

Facile synthesis of nanoporous anatase spheres and their environmental applications†

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Highly nanoporous TiO₂ (anatase) spheres with an excellent ability in environmental applications have been successfully prepared via *in situ* hydrolysis of titanium glycolate precursor spheres.

Nanoporous materials with pore sizes ranging from one to hundreds of nanometres are attractive candidates in many application areas of modern science and technology, including catalyst, adsorbent, medical diagnosis, sensor and electrochemical energy conversion.^{1–6} Recent studies have uncovered that nanoporous materials possess physical or chemical properties that are not found on the corresponding bulk materials.^{7,8} For example, hierarchically mesostructured ceria exhibits a photovoltaic response, while normal ceria does not show this response.⁹ Such new properties are most likely due to the size effect.

The ability to manipulate the morphology and chemical composition of the porous materials on a nanometre scale would enable greater control of the physical or chemical properties. Thus, it is a significant progression to develop a general synthetic approach for nanoporous materials with control over both the composition and the morphology. Many different routes have been reported so far for the preparation of nanoporous structure. The most common route is template-based method, which includes soft template (block copolymers, surfactants, chelating agents, *etc.*)^{10–13} and hard template (porous anionic alumina, carbon nanotubes, zeolite, *etc.*)^{14–17} However, there are few reports on the preparation of nanoporous structure under template free condition. Recently, Guo *et al.* used a TiO₂–CdSO₄ composite as an intermediate to prepare hierarchically mesoporous TiO₂ (anatase) sub-micron spheres with high Li storage capacity and good cycling performance in lithium battery studies.¹⁸ Herein, we develop a simple strategy to synthesize nanoporous TiO₂ (anatase) based on *in situ* hydrolysis of titanium glycolate. The as-obtained nanoporous TiO₂ spheres possess a highly specific surface area and large pore volume, and exhibit an excellent removal ability for As(v) and high photocatalytic activity for photodegradation of eosin B, demonstrating a promising potential in environmental applications.

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This method to prepare nanoporous TiO₂ is essentially a two-step process. The first step is to prepare titanium glycolate spheres. In the second step, the titanium glycolate is mixed with water at refluxing temperature, and the titanium glycolate reacts with water to form the hierarchically nanoporous TiO₂. Titanium glycolate spheres are prepared by the well documented ethylene glycol mediated process.^{19–23} Detailed synthesis procedures can be found in the ESI.†

The scanning electron microscopy (SEM) image of the as-prepared titanium glycolate (Fig. 1a) shows that mono-dispersed spheres are obtained (*ca.* 200 nm in diameter). The transmission electron microscopy (TEM) image of the titanium glycolate (Fig. 1b) indicates that the surfaces of the spheres are rather smooth. The titanium glycolate seems to be fluffy powder, indicating low bulky density. In addition, the XRD pattern of titanium glycolate shows its amorphous nature (Fig. S1 in ESI†).

After one hour reaction between titanium glycolate and water at 100 °C, SEM image of the product (Fig. 1c) reveals that titanium glycolate spheres with dense structures and

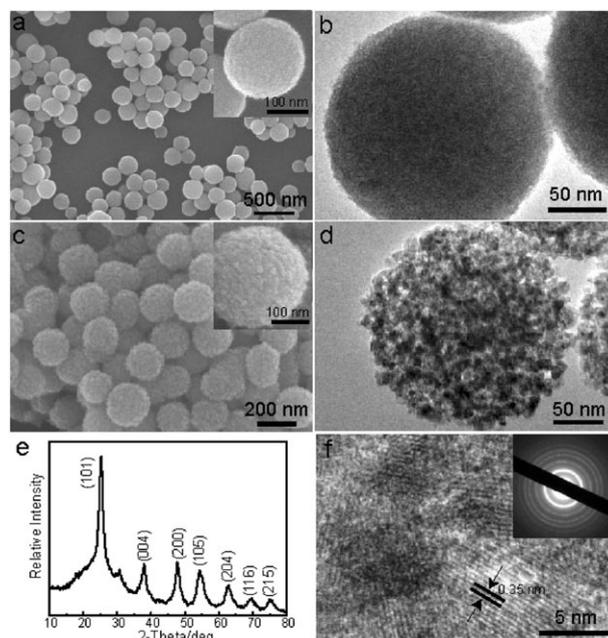


Fig. 1 SEM image (a, with the larger magnification in the inset) and TEM image (b) of the titanium glycolate precursor spheres; SEM image (c, with the larger magnification in the inset), TEM image (d), XRD pattern (e) and HRTEM image (f, with the SAED pattern in the inset) of the nanoporous TiO₂ spheres.

smooth surfaces have been transformed into porous spheres with hierarchical structures, consisting of interconnected nanoparticles of *ca.* 10 nm size. The TEM image (Fig. 1d) also confirms the nanoporous nature of the material with the pore size of several nanometres. The powder X-ray diffraction (XRD) pattern (Fig. 1e) indicates that the as-obtained sample is made of pure anatase (JCPDS Card No. 21–1272). High-resolution TEM (HRTEM) image indicates the polycrystalline characteristic of the material (Fig. 1f). The lattice fringes with a spacing of 0.35 nm are due to the spacing of the (101) planes of the anatase. Continuous sharp circles on the selected-area electron diffraction (SEAD) pattern (inset of Fig. 1f) further confirm that the product is composed of polycrystalline anatase nanostructures.

