Angewandte Chemie International Edition

Porous Single Crystals

DOI: 10.1002/anie.201303849

Fast Electron Transport and High Surface Area: Potential Application of Porous Anatase Single Crystals in Solar Cells

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electron mobility · mesoporous materials · nanoparticles · solar cells · titanium dioxide

In 1991 when Grätzel and O'Regan used TiO_2 nanoparticles[1] instead of large single crystals[2] to create the prototype of today's dye-sensitized solar cells (DSSCs), the key result was a 1000 times increased light conversion efficiency (IPCE)[3] (see Figure 1 a,b and d,e). This indicated that the key to high solar-cell efficiency is surface area, when a monolayer of dye is adsorbed on TiO_2 as a light absorber. Nevertheless, a fundamental drawback of photoanodes based on sintered or compacted anatase nanoparticles is the drastic decrease in electron mobility. This originates from the high number of grain boundaries and a lack of directional charge transfer to the back contact, in other words, the long electron-diffusion paths (random walk through the particle network)[4] that is introduced by the particle structure. As a result, the electron mobility of sintered nanoparticle layers of anatase and that of an anatase single crystal[4–6] differ by 6–8 orders of magnitude (Figure 1 f). So, simply the best of all worlds would be a single crystal of anatase with a maximum surface area for dye attachment. This is exactly what Snaith and his colleagues[7] achieved—the growth of a large, porous single crystal.

For this, they used a nanotemplate consisting of a close-packed assembly of silica nanospheres (see Figure 2) that was seeded with a number of anatase nuclei. A suitably low density of nuclei then makes it possible to grow comparably large anatase crystallites throughout the template by hydrothermal treatment in TiF_4 solution. This procedure had been originally developed by Yang et al.[9] and Zhang et al.[10] The seeding procedure is crucial, as it eliminates the higher energy nucleation step in a crystal nucleation–growth sequence. This step can be conducted at sufficiently low temperatures such that anatase growth occurs only within the seeded silica template and not in the solution or at other random intitation sites. For seeding, Snaith et al. use a classic approach to decorate the nanostructures with nanosize anatase particles, $TiCl_4$ hydrolysis,[7] but at a concentration in the μM range to establish an active seed-to-seed spacing in the range of micrometers. Seed creation is the only high-temperature step (500 °C) in the entire process; the hydrothermal growth is carried out at 200 °C. After the template is removed (by dissolving the silica spheres in aqueous NaOH), mesoporous single crystals (MSCs) of anatase are obtained (Figure 2).

Anatase is the phase of choice in all TiO_2 applications that require electron transport such as solar cells and other photoelectrochemical devices, as its electron conductivity is approximately 100 times greater than that of rutile. It should be pointed out that the growth of large single-crystal anatase is still considered very difficult since at large scale rutile is the thermodynamically more stable phase. As a result, most research on anatase surfaces and its properties still relied on natural single crystals.

Two elements are key to the successful anatase growth in Snaith's work: 1) the applied $TiCl_4$ seeding technique that indeed produces anatase particles,[8] and 2) the use of fluoride-containing precursors (TiF_4) in the hydrothermal growth step. Fluorides possess the virtually unique ability to reverse the thermodynamic stability of TiO_2 crystal facets.[9–11]

A rather remarkable point is also that the self-assembled template of SiO_2 nanospheres is apparently porous enough to produce a uniform TiO_2 crystal, which after template removal, can be filled with dye sensitizer and a solid-state electrolyte.

The approach used by the Snaith group seems scalable; that is, SiO_2 nanospheres of different diameters (20–200 nm) can be used to generate corresponding cavities in the single crystal. The use of 20 nm cavities leads to a BET surface area of 80–100 $m^2 g^{-1}$, very similar to typical surface areas available for dye adsorption in classic Grätzel-type solar cells. Therefore, Snaith and his co-workers demonstrated the use of their anatase crystallites in dye-sensitized solar cells, where a remarkable efficiency of 3.1 % in low-temperature-fabricated dye-sensitized single crystals was obtained.[7] Additionally, they showed that sensitization with a "perovskite dye" leads to an efficiency at 7.2 % in a solid-state device. However, in the case of the perovskite-type sensitization it may be argued that for these cells electron transport in the supporting structure does not really matter.[12]

