Synthesis of hierarchical nanoporous F-doped TiO₂ spheres with visible light photocatalytic activity†

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Hierarchical porous F-doped TiO₂ microspheres exhibiting high visible light photocatalytic activity have been fabricated by a one-step low-temperature hydrothermal approach without using any templates.

Since the discovery of photo-induced water decomposition on TiO₂ electrodes under ultraviolet light irradiation,[1] TiO₂ has received much attention as a photocatalytic material. However, the widespread technological use of TiO₂ is impaired by its wide band gap (3.2 eV), which requires ultraviolet irradiation for activation. Asahi *et al.* reported in 2001 that N-doped TiO₂ with a narrow band gap could be synthesized by sputtering TiO₂ targets in a N₂–Ar gas mixture followed by annealing in N₂ gas at 550 °C.[2]

Many studies have since revealed that doping TiO₂ with nonmetal atoms, such as N,[3] S,[4] C,[5] I,[6] Br and Cl[7] shifts the optical absorption edge of TiO₂ to lower energies, thereby increasing the photocatalytic activity in the visible region. It was also demonstrated that F-doping in TiO₂ could induce visible-light-driven photocatalysis by the creation of oxygen vacancies.[8]

In the present work, we use a simple approach for the synthesis of F-doped TiO₂ photocatalysts by low-temperature hydrothermal treatment of TiF₄ powder in HCl solution at 180 °C. The reaction condition is much milder than that of conventional methods, which require a fluorine-conditioning atmosphere and very high temperatures. Another advantage is that our products show an interesting hierarchical nanoporous spherical structure. Traditionally, hierarchical nanoporous structures are constructed by using various organic templates as scaffolds. The templates must then be removed by thermal treatment, resulting in high energy consumption and environmental pollution.

It is well-known that porous solids have excellent adsorptive properties which possess numerous applications in catalysis and separation.[9] Chemical reactions can occur more easily when the transport paths, through which molecules move into or out of the porous materials, are included as an integral part of the architectural design. These transport paths may be realized through a hierarchical combination of smaller and larger mesopores. It is reported that the transport of small molecules in media featuring hierarchical nanoporous structure can approach rates of diffusion comparable to those in open media.[10] In addition, calculations and simulations have demonstrated that the catalytic process would occur more efficiently in materials with hierarchical pore size distribution on the nanoscale.[11] Thus, it is expected that the photocatalytic efficiency should be greatly enhanced for a hierarchical porous material. As such we have proven that hierarchical porous TiO₂ shows much enhanced photocatalytic activity.[12] Here we report for the first time that hierarchical porous F-doped TiO₂ microspheres can be synthesized through a one-step, template-free hydrothermal approach exhibiting visible light photocatalytic activity.

In a typical procedure, titanium tetrafluoride (Aldrich) was used as both a source of fluorine dopant and a precursor of titanium. Titanium tetrafluoride was dissolved in HCl solution (1 M) to give a TiF₄ concentration of 0.5 to 5 M. The above TiF₄ solutions were then placed in a 200 ml Teflon-lined stainless steel autoclave until 80% of its volume was filled. The autoclave was maintained at 180 °C for 6–12 h and then air cooled to room temperature. After this hydrothermal reaction, the resulting samples were collected by centrifugation, gently washed with deionized water several times and dried in an oven at 100 °C. As a control experiment, TiS₂, TiC, TiN and TiCl₄ were used instead of TiF₄ for the hydrothermal process and all other conditions were kept the same.

The X-ray diffraction (XRD) patterns of F-doped TiO₂ spheres indicate that all peaks can be indexed as the anatase phase of TiO₂ (JCPDS file No. 21-1272) (Fig. S1†). According to the Scherrer equation, the average crystallite sizes are *ca.* 11–15 nm. The morphology of the samples was investigated by scanning electron microscopy (SEM). Fig. 1 shows the SEM images of F-doped TiO₂ spheres with different magnifications. Spherical particles of micrometre size were observed in the hydrothermally treated samples (Fig. 1a and b). The porous structure of the F-doped TiO₂ spheres can be better seen from the SEM images with higher magnification (Fig. 1c and d). As shown in the images, the samples exhibit a unique nanoporous spherical structure. Fig. 1e shows an image of a single nanoporous sphere with about 1 μm in diameter and it is composed of numerous small crystallites. It should be emphasized that these small crystallites aggregate to form a nanoporous spherical structure. Large mesopores in the range of 20 to 50 nm were observed between these small crystallites.

