



# Enlightening the synergic effect of anatase/rutile mixtures in solar cells



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## ABSTRACT

The synergic effect, observed in dye sensitized solar cells assembled with mesoporous electrodes made of mixtures of anatase and rutile nanoparticles, was revealed to depend on a delicate balance of competing contributions from chemical capacitance and resistance to electron diffusion instead of a longer electron lifetime in TiO<sub>2</sub> conduction band, as consequence of a slower electron recombination rate at the electrode/electrolyte interface. The parameters influencing the charge diffusion in actually running dye-sensitized solar cells (DSCs) were carefully evaluated by impedance spectra simulation and correlated with the percentage of rutile and anatase in the respective mesoporous electrode. Cells were assembled with mesoporous titanium dioxide (TiO<sub>2</sub>) electrodes fabricated with sixteen different anatase/rutile mixtures, ranging from pure anatase to pure rutile. All measurements were carried out in triplicate in order to give statistically validated results. The enhanced charge diffusion at 15% of rutile in the mixed film cells was found to be associated with the presence of isolated rutile islands embedded in a more conducting anatase phase, as confirmed by confocal Raman microscopy.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) continues to be an extensively studied material particularly due to its photochemical and optical properties allied to low toxicity and availability in large scale. TiO<sub>2</sub> is a polymorph that can be found in three main crystalline forms (rutile, anatase and brookite), but studies with the last one has been inhibited by the low stability and difficulties for preparation of pure materials in that crystalline phase [1]. In contrast, rutile is been widely used as white pigment in inks, as UV absorber and optical coating because of its low cost, high stability and refractive index. On the other hand, anatase is more commonly used in energy conversion devices and photocatalysis because of its wider band-gap, higher photoactivity, higher electron mobility and adsorption capability combined with lower electron-hole recombination rates [2,3].

Despite the large number of reports evidencing the occurrence of synergic effects in photocatalytic reactions and in dye-sensitized solar cells (DSCs), this subject continues to draw considerable attention. In fact, larger efficiencies have been reported when materials containing mixtures of anatase and rutile nanoparticles (NPs) in suitable proportions are used instead of the respective pure materials. Such a synergic effect has been exploited to increase the photocatalytic decomposition of organic

contaminants [4], and in the fabrication of self-cleaning windows [5], as well as to enhance DSCs efficiency [6–11]. However, the actual reasons responsible for that phenomenon were not completely clarified yet. The first hypothesis was forwarded by Bickey et al. [12] who assigned the enhanced photocatalytic activity of mixed phase TiO<sub>2</sub> to a more effective electron-hole pair separation at the anatase/rutile interface. Then, Hurum et al. demonstrated by EPR spectroscopy that electrons are transferred from rutile conduction band to lower energy trapping sites present in anatase [13] thus increasing the efficiency of the photoinduced charge-separation process.

In fact, the efficiency of DSCs tend to be maximized when the mixed phase mesoporous electrode contains 15–20% of rutile NPs and 85–80% of anatase NPs [6–11]. This phenomenon is generally assigned to a significant decrease of the electron recombination rate at mesoporous TiO<sub>2</sub> electrode/electrolyte interface, and consequent increase of electron lifetime in the semiconductor conduction band. Nevertheless, this model considers only the short-range diffusion of electrons and not the diffusion throughout the mesoporous film, the fundamental process associated with the density of photocurrent and the overall cell efficiency [14,15]. Moreover, to the best of our knowledge, no systematic and statistically validated study was carried out considering all possible effects influencing the charge transport in dye-sensitized solar cells.

Accordingly, the parameters influencing the charge diffusion in actually running DSCs were carefully evaluated by modeling the electrochemical impedance spectra of a series of devices, which

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were assembled with mesoporous electrodes prepared with sixteen different proportions of anatase and rutile NPs ranging from pure anatase to pure rutile. Finally, those parameters were correlated with the respective percentages of rutile (%rutile) in the mesoporous TiO<sub>2</sub> electrodes in order to find tendencies or profiles. As a consequence, the overall decay in cell performance as a function of %rutile was confirmed to be associated with the lower surface concentration of N719 ruthenium dye on rutile NPs, whereas charge diffusion was shown to be the main parameter responsible for the synergic effect in running dye sensitized solar cells. This parameter was shown to depend on the competing contributions of chemical capacitance and resistance to electron diffusion in TiO<sub>2</sub> mesoporous films containing isolated rutile islands embedded in anatase NPs matrix, as revealed by confocal Raman microscopy.

