports show that one such metal, in particular–platinum (Pt)–can completely extract excited electrons from a semiconductor [26,27]. This ability to efficiently deplete excited electrons, together with its well-known superior catalytic activity, makes Pt a good potential co-catalyst. With this in mind, we decorated the outer surface and the interior cavity of the TiO_2 hollow shells with Pt to improve their photocatalytic activity. With these great features, Pt-decorated TiO_2 shells show promise as an alternative way to more efficiently remove organic pollutants such as Methylene Blue (MB) from aqueous solutions.

2. Materials and methods

2.1. Materials

Titanium *n*-butoxide (TBT), ethoxylated trimethylolpropane triacrylate (ETPTA), 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP), Pluronic F108, chloroplatinic acid, sodium borohydride, isopropanol (i-PrOH), and MB were all of analytical grade quality and purchased from Sigma–Aldrich.

2.2. Characterization methods

Crystallographic analysis was carried out by X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 0.15478$ nm) (Bruker Eco D8 Advance AXS system). The production of emulsion drops is observed using an inverted optical microscope (DMIL LED, Leica) equipped with a high-speed camera (MicroLab 3a10, Vision Research). The surface morphology and distribution of the microparticles were observed by using a field-emission scanning electron microscope (SEM, LEO FESEM, LEO 1550) equipped with an Energy-Dispersive X-ray spectroscopy (EDS) system for analyzing the chemical composition of the samples. The particle size and distribution of the Pt nanoparticles were obtained by high-resolution transmission electron microscopic (HRTEM, FEI-F20-TEM-STEM, 200 kV) studies. X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of samples using a Surface Science Instruments Model SSX-100 XPS system. Fourier Transform-Infrared Spectroscopy (FTIR) spectra was recorded at the 4000–400 cm^{-1} region on Shimadzu FTIR Model-IRAffinity-1S (MIRacle 10). Photoluminescence (PL) emission spectra were recorded using a Spectrofluorophotometer (RF-6000, Shimadzu) with excitation wavelength at 320 nm. UV–vis diffuse reflectance (DRS) was measured using a UV–vis spectrophotometer (Shimadzu, UV-2600) equipped with an integrating sphere unit (Shimadzu, ISR-2600 Plus). The total organic carbon (TOC) measurements were carried out using a TOC analyzer (Model 1010, OI Analytical, College Station, TX).

2.3. Photocatalytic experiments

Photocatalytic removal experiments were carried out at room temperature in a batch quartz reactor. Artificial irradiation was provided by an 8 W mercury lamp (model UVLS-28 EL Series) emitting at around 356 nm, situated on top of the batch quartz reactor. The distance between the solution surface and the light source was 10 cm. In each test, 40 mg of catalyst suspension, dispersed in water for 15 min using an ultrasonic bath (Symphony™ Ultrasonic Cleaners, VWR, 35 kHz, 144 W), and 10 mg L^{-1} of MB were transferred into the reactor and stirred for 30 min to achieve the adsorption equilibration in the dark before irradiation. The photocatalytic reaction was started by turning on the light