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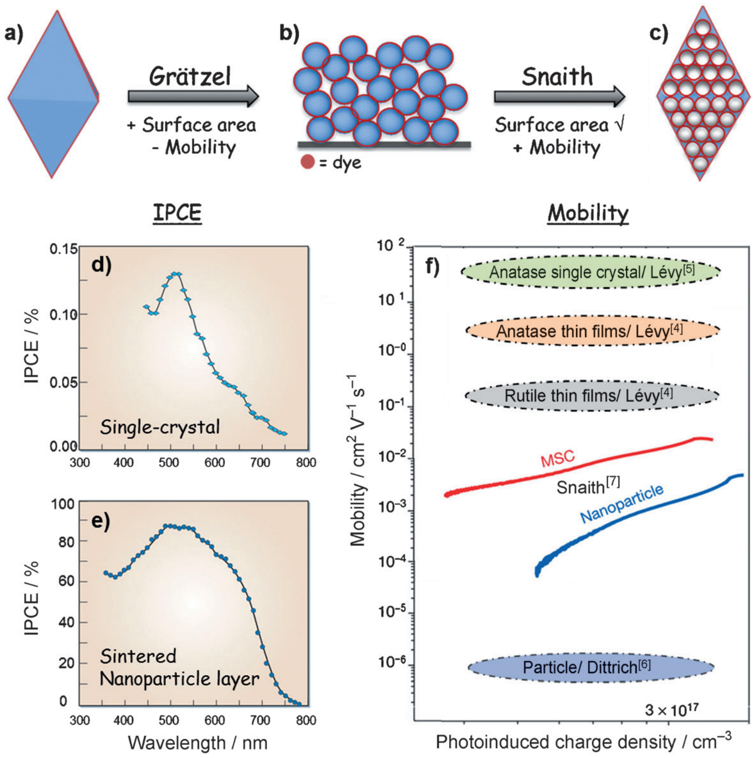

Figure 1. a) Anatase single crystal; b) Grätzel-type layer of TiO_2 nanoparticles; c) Snaith's MSC; d,e) incident-photon-to-current conversion efficiency (IPCE) of an anatase single crystal (d) and of a layer of nanoparticles (e);[3] f) electron mobility for various forms of TiO_2. Reproduction from Ref. [3] with permission from Macmillan Publishers Ltd.

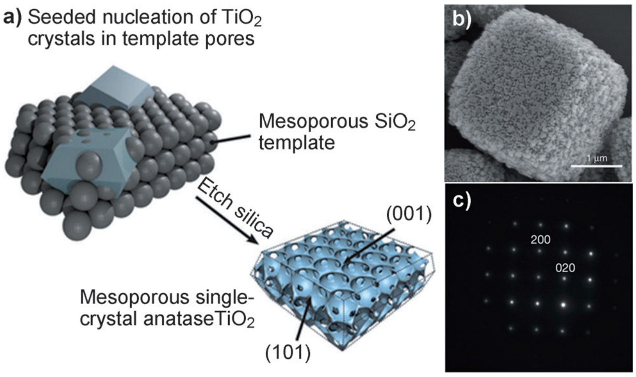

Figure 2. a) Schematic of MSC nucleation and growth within a mesoporous template. b) Fully mesoporous TiO_2 grown by seeded nucleation in the bulk of the silica template. c) Electron diffraction Laue pattern collected from a complete mesoporous crystal assigned to anatase TiO_2 with [001] beam incidence. Reproduction from Ref. [7] with permission from Macmillan Publishers Ltd.

The fact that the electron mobility in these produced single crystals is still considerably lower than that in a natural anatase single crystal (see Figure 1 f) leaves much room for further investigations. Is the low electron mobility due to bulk defects or impurities, or a comparably high number of recombination states at the "rounded" crystal surfaces? Can this gap be overcome by optimized growth conditions or by surface passivation? Or is it better to use single-crystal one-dimensional structures such as nanowires or nanotubes?[13]

In any case it is already clear that a main advantage of the MSCs is the possibility to process solar cells at low temperatures. This is of tremendous interest in view of the compatibility with organic solar-cell materials and the use on flexible (plastic) substrates. Furthermore, the principle shown in Snaith's work—seeded growth in a nanotemplate—may have broad implications as a general strategy for growing porous single-crystalline materials. Thus, not only applications in solar cells but also in sensing, drug delivery, and photocatalysis may benefit from this innovative work.

Received: May 5, 2013
Published online: July 2, 2013

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