Fabrication of Porous Titania (Brookite) Microparticles with Complex Morphology by Sol−Gel Replication of Pollen Grains

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Nature is replete with complex, elaborate structures that have high functional specificity. Recently, there has been widespread interest in the replication of these biostructures for use as biomimetic materials in a variety of potential applications. For example, cedar wood has been exploited in the preparation of macroporous silica with potential uses in the separation, catalysis, and adsorption of high molecular weight molecules.[1] Similarly, stable biosubstrates such as bacterial[2] and fungal colonies,[3] insect wings and plant leaves,[4] and spider silk[5] have been utilized as templates for the fabrication of functional inorganic materials with novel architectures and form. The scope of these replication processes is often compromised, however, by the limited availability of appropriate chemical precursors as well as by significant levels of shrinkage and deformation associated with thermally induced removal of the biotemplate. In this respect, pollen grains are excellent candidates for inorganic replication because they are relatively resistant to heat and oxidative attack,[6] and although the grains shrink on heating, the hardiness of the outer layer (exine) limits deformation such that high fidelity replication should be possible for a wide range of inorganic materials. Pollen is a ubiquitous and inexpensive natural product that is environmentally benign and easy to harvest and store. Moreover, the grains are uniform in particle size, are of high surface area, and have species-specific morphologies that are often highly elaborate and complex in surface morphology.[7]

We have recently described the use of pollen as a template to produce porous silica, calcium phosphate, and calcium carbonate microspheres prepared in aqueous reaction solutions.[8] In this paper, we describe a nonaqueous route to morphologically complex porous particles of titania (brookite)[9] using hydrated pollen grains exposed to titanium isopropoxide (TIP) reaction solutions. We use dandelion (*Taraxacum*) pollen grains because the tough outer exine layer exhibits a series of complex microscale surface features that require the development of high-resolution replication procedures. In addition, our work has focused on titanium dioxide because of the wide ranging interest in the use of high surface area titania particles in areas such as solar cells, self-cleaning surfaces, and the treatment of cancer by decomposition of tumor cells.[10]

Dandelion pollen was pretreated by immersion in ethanol/water mixtures to produce hydrated grains so that the surface could react specifically with nonaqueous reaction solutions of TIP. No reaction was found with native grains.[11] Scanning electron microscopy (SEM) images indicated that the native/hydrated pollen grains were 20−25 μm in size and decorated with elaborate surface features in the form of 700-nm-thick echinate spines and 4-μm-wide lophate ridges, which were interspaced with depressions of the softer cellulose-rich intine (Figure 1a). Immersion of hydrated pollen grains in a 2-propanol solution of TIP for 15 min followed by centrifugation and calcination at 500 °C for 3 h of the air-dried material[12] produced a black powder that consisted of porous 5-μm-sized inorganic particles with complex microstructure (Figure 1b). The inorganic microstructures were intact and uniform in size but notably reduced in dimension compared with the native grains, presumably because of thermally induced shrinkage. Significantly, the fine-structure details associated with the lophate ridges and echinate spines of the native pollen grains were preserved albeit at a smaller length scale (0.5 μm and 100 nm in width, respectively) as the

