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Fabrication of Aligned Anatase TiO_2 Submicron Spheres Using Porous Carbon

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Porous TiO_2 film is the most important light-absorption and electron-transport material for photovoltaics and photocatalysis [1].

Here we show a porous carbon template approach to synthesizing aligned and interconnected TiO_2 submicron spheres. An inverse opal of carbon was prepared by carbonizing a carbon precursor infiltrated into a lattice of packed SiO_2 submicron spheres and then dissolving these SiO_2 submicron spheres (Fig. **a**). A high-magnification scanning electron microscope (SEM) image shows the hexagonal order of the carbon framework (Inset of Fig. **a**). The high porosity allowed this carbon framework to be filled with the precursor of $Ti(OC_4H_9)_4$ with the assistance of suction. Next, we made a layer of gel on the top of the $Ti(OC_4H_9)_4$ filling the carbon framework by hydrolysis of $Ti(OC_4H_9)_4$. The porous carbon containing $Ti(OC_4H_9)_4$ were reversely attached on a Si substrate and dried at 70 °C for 3 h. After calcination at 400 °C for 2h, submicron spheres were formed in the inverse opal of carbon standing on the TiO_2 layer derived from the gel (Fig. **b**). Energy-dispersive X-ray (EDX) analysis reveals that these submicron spheres were TiO_2 (Fig. **c**). After further calcination at 700 °C for 1 h, the carbon framework was completely removed. SEM analysis demonstrated that as-synthesized TiO_2 submicron spheres had a size range from 180 nm to 220 nm and were packed in an opal structure (Fig. **d**). A high magnification SEM image of a portion of the sample is shown in the inset of Fig. **d**. Most of exposed TiO_2 submicron spheres have a relative smooth surface with the exception of some rough areas resulting from broken bridges to neighboring TiO_2 submicron spheres. This indicates that among the packed TiO_2 submicron spheres, each sphere is firmly connected to six sideward spheres. The solid connections between neighboring TiO_2 submicron spheres provide an advantage for electron transport during the separation of photon-induced electron-hole pairs [2]. The internal structure of TiO_2 submicron spheres was characterized using a FEI Tecnai F-20 transmission electron microscope (TEM). Fig. **e** shows that the as-synthesized TiO_2 submicron spheres are polycrystalline, which was confirmed by their corresponding electron diffraction (ED) pattern. The product was further analyzed using a HORIBA Jobin Yvon LabRAM HR Raman microscope (Fig. **f**). Raman spectrum of as-synthesized TiO_2 submicron spheres demonstrates the six Raman-active modes ($3E_g + 2B_{1g} + A_{1g}$) of octahedral anatase TiO_2 [3]. This indicates that these TiO_2 submicron spheres are anatase. Further modifying the sphere size of the TiO_2 spheres will be conducted to optimize the light-absorption of the opal-like TiO_2 porous structures.

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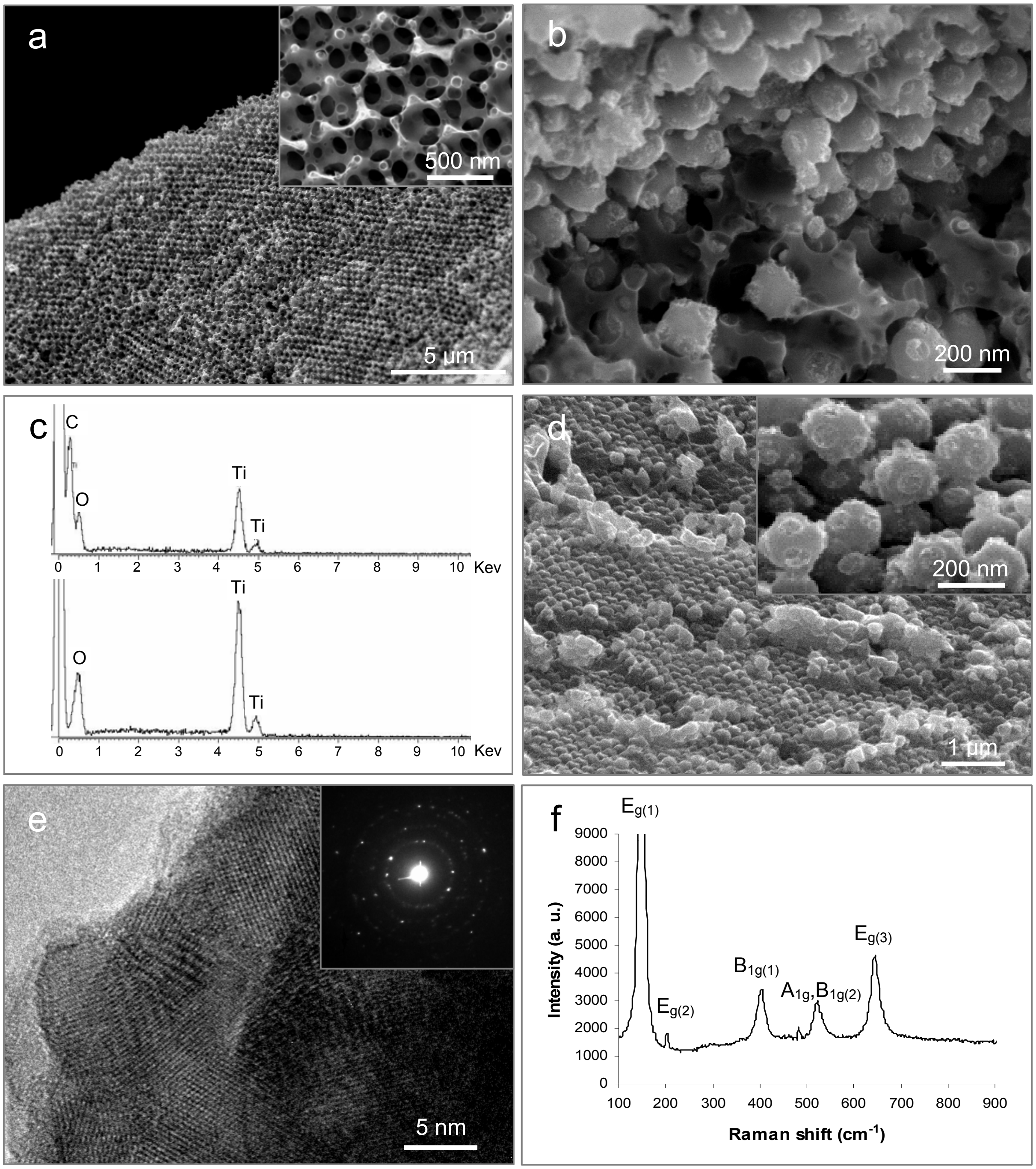

FIG. (**a**) SEM image of porous carbon; the inset is part of (**a**). (**b**) The submicron spheres formed in the inverse opal of carbon after calcination at 400 °C for 2h. (**c**) EDX spectra of the carbon frame-rich area (upper) and the submicron spheres (bottom) shown in (**b**), respectively. (**d**) Orderly packed TiO_2 submicron spheres obtained after calcination at 700 °C for 1h; the inset is a high magnification SEM image of a portion of the packed TiO_2 submicron spheres. (**e**) Representative TEM image of TiO_2 submicron sphere, the inset is the corresponding electron diffraction pattern. (**f**) Ambient pressure Raman spectra of packed TiO_2 submicron spheres excited using a laser with a wavelength at 532 nm.

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