Chemical composition analysis using energy-dispersive X-ray (EDX) spectroscopy (Fig. 1f) illustrates that the porous microspheres are mainly composed of Ti, O and F. These results are consistent with those from X-ray photoelectron spectroscopy (Fig. S2†), in which titanium, oxygen, fluorine and carbon are found in the microsphere sample after the hydrothermal process. A

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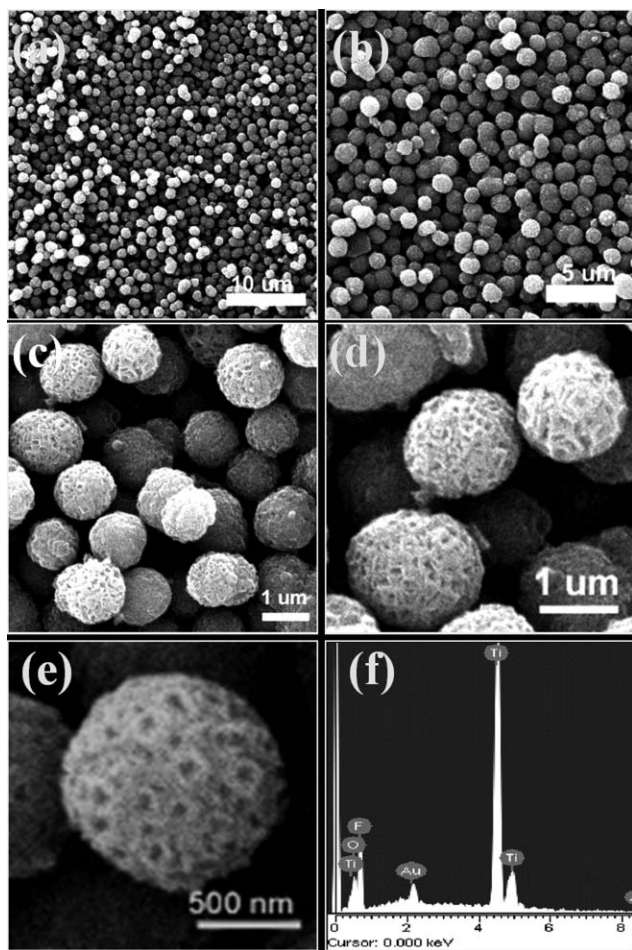
Fig. 1 SEM images of (a–d) porous F-doped TiO_2 microspheres with different magnifications; (e) an individual single microsphere showing detailed texture and porosity (*ca.* 1 μm in diameter); (f) EDX microanalysis spectrum of porous F-doped TiO_2 microspheres.

Fig. 2 Pore size distribution curve and (inset) corresponding isotherm of hierarchical porous F-doped TiO_2 microspheres.

high-resolution spectrum of the F 1s region displays a peak at 687.8 eV which can be attributed to the doped F-atoms in the TiO_2. It is close to the value reported by our group[13] and Li *et al.*[8] for substitutional F-atoms in TiO_2. This confirms that F-atoms are doped into the oxygen sites of the TiO_2 crystal lattice. It should be mentioned that when the −1 fluoride ions replace the −2 oxide ions in the lattice, a charge imbalance is created. The extra positive charge is probably neutralized by the hydroxide ions by forming surface adsorbed hydroxyl groups.

Fig. 2 shows the pore size distribution curve calculated from the desorption branch of a nitrogen isotherm by the BJH method using the Halsey equation. The powder contains small mesopores (3.6 nm) and large mesopores with a maximum pore diameter of *ca.* 37 nm. The inset shows the corresponding nitrogen isotherm of the F-doped TiO_2 sphere. Two distinct capillary condensation steps can be clearly seen on the N_2 adsorption–desorption isotherm. These results confirm the hierarchical combination of independently connected mesopores. The first hysteresis loop of the samples is at $0.42 < P/P_0 < 0.81$, corresponding to the filling of the framework confined smaller mesopores formed between intra-agglomerated primary particles. The second hysteresis loop is at $0.83 < P/P_0 < 1$, corresponding to the filling of larger textural mesopores produced by inter-aggregated secondary particles.
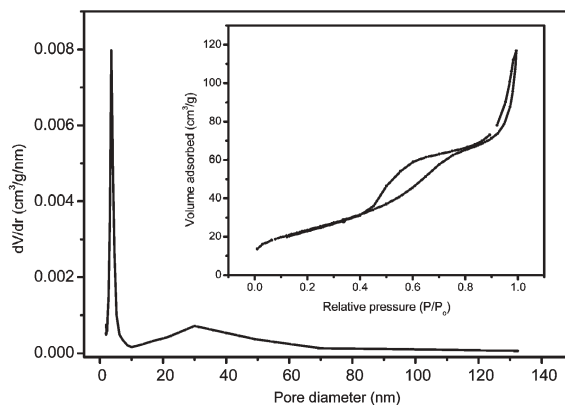
The formation of hierarchical porous F-doped TiO_2 microspheres can be attributed to the HF generated during the hydrothermal process. First, a titanium dioxide cluster or crystal nucleus is formed in solution phase by the slow hydrolysis and condensation of TiF_4. The nucleus is then agglomerated and grows into a larger particle with framework confined small mesopores. At the same time, HF, which is a corrosive chemical etchant, is formed *in situ* as a hydrolysis product from TiF_4 in the production of TiO_2 (*i.e.* $TiF_4 + 2H_2O \rightarrow TiO_2 + 4HF$). This process will create a localized HF-rich zone in the region around the TiO_2 particle. When the particle reaches a critical dimension, the area created will then attract a new cluster crystallizing on it. The cluster will later develop into a larger one, and the new area will become more inviting to a new nucleus. Through the repetition of the above steps due to the chemical etching of hydrolysis products, secondary large textural mesopores are gradually produced. Finally, this interaggregation process will lead to the formation of hierarchical porous F-doped TiO_2 spheres. In a control experiment where TiF_4 was replaced by TiS_2, TiC, TiN or $TiCl_4$ to avoid HF formation in the synthesis, no spherical structure could be found from the final product. This confirms the crucial role of HF in the formation of porous spherical structures.

