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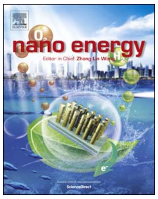

# Monodisperse mesoporous $TiO_2$ microspheres for dye sensitized solar cells

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## ABSTRACT

Uniform discrete mesoporous titania microspheres have been synthesized via a facile and controllable interface-directed co-assembly approach by using 3-dimensional macroporous carbon (3DOMC) as the nanoreactor for the confined co-assembly of template molecules and titania source. By adjusting the synthesis parameters, hollow mesoporous microspheres and hemi-microspheres can also be synthesized. The obtained mesoporous $TiO_2$ microspheres possess a large pore size (4.7 nm), high accessible surface area (145 $m^2/g$), large pore volume (0.26 $cm^3/g$) and highly crystallized anatase pore walls. The dye-sensitized solar cell based on the mesoporous $TiO_2$ microspheres exhibits high photoconversion efficiencies up to 8.5%, which are largely attributed to their intrinsic high surface area, high porosity and well-connected crystalline framework.

## 1. Introduction

Over the past few decades, mesoporous materials have attracted increasing attention because of their unique properties such as multiform framework compositions, uniform and large pore sizes, and high surface areas [1–3]. Titania ($TiO_2$) is an inexpensive and readily available semiconductor material, and it possesses substantial photocatalytic activity, low toxicity and excellent chemical stability, which has potential applications in photocatalysis [4,5], sensors [6,7], dye-sensitized solar cells (DSSCs) [8–26], energy storages [27–29] and so forth [30,31]. Most of these applications strongly depend on the large surface area, diverse nanostructures, and high crystallization degree. Compared to the common solid titania powder, the mesoporous counterpart can provide a huge amount of interfaces for interacting with guest molecules, not only at the surface but also in the ordered internal pore system with diverse mesostructures [31]. Antonelli et al. firstly synthesized mesoporous titania by using titanium isopropoxide as precursor and alkylphosphate as template via soft-template method [32]. Solvent evaporation induced self-assembly (EISA) was also employed to synthesize ordered mesoporous titania by using commercial Pluronic triblock copolymers like poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), $PEO_{20}$-$PPO_{70}$-$PEO_{20}$ (P123), and $PEO_{106}$-$PPO_{70}$-$PEO_{106}$ (F127) as templates. Yang et al. developed the cooperative assembly route to synthesize mesoporous $TiO_2$ with partially crystallized framework in nonaqueous solutions [33]. Tian et al. reported an “acid-base pair” route, wherein a mixture of titanium alkoxide and $TiCl_4$ was adopted as a novel precursor for fabrication of ordered mesoporous titania [34], the former component of the mixture being the main precursor and the latter one acting as the pH adjustor and hydrolysis-condensation controller. This method can significantly shorten the synthetic time and improve the mesostructural regularity. Zhang et al. demonstrated a novel ligand-assisted assembly method for the synthesis of highly ordered mesoporous titania with crystallized anatase framework by virtue of the supporting effect of residual carbon derived from poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS) during

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calcination in $N_2$ [35]. The obtained flake-like mesoporous titania materials possess large nearly spherical mesopores of about 16 nm and high surface area of 112 $m^2/g$, and the dye sensitized solar cell based on the obtained mesoporous titania revealed a power-conversion efficiency of 5.45% in combination with the N719 dye.