To study the formation process of the nanoporous structure, a sample is collected after refluxing for only 15 min and investigated by SEM and TEM (Fig. S2 in ESI†). The surface of the intermediate is not as rough and porous as that of the final product. There aren't sharp diffraction rings in the SEAD pattern of the intermediate, indicating an intermediate state from titanium glycolate to the final nanoporous TiO₂. We also investigated the effect of reaction temperature on the formation process. A similar nanoporous structure (Fig. S3 in ESI†) is also obtained when the reaction temperature is lowered to 50 or 25 °C. Titanium oxide crystals are more stable than amorphous titanium glycolate in an aqueous medium, so the latter is prone to be converted into titanium oxide crystals even at room temperature. However, a longer time is needed to complete the conversion process due to the lower reaction rate.

Nitrogen sorptometer measurements are conducted to further investigate the porous structure of the as-obtained TiO₂ spheres. The N₂ adsorption–desorption isotherm of the nanoporous TiO₂ shows characteristics of mesoporous materials (Fig. 2a). The Barrett–Joyner–Halenda (BJH) pore size distribution (Fig. 2b) obtained from the isotherm indicates pores ranging from 2 nm to 10 nm. The BET specific surface area and pore volume of the sample are 244.6 m² g⁻¹ and 0.324 cm³ g⁻¹, respectively, from which the porosity of the nanoporous TiO₂ spheres is calculated to be about 56 %. All these data strongly support the fact that the product has a nanoporous structure.

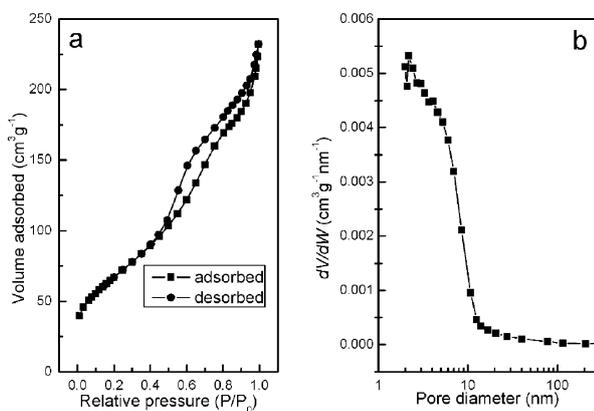


Fig. 2 Nitrogen adsorption–desorption isotherm (a) and BJH pore size distribution plot (b) of the nanoporous TiO₂ spheres.

From the above discussion, we can see that, simply by treating the titanium glycolate precursor with water at refluxing temperature, nanoporous TiO₂ (anatase) could be easily obtained without the addition of any surfactant as the template. The nanoporous TiO₂ retains the sphere morphology and the diameter of the titanium glycolate spheres. Thus, it is rather convenient to control the size of the nanoporous TiO₂ spheres by using the titanium glycolate spheres with different sizes, which can be easily controlled by varying the preparation parameters.^{19–23}

By comparison, direct calcination of the titanium glycolate at 500 °C in air for 2 h also produces anatase TiO₂. However, as shown in supporting information Figure S4,† the sample obtained by calcination possesses a rather solid structure, and has a low BET surface area (29.1 m² g⁻¹). More significantly, the mean diameter of each sphere has been reduced by 15%, indicating that from titanium glycolate to titanium oxide, the titanium glycolate spheres shrank due to the density difference of the two materials. As mention earlier, the density of the titanium glycolate is quite low. However, for the titanium oxide prepared from the hydrolysis route, the titanium oxide spheres retain the original sizes. As a result, porous structures were produced inside the sphere to account for the density change.

Fig. 3 illustrates our proposed mechanism to explain how porous structure is generated and the original sphere sizes are preserved during the titanium glycolate hydrolysis. Once the precursor sphere is added to water at reflux temperature, as titanium glycolate is not stable in aqueous medium, the titanium glycolate on the outer sphere surface will react with water to form a thin TiO₂ shell. The density difference between titanium glycolate and titanium oxide results in cracks on the shell. Since the titanium glycolate spheres are amorphous, and the whole sphere is quite loose, water can penetrate through the cracks on the shell and enter the inner part of the titanium glycolate spheres as showed in step (1) in Fig. 3. Thus, hydrolysis also occurs within the precursor spheres and forms small TiO₂ clusters. These small TiO₂ clusters could act as nuclei for further growth. With the hydrolysis proceeding, the TiO₂ clusters grow gradually into interconnected nanoparticles. Because the lattice density of anatase is higher than that of titanium glycolate, void spaces are produced within each TiO₂ nanoparticles as showed in step (2) in Fig. 3. The hierarchical nanoporous structure of TiO₂ is thus formed.

