

Addition of Carbon to Anatase TiO₂ by *n*-Hexane Treatments – Surface of Bulk Doping?

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The use of anion dopants are a recent and exciting development in efforts to enhance the visible light absorption in metal oxide photoelectrodes for water splitting and other photochemical processes [1-3]. We recently reported on the deposition of carbon-doped anatase TiO₂ thin films by spray pyrolysis of an ethanolic titanium-tetra-isopropoxide solution under a CO₂ atmosphere [4]. The carbon-doped TiO₂ photoelectrodes show a significant increase of the photocurrent in the UV region compared to undoped TiO₂ [4]. However, no photocurrent was observed in the visible part of the spectrum due to a too low carbon content [3,4]. Here, we report on our efforts to increase the carbon concentration in undoped anatase TiO₂ by a post-deposition thermal treatment in an argon/hexane gas mixture.

Both thin dense films (TF) as well as nanoparticulate films (HT) have been investigated. The preparation of the thin dense films is reported elsewhere [4]. The nanoparticle films were prepared by doctor-blading a paste of 9 nm TiO₂ particles (Solaronix) onto these thin film samples. After preparation, all films were annealed at 450°C in air to improve the stoichiometry and crystallinity. The resulting HT and TF films were homogeneous and optically transparent. To incorporate carbon, the films were annealed in a *n*-hexane/argon atmosphere for 4 hours at 500 °C. The gas mixture was prepared by bubbling argon through pure hexane at room temperature. To study the stability of these modified films, a thermal anneal in air for 6 h at 450 °C was carried out (re-oxidation). X-ray diffraction showed that all films (untreated, hexane-treated and re-oxidized films) have the anatase structure.

It is observed that after the hexane/argon treatment, the HT TiO₂ films turn completely black, while the TF TiO₂ films have only a slightly blackish appearance (Figure 1B). The black color disappears completely after subsequent oxidation in air (see Figure 1C). Since no blackening is

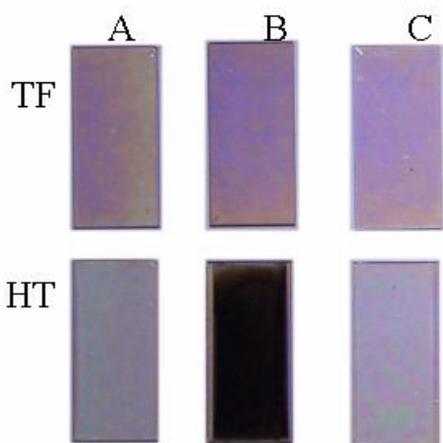


Figure 1. Camera image of TF and HT TiO₂ films. A) TiO₂ pure sample; B) TiO₂ annealed in hexane/argon at 500 °C for 4h; C) TiO₂ re-oxidized in air for 6h at 450 °C.

observed on bare quartz substrates, it appears that the hexane reacts with the oxygen-terminated sites at the TiO₂ surface. The amount of material in the thin films (TF, ~200 nm dense film) is about 6 times less than for the nanoparticle films (HT, ~200 nm dense film + 1 mm nanoparticle film with a porosity of ~50%). The difference in the blackening of the TF vs. HT films in Figure 1B is, however, much larger than a factor of 6. From this, we conclude that the black color of the nanoparticulate film is due to surface adsorption of carbon species, and not to bulk diffusion of carbon into the TiO₂ lattice.

In order to have a more detailed insight into the optical changes, absorption measurements are performed. In Figure 2, the optical absorption spectra of the films are presented. The black color corresponds to an overall increase of the absorption over the entire range of the spectrum (Figure. 2F). A small shift of the absorption edge towards the visible part of the spectrum (Figure. 2, A-B vs. D-E) is observed, even after re-oxidation of the hexane treated films. A similar shift was also found in the case of C-doped TiO₂ films made by spray pyrolysis under a CO₂ atmosphere [4].

