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Addition of carbon to anatase TiO_2 by *n*-hexane treatment—surface or bulk doping?

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Abstract

Anatase TiO_2 can be sensitized to visible light by adding carbon as a dopant. Towards this end, TiO_2 photoelectrodes were subjected to a thermal treatment in a hexane-rich environment. By comparing the optical and photoelectrochemical characteristics of both thin film and nanocrystalline nanoporous photoelectrodes, carbon is found to be located mainly at the surface of the TiO_2. The amount of carbon that diffuses into the bulk of the material is too small to significantly enhance the visible light response and only a small shift of the absorption edge towards higher wavelengths is observed. The presence of carbon in TiO_2 shifts the anatase-to-rutile transformation temperature beyond 800 °C, and X-ray diffraction shows that spray deposition of TiO_2 under a CO_2 atmosphere results in a higher bulk carbon concentration than a post-deposition thermal treatment in a hexane-rich environment.

Keywords: Anatase; Titanium oxide; Photoelectrode; Thin films; Carbon dopant; Surface defects; Photoconductivity

1. Introduction

Transition metal oxide photoelectrodes continue to receive widespread attention because they appear to be the only low-cost and stable class of materials that enables photo-assisted splitting of water. Titanium dioxide (TiO_2) is a particularly interesting photocatalyst due to its high catalytic activity and excellent photochemical stability. However, it only absorbs in the UV region of the solar spectrum due to its large band gap (3.2 eV). UV radiation represents only 4% of the incoming solar energy and, therefore, considerable efforts have been directed to extend the absorption of TiO_2 towards the visible part of the spectrum. Numerous attempts have been made during the last three decades to enhance the visible light absorption of TiO_2 by introducing cation dopants, for example Fe [1,2], Cr [3,4], and V [5]. These dopants introduce additional energy levels in the bandgap from which electrons can be excited into the conduction band with

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less energy than is needed for band-to-band excitation. Unfortunately, the localized nature of these electronic states presents two problems: (i) it prevents efficient transport of photogenerated holes to the surface of the photoelectrodes (holes have to 'hop' from one dopant site to the next), and (ii) the energy levels of these states are often located deep within the bandgap, which makes them efficient recombination centers [6]. Clearly, efficient sensitization of TiO_2 to visible light requires a different approach.

Recently, various anion dopants, such as carbon [7–11], nitrogen [12–20], and sulfur [21–23] have been shown to significantly enhance the visible light absorption of TiO_2. Theoretical calculations by Asahi et al. [12] suggest that the p-orbitals of these anions, which were assumed to reside on the oxygen sites, show a significant overlap with the O-2p orbitals from the valence band of TiO_2. This orbital overlap should facilitate hole transport, while the less localized nature of the anion dopants would limit the amount of recombination.

Most studies on carbon-doped TiO_2 have been carried out on suspensions of nano- or micro-sized particles [8–11,24–26]. In contrast, the number of reports on carbon-doped TiO_2 photoelectrodes is limited [7,27]. Recently, we reported on the deposition of carbon-doped anatase TiO_2 thin dense films prepared by spray pyrolysis (SP) of an ethanolic titanium-tetra-isopropoxide solution under a CO_2 atmosphere [28]. The use of the thin dense films allowed us to measure, for the first time, photocurrent and donor densities of carbon-doped TiO_2.The carbon-doped TiO_2 photoelectrodes showed a significant increase of the photocurrent in the UV region compared to undoped TiO_2. However, no photocurrent was observed in the visible part of the spectrum due to a too low carbon content [8]. Here, we report on our efforts to incorporate carbon into anatase TiO_2 by a post-deposition thermal treatment in an argon/hexane gas mixture. Special attention will be given to the high-temperature stability of these hexane-treated photoelectrodes under oxidizing conditions.

2. Experimental

Spray pyrolysis was used to prepared undoped TiO_2 thin films. The precursor solution consisted of 1.8 ml titanium(IV)tetraisopropoxide (TTiP, >99%, Acros Organics) in 27 ml ethanol (>99.9%, J.T. Baker) with 1.2 ml 2,4-pentanedione (>99%, Aldrich) added to prevent cracking of the films [29]. The substrate temperature was 350 °C, and a 3 s on, 60 s off spraying-cycle was used to allow the solvent to evaporate before depositing the next layer. The film thickness was typically 200 ± 20 nm. The films were deposited on 1 mm thick fused silica (quartz) substrates (Heraeus, Suprasil 1) for optical characterization and on transparent conducting glass ($15\ \Omega\ cm^{-2}$ $F{:}SnO_2$, TEC 15, Libbey-Owens-Ford) for photoelectrochemical studies. Nanocrystalline nanoporous (mesoporous) films with a thickness of 1 μm were prepared by doctor-blading a paste of 9 nm TiO_2 particles (Solaronix, surface area $165\ m^2\ g^{-1}$) onto the spray-deposited thin-film samples described above. The underlying dense TiO_2 film is necessary to avoid direct contact and, therefore, high leakage currents between the aqueous electrolyte and the conducting $F{:}SnO_2$ substrate.

All films are subjected to a post-deposition annealing procedure at 450 °C in air for 6 h in order to further improve the stoichiometry and crystallinity, and to sinter the particles in case of the mesoporous films. To incorporate carbon, the films were annealed in a *n*-hexane/argon atmosphere for 4 h at 500 °C. The gas mixture was prepared by bubbling argon through pure hexane at room temperature at a flow rate of $58\ cm^3\ min^{-1}$.

Optical transmission and reflection spectra of the thin and mesoporous TiO_2 films were recorded using a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere (Labsphere). X-ray diffraction (XRD) measurements were carried out with a Bruker D8 Advance diffractometer in grazing incidence mode, using Cu Kα radiation.

Photoelectrochemical experiments were performed in a three-electrode cell, with a quartz window, a platinum counter electrode, and a saturated calomel reference electrode (XR 300, Radiometer Analytical). A solution of 0.1 M KOH (J.T. Baker) in demineralised and deionized water (Milli-Q, 18.2 MΩ cm) was used as the electrolyte. N_2 was bubbled through the solution to remove any dissolved oxygen. Electrical contacts were made by gluing copper wires to the conducting substrate with silver paint (Bison