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(11) Dandelion (*Taraxacum*) pollen was purchased from http://www.pollen-online.com. In a typical preparation, 0.01 g of dry *Taraxacum* pollen powder was added to 1 mL of a 50 wt % aqueous solution of ethanol (Merck; grade, absolute extra pure) in a 1.5 mL Eppendorf centrifuge tube, sonicated for 15 min followed by centrifugation at 13 200 rpm for 5 min and removal of the supernatant. A total of 1.5 mL of water (Milli-Q, 18.2 MΩ) was added to the pollen pellet, and the mixture was sonicated for 15 min prior to agitation overnight at 1000 rpm. The sample was then centrifuged at 13 200 rpm for 5 min, and the supernatant was removed leaving damp grains which directed the hydrolysis.
(12) Preparation of titania-infiltrated pollen grains was based on a recent protocol developed for the growth of anatase on cotton fibres.[15] A wide range of conditions were investigated; optimum conditions for producing high fidelity titania replicas are described as follows. A total of 1 mL of 100 μM TIP (97% in propanol, Aldrich, used as supplied) in 2-propanol was added to pelleted pollen grains prepared as as already described,[11] and the sample was left for 15 min prior to centrifugation at 13 200 rpm for 5 min followed by removal of the supernatant and drying under vacuum. In some samples the sol was added above the solid; that is, the sol was allowed to percolate through the solid. In others the solid was added on top of the sol. Percolation was found to be the easiest approach. The pollen template was subsequently removed by calcination at 500 °C for 3 h to produce titania replicas. Samples for SEM were prepared by mounting replicated grains on gummed carbon pads adhered to aluminum stubs with a diameter of 10 mm. Samples were also coated with a 15-nm-thick platinum film. Titania replicas were investigated by TEM using samples sonicated in ethanol prior to air drying these dispersions onto carbon-coated grids.

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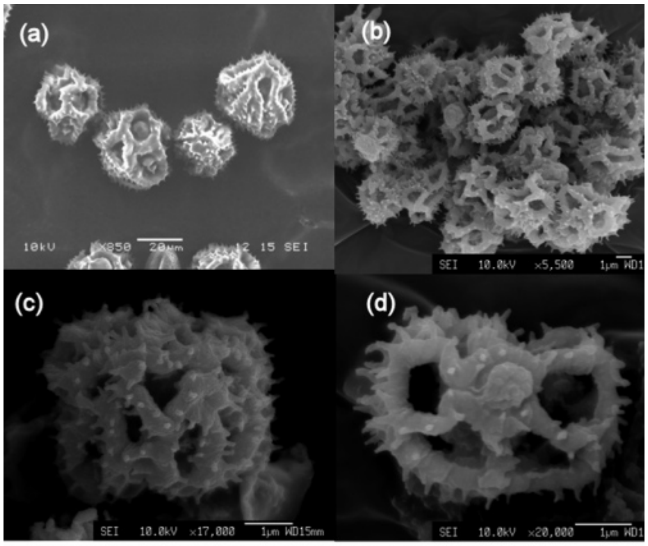

Figure 1. SEM images of (a) native dandelion (*Taraxacum*) pollen grains. Scale bar: 20 μm. (b−d) SEM images of titania replicas produced by pollen grain templating and calcinations; scale bars, 1 μm. (b) Low magnification image, (c, d) single titania particles showing porous architecture, and replicated lophate ridges and echinate spines.

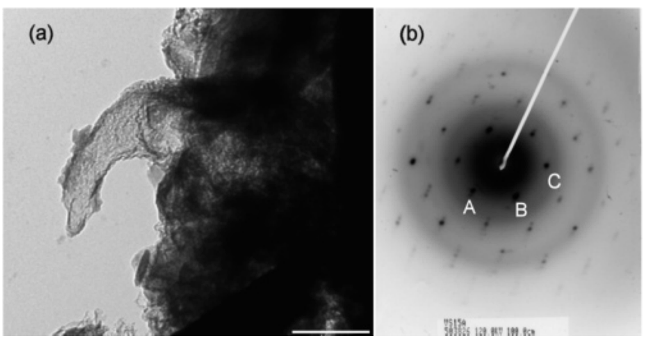

Figure 2. (a) TEM image showing titania replica of an individual echinate spine. Scale bar: 200 nm. (b) Single-crystal electron diffraction from the fractured area of titania replica. Reflections: A = (030), B = (111), and C = (121). Interplanar angles: A ∧ B = 68°, B ∧ C = 62°, and A ∧ C = 47° agree with the literature values for the brookite polymorph of titania. The *d* spacing of 2.93 Å (030) in particular discounted the presence of both anatase and rutile, as neither polymorph has a major reflection around 2.9 Å. The presence of rings in the electron diffraction pattern indicate a degree of polycrystallinity.

replicas decreased in size by approximately a factor of 5 (Figure 1c,d). During the shrinkage process it is assumed that the echinate spines became to a large extent solid. In contrast, the softer intine regions were mainly absent, with the consequence that the inorganic particles contained well-defined micrometer-sized apertures (Figure 1d).