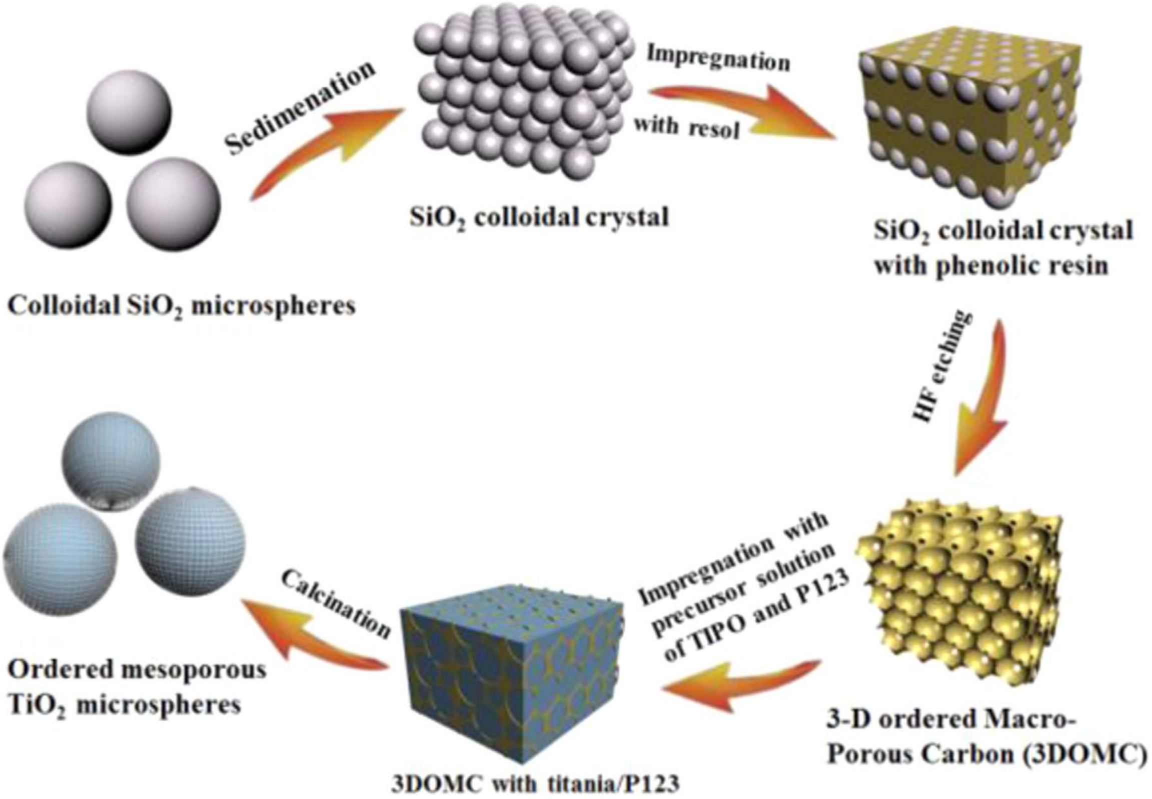
To improve the application performances, much work has been done to fabricate $TiO_2$ with different morphologies, including film [5,17,18,35], nanohelixs [6], nanorods [8,36], hollow microspheres [28,37,38], spherical particles [24,25,39,40], nanotubes [41], sub-microbox [27,29] and so on. Among them, monodisperse mesoporous titania microspheres have drawn particular attentions due to their superior surface permeability and accessibility, low density, and high mechanical stability. Particularly, spherical titania particles with mesoporous structure have attracted great interest, because they can shorten the diffusion path of guest molecules within frameworks. However, the synthesis of mesoporous titania microspheres with well-defined pore structure remains a grand challenge due to the difficulty in controlling the co-assembly of template molecules (*i.e.* structure directing agent) and titania precursor in a spherical morphology. Recently, an interesting and powerful interface-directed co-assembly approach(IDCA) has been developed to synthesize highly uniform mesoporous particles of carbon and silica by using 3-dimensional macroporous silica and carbon as the nanoreactor, respectively, for the confined co-assembly of template molecules with precursors [42,43]. The size of microspheres can be easily tuned by simply changing the 3-dimensional macroporous scaffold with different macropores sizes.

Herein, the IDCA strategy was extended to synthesize monodisperse mesoporous $TiO_2$ microspheres via the confined solvent evaporation induced co-assembly process in 3-D ordered macroporous carbon (3DOMC) template by using amphiphilic template molecules P123 as structure directing agent, titanium isopropoxide (TIPO) as titania source (Scheme 1). The obtained mesoporous $TiO_2$ microspheres possess a large pore size (4.7 nm), high accessible surface area (145 $m^2/g$), large pore volume (0.26 $cm^3/g$) and highly crystallized anatase pore walls. Moreover, by controlling the amount of the precursor solution, the morphology of the mesoporous $TiO_2$ materials can be well tuned from solid mesoporous microspheres to hemi-microspheres and even to hollow mesoporous microspheres. The dye-sensitized solar cells based on solid mesoporous $TiO_2$ microspheres shows high photoconversion efficiencies up to 8.5%, which are largely attributed to their intrinsic high surface area, high porosity as well as high crystallized anatase walls. This work may open up a new opportunity for designing mesoporous $TiO_2$ microspheres with desired mesostructure for applications in catalysis, sensors, and optical devices, etc.

## 2. Experimental section

### 2.1. Chemicals

Pluronic block copolymers poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) (P123, Mw=5800, $EO_{20}PO_{70}EO_{20}$) were purchased from Aldrich Corp. TIPO was purchased from Acros. Ethanol, tetraethyl orthosilicate (TEOS), concentrated ammonia solution (28 wt%), hydrochloric acid, hydrofluoric acid, sodium hydroxide, nitric acid and concentrated sulfuric acid, were purchased from China Medicines Corp. Resol, a soluble phenolic resin with low molecular weight (~500 g/mol), was prepared according to the method reported previously [44] and dissolved in ethanol to form a solution with a resol concentration of 20 wt% for further use. P25, a mixture of anatase and rutile titania (rutile: 20–30 wt%) was purchased from Degussa.



**Scheme 1.** Schematic illustration of the formation process of $TiO_2$ microspheres with ordered mesopores.