TiO₂ has been widely used in the photovoltaic cell, water splitting, pollution abatements and electrochemical cell.^{18,24–27} In these applications, TiO₂ is usually used in the form of

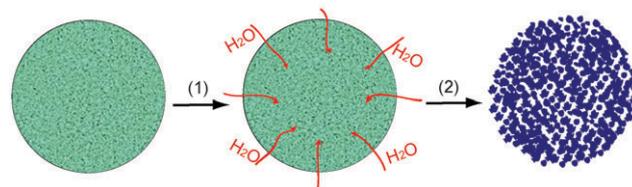


Fig. 3 Illustration of the formation mechanism of the nanoporous TiO₂. (1) Water penetrating into the precursor sphere; (2) complete conversion of titanium glycolate into nanoporous TiO₂ through *in situ* hydrolysis.

nanoparticles for high specific surface area and activity. Prompted by the hierarchical nanoporous structure, high surface areas and high pore volumes, we expect that the as-obtained TiO₂ in this study to be also useful in these applications.

The arsenic ion (As(v)) is one of the most toxic pollutants found in the underground water source, and its efficient removal is one of the top priorities in pollution abatements. Recently, TiO₂ nanoparticles have been investigated for effective removal of As(v) ions.^{28–31} Herein, we use the as-obtained nanoporous TiO₂ as adsorbent to remove As(v) ions. Fig. 4a shows the adsorption isotherms of As(v) on the different adsorbents at different initial concentrations of As(v). The as-obtained nanoporous TiO₂ possesses a much higher removal capacity for As(v) than the commercial anatase (Alfa Aesar, with BET surface area of 45 m²g⁻¹) and TiO₂ obtained by direct calcination of the precursor. For example, when the initial concentration of As(v) is 184.8 ppm, the removal capacity of the nanoporous TiO₂ is 51.8 mg g⁻¹, while only 14.2 mg g⁻¹ and 15.1 mg g⁻¹ are found for commercial and directly calcined control samples, respectively. The mechanism for the removal of As(v) is proposed to be through the formation of bidentate binuclear surface complexes between TiO₂ and As(v) species in the solution.³⁰ So much higher surface area and facile mass transportation on nanoporous TiO₂ enable it to remove more As(v) from water.

The as-obtained nanoporous TiO₂ also exhibits excellent photocatalytic activity for photodegradation of eosin B. As revealed by Fig. 4b, which shows the time-dependent concentration of eosin B under exposure to UV light using different TiO₂ samples as photocatalysts. The as-obtained nanoporous TiO₂ is able to completely degrade eosin B within 16 minutes, much faster than the other two comparing samples. We attribute the better performance of nanoporous TiO₂ to two features: more active sites due to the higher specific surface area; and facile diffusion of reactants and products during the reaction because of the highly porous structure. In addition, separation and recycle by means of a simple filtration step are

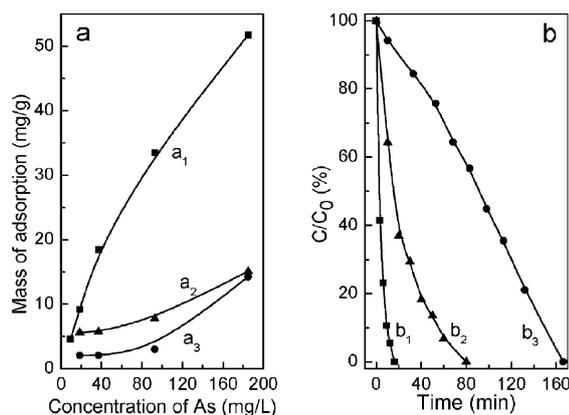


Fig. 4 The application of the as-obtained nanoporous TiO₂ for As(v) removal and photodegradation of eosin B. (a) Adsorption isotherms of As(v) by different adsorbents: (a₁), nanoporous TiO₂ spheres; (a₂), commercial anatase nanoparticles; (a₃), TiO₂ obtained by calcination of the precursor; (b) Photodegradation of eosin B by different photocatalysts: (b₁), nanoporous TiO₂ spheres; (b₂), commercial anatase nanoparticles; (b₃), TiO₂ obtained by calcination of the precursor.

facile because of the relatively large diameter of the nanoporous spheres compared with true nanoparticles.

In summary, nanoporous titania spheres are synthesized through a facile aqueous route. They are promising adsorbents and catalysts. Future work will focus on expanding the applications of this material.

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