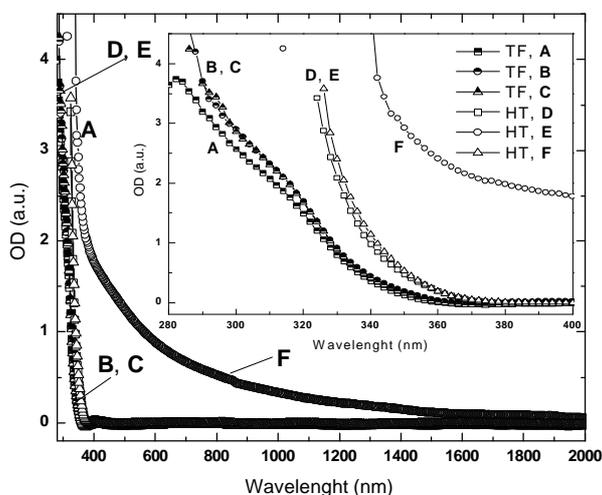


Figure 2. Optical absorption spectra for TF and HT TiO_2 films. A, D) TiO_2 pure sample; B, E) TiO_2 annealed in hexane/argon at 500°C for 4h; C, F) TiO_2 re-oxidized in air for 6h at 450°C .

carbon is supported by our observation that the phase transformation from anatase to rutile in these materials requires much higher temperatures than for undoped anatase (not shown). The increased temperature required for the anatase-to-rutile transformation has also been observed by other workers [5].

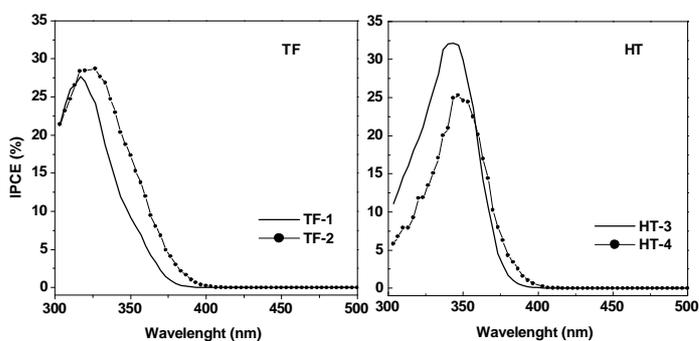


Figure 3. Photocurrent spectra of TF and HT TiO_2 . TF-1 and HT-3 are annealed for 6h in air at 450°C (before hexane treatment). TF-2 and HT-4 are samples treated in hexane at 500°C for 4h and re-oxidized in air for 1h at 450°C . The spectra were obtained in an aqueous 1.0 M KOH solution, at a potential of +0 V vs. SCE.

The photocurrent spectra for the hexane-treated samples are shown in Figure 3. It should be noted that the hexane-treated films require a minimum re-oxidation time of 30 minutes before any photocurrent could be observed. Presumably, the alkane chains attached to the TiO_2 surface prevent electron transfer across the semiconductor/electrolyte interface. Again, a shift of the absorption towards the visible part of the spectrum is observed for both TF and HT TiO_2 films after re-oxidation. Straightforward reduction of TiO_2 in an argon/hydrogen atmosphere followed by re-oxidation does not result in any shift of the absorption edge. Hence, we attribute the shift of the absorption edge to the presence of small amounts of carbon in the bulk of the material. The presence of bulk

In summary, we found that the carbon introduced by thermal treatment in a hexane-containing environment is mainly located at the surface of the anatase TiO_2 . These surface species are responsible for the black coloration of the nanoparticles, and do not lead to enhanced photocatalytic activities in the visible part of the spectrum. A small fraction of the carbon is located in the bulk of the material, where it causes a small shift ($\sim 0.05\text{-}0.1\text{ eV}$) of the absorption edge towards the visible part of the spectrum. More details about this work will be published elsewhere.

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