The self-generated etchant HF not only provides the nucleation center for the growth of porous spheres, but also acts as the source of F-dopant. When TiF_4 was used as the starting material, most of the fluorine in TiF_4 was hydrolyzed and the residual fluorine would naturally remain as a dopant in the TiO_2 lattice. This phenomenon is similar to the situation of the conventional method in the synthesis of N-doped,[3b] S-doped[4a,b] and C-doped TiO_2[5b,c] by oxidative annealing of TiN, TiS_2 and TiC.

The absorption spectra of the F-doped TiO_2 spheres with different F-dopant contents indicate that F-doping does not cause a shift in the fundamental absorption edge of TiO_2 (Fig. S3†). This conclusion is consistent with the theoretical band calculations for F-doped TiO_2 reported by Asahi *et al.*[2,3b] and Yamaki *et al.*[14] When TiO_2 is doped with fluorine, localized levels with high density appear below the valence band of TiO_2. These levels consist of the F 2p state without any mixing with either the valence band or the conduction band of TiO_2. Since the F-doped TiO_2 does not absorb in the visible spectrum, it is not expected to show high visible-light-driven photocatalytic activity.[8,15] Therefore, studies on F-doped TiO_2 are almost always carried out under UV irradiation.[13,15,16]
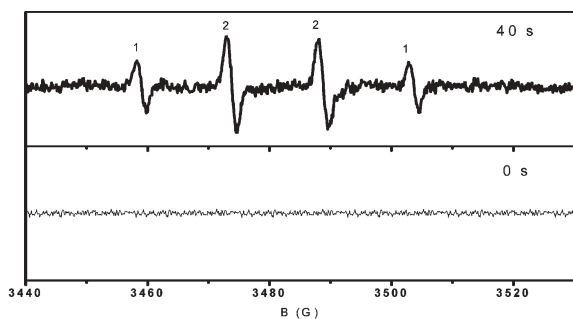
Fig. 3 ESR signals of the DMPO–OH˙ adduct in a porous F-doped TiO₂ microspheres–DMPO dispersion. The signals were recorded before and after illumination for 40 s with a Quanta-Ray Nd:YAG pulsed laser operated in the continuous mode at 10 Hz frequency.

Surprisingly, our hierarchical porous F-doped TiO₂ microspheres are very effective in the photocatalytic degradation of 4-chlorophenol under visible light illumination (Table S1†). It has been reported that the photoexcitation of extrinsic absorption bands of a catalyst can also lead to surface photoreactions.[17] The extrinsic absorption originates from the photoionization of original or newly formed defects and the excitation of surface states. Such extrinsic absorption requires less energy to activate. Thus, it is possible to generate free charge carriers to induce surface chemical reactions by using visible light. A recent study indicates that F-doping in TiO₂ can also induce visible-light-driven photocatalysis by extrinsic absorption through the creation of oxygen vacancies.[8] The high photocatalytic activity of our F-doped TiO₂ microspheres is probably due to the excitation of the extrinsic absorption bands by these oxygen vacancies rather than the excitation of the intrinsic absorption band of bulk TiO₂. Fig. 3 illustrates the ESR spectrum of the DMPO–OH˙ spin adduct with pulsed laser illumination. In the dark (0 s), no signal can be detected. After visible light irradiation, the characteristic 1 : 2 : 2 : 1 quadruple peaks of the DMPO–OH˙ adduct are observed, which indicates that the photocatalysts are activated when exposed to visible light and generate reactive oxygen species such as hydroxyl radicals. This further confirms the existence of oxygen vacancies, which can generate hydroxyl radicals from the F-doped TiO₂ microspheres for the photocatalytic degradation of 4-chlorophenol.[18]

Our template-free hydrothermal approach offers another benefit. The final products possess an unusual hierarchical porous structure. This allows more efficient transport for the reactant molecules to get to the active sites on the framework walls, hence enhancing the efficiency of photocatalysis.[19] To the best of our knowledge, this is the first evidence of hierarchical nanoporous F-doped TiO₂ spheres showing visible light photocatalytic activity. We believe that the preparation of hierarchical porous inorganic microspheres is of great interest in catalysis, separation technology, biomedical engineering and nanotechnology.[20]

In summary, hierarchical porous F-doped TiO₂ spheres were fabricated by a simple and template-free hydrothermal approach. The new photocatalysts show high visible light photocatalytic activity on the degradation of 4-chlorophenol. We also demonstrate that the visible light photocatalytic activity of F-doped TiO₂ microspheres was achieved by the creation of oxygen vacancies rather than by the improvement of the absorption of bulk TiO₂ in visible light region.

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