Transmission electron microscopy micrographs of the sonicated replicas indicated that the microstructures comprised a continuous titania gel matrix with a surface texture which replicated exactly the underlying morphology of the pollen grain template. High magnification images of the replicated echinate spines confirmed the presence of titania spikes that were often less than 100 nm in width (Figure 2a). Corresponding electron diffraction analysis from selected areas of the sonicated inorganic replicas gave single crystal or polycrystalline patterns that were indexed to the relatively uncommon titania polymorph, brookite, with an orthorhombic unit cell with parameters, $a = 5.455\ 80$ nm, $b = 9.181\ 90$ nm, and $c = 5.142\ 90$ nm (Figure 2b). Formation of brookite

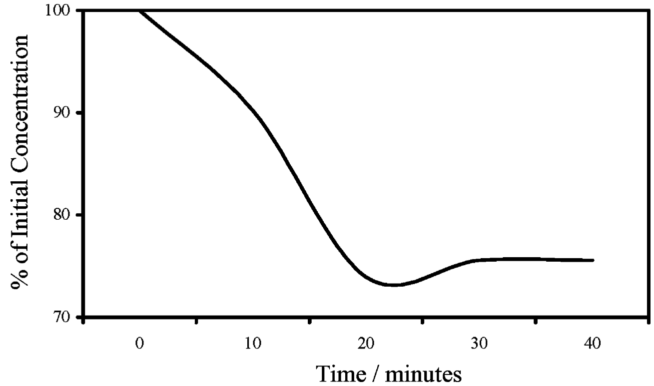

Figure 3. Plot showing time-dependent decomposition of methyl blue in the presence of titania replicas produced by pollen grain templating.

was confirmed by powder X-ray diffraction, which showed broad, low intensity peaks at *d* spacings of 3.52 (210) and 2.14 (221). The low level of crystallinity was consistent with the relatively low-temperature processing of titania produced by sol−gel synthesis at neutral pH.[13] Increasing the calcination temperature to 800 °C produced a whitening of the black powder and enhancement in crystallinity, as evidenced by an increase in the sharpness and intensity of brookite reflections at $d = 3.52$ (210), 2.26 (202), 2.12 (221), 1.94 (302), and 1.66 (421). Reflections corresponding to rutile ($d = 3.32$ (110), $d = 2.22$ (111)) were also observed under these conditions as a result of solid-state transformation of brookite to the more stable titania polymorph (transition temperature, 750 °C). SEM images of these replicas showed that they retained their original morphology.

The titania replicas were assessed for photocatalytic activity by monitoring the decomposition of methyl blue in aqueous solution[14] in the presence of UV light. A linear decrease in methyl blue concentration was observed over an initial period of 20 min, which corresponded to about 20% decomposition of the organic molecule (Figure 3). The reaction runs for 20 min, after which time the surface is poisoned by decomposition products and the reaction is unable to continue. The replica sample was run in tandem with the same mass of Degussa P25, a highly photoactive rutile−anatase combination material, so that a comparison could be made. These data indicate that the replicas show some photoactivity, although not as much as the highly photoactive standard. This is disappointing with respect to the immediate application of the replicas produced in this work but consistent with the extent of crystallinity shown by XRD spectra. However, there is potential for this method to be developed to encourage a more crystalline product and potentially a strong photocatalytic material, particularly in combination with anatase.

In conclusion, we have developed a method for the high fidelity replication of dandelion pollen grains in the form of morphologically complex porous titania (brookite) micro-

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particles. Our results indicate that hydrated pollen grains can be used as elaborate templates in nonaqueous sol–gel synthesis, thereby broadening the potential range of mineral phases attainable via this bioreplication route. The use of facile processes to fabricate titania microstructures with complex form is not only of significant academic interest but also of potential interest with regard to the widespread use of titania colloids in numerous applications.

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