

# PHOTOELECTROCHEMICAL AND OPTICAL PROPERTIES OF NITROGEN DOPED TITANIUM DIOXIDE FILMS PREPARED BY REACTIVE DC MAGNETRON SPUTTERING

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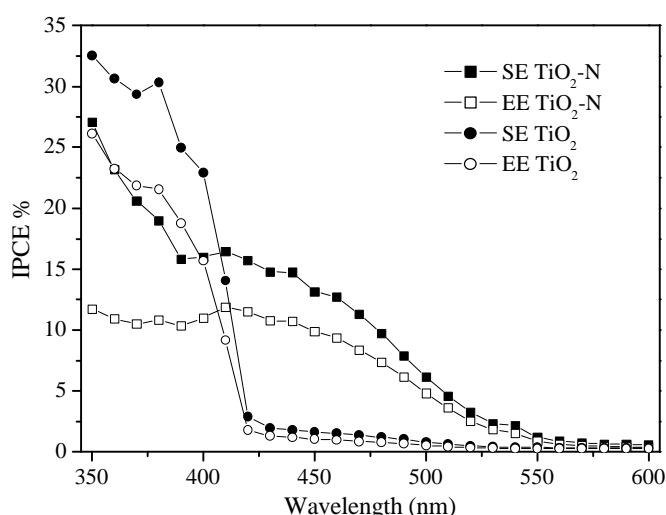
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Titanium dioxide, TiO<sub>2</sub>, has been largely studied for photoelectrochemical and photocatalysis applications due to its high corrosion resistance, reasonable cost and harmless characteristics.<sup>1</sup> Despite these advantages, this material has a large band gap (3.0 eV for rutile and 3.2 eV for anatase) allowing only absorption of the UV light of the solar irradiation. Therefore, many attempts have been made to shift the spectral response into the visible region. One of the strategies is to sensitize TiO<sub>2</sub> with a dye (often ruthenium polypyridine complexes) leading to a conversion of incident photons into electric current nearly quantitative over a large spectral range.<sup>2</sup> Unfortunately these dye-TiO<sub>2</sub> systems are not stable in water due to hydrolysis of the carboxylate functions anchored to the semiconductor. Since one of our goals is to achieve direct water splitting into hydrogen and oxygen by solar light, we have focused in another alternative to increase the solar spectrum absorption: to decrease the band gap of TiO<sub>2</sub> by means of doping. Recently, Taga *et al.*<sup>3</sup> reported that nitrogen-doped TiO<sub>2</sub> (TiO<sub>2-x</sub>N<sub>x</sub>) show a narrower band-gap and a better photocatalytic activity under visible light than the corresponding undoped TiO<sub>2</sub>. With this in mind, we have synthesized and characterized nitrogen doped TiO<sub>2</sub> films by means of reactive magnetron d.c. sputtering.<sup>4</sup> By changing the amount of nitrogen used in the chamber during deposition, the crystal structure could be obtained as rutile or anatase, or a mixture of both. SEM studies revealed rough surfaces with protruding nodules. All nitrogen doped samples showed an optical response in the range 400 to 535 nm.

The photoelectrochemical behavior of these electrodes was investigated in non-aqueous electrolyte as well as in water solutions. Both 2-electrode and 3-electrodes experiments were performed to reveal the photoelectrochemical properties. The effect of light intensity, pH of the electrolyte and light source were studied. The photocurrent onset potential shifts with pH following a Nernstian behavior. The IPCE onset was located around 535 nm (see Figure), which corresponded well with the optical response. The photoelectrochemical properties showed that the new band gap states created by doping indeed improved the photoresponse in the visible region. Apart from decreasing

the bandgap by shifting the valence band edge it was found that nitrogen doping also introduce states close to the conduction band. These states were studied by chronoamperometric measurements.

In conclusion, this study shows that band gap narrowing of  $\text{TiO}_2$  by nitrogen doping improves the photoresponse in the solar spectrum. This could be of special interest for direct water splitting and photocatalytic applications. To some extent the photoresponse is limited by recombinations caused by states introduced by nitrogen.



**Figure.** Action spectra of undoped and nitrogen doped  $\text{TiO}_2$  electrodes in three electrodes set-up. Aqueous 0.1 M NaOH was used as electrolyte. The samples were irradiated through substrate-electrode (SE) and electrode-electrolyte (EE) interfaces.

Very recently it has been also reported efficient photoelectrochemical water splitting by a chemically modified  $\text{n-TiO}_2$ .<sup>5</sup> This time, the carbon was the element incorporated in the  $\text{n-TiO}_2$  films.

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<sup>2</sup> O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737.

<sup>3</sup> (a) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, 293, 269. (b) Morikawa, T.; Asahi, R.; Ohwaki, T.; Aoki, K.; Taga, Y. *Jpn. J. Appl. Phys.* **2001**, 40, L561.

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<sup>5</sup> Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B. Jr. *Science* **2002**, 297, 2243.