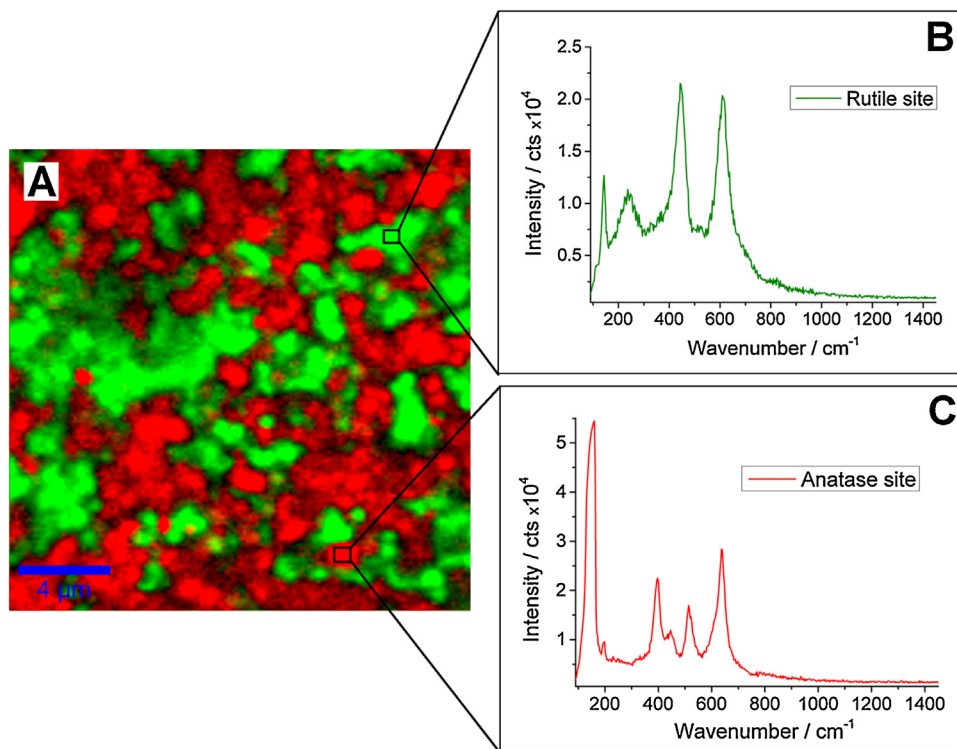
## 2. Experimental

Nanocrystalline anatase (<25 nm particles, 99.7%) and rutile (40 nm long and 10 nm diameter, 99.5%) samples were purchased from Aldrich and used in the preparation of organic TiO<sub>2</sub> pastes based on terpeneol and ethylcellulose, as described in the literature [16]. Typically, 3 g of anatase NPs (or rutile NPs) were gently dispersed in a mixture of 0.5 mL of acetic acid, 2.5 mL of Milli-Q DI-water and 15 mL of ethanol for about 40 min, in a mortar with a pestle. The slurry was transferred to a beaker with 100 mL of ethanol, then 10 g of terpeneol and 16.5 g of ethylcellulose in ethanol solution (10% m/m) were added into, and the mixture kept under stirring for 1 h. Viscous anatase NPs and rutile NPs pastes were obtained after partial removal of the solvent (water and ethanol) in a flash evaporator. Suitable amounts of pure anatase and pure rutile pastes were carefully mixed together in order to get pastes containing mixtures of anatase and rutile NPs in the following proportions: (a) 100/0, (b) 95/5, (c) 90/10, (d) 87.5/12.5,

(e) 85/15, (f) 82.5/17.5, (g) 80/20, (h) 77.5/22.5, (i) 75/25, (j) 72.5/27.5, (k) 70/30, (l) 65/35, (m) 60/40, (n) 50/50, (o) 30/70 and (p) 0%/100%. The electrode area ( $A = 25 \text{ mm}^2$ ) was delimited on conducting FTO glass substrates ( $R \approx 15 \Omega \text{ sq}^{-1}$ ) with a Scotch tape and a TiO<sub>2</sub> paste spread homogeneously by spin-coating instead by the conventional doctor blade technique [17]. After some time, the tape mask was removed, kept at 100 °C for 1 h, and then sintered at 450 °C for 30 min in a furnace to produce FTO electrodes with a 20 μm thick mesoporous TiO<sub>2</sub> film on the conducting face. As soon as the temperature decreased to about 40 °C they were immersed in  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  N719 (Aldrich) solution in tert-butanol/ acetonitrile 1:1 v/v for dye adsorption. A dye-sensitized electrode was hot-pressed (110 °C) together with a platinum doped FTO counter electrode and a 40 μm thick Surlyn spacer intercalated in between. A small hole was drilled in the counter electrode and a I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte solution ( $0.5 \text{ mol dm}^{-3}$  tert-butylpyridine,  $0.6 \text{ mol dm}^{-3}$  tetrabutylammonium iodide,  $0.1 \text{ mol dm}^{-3}$  LiI,  $0.1 \text{ mol dm}^{-3}$  I<sub>2</sub> in methoxypropionitrile) injected through it after making vacuum inside, and sealed in order to get functional DSCs.

The I–V curves and EIS measurements were carried out using an Autolab PGSTAT30 potentiostat/galvanostat while irradiating the cells with an ABB class Oriol solar simulator (AM 1.5, IEC, JIS, ASTM), whose illumination potential was adjusted to  $100 \text{ mW} \cdot \text{cm}^{-2}$  (1 sun) with a Si cell (VLSI standards, Oriol P/N 91150V). Electrochemical impedance spectra were registered from 0.01 to 100,000 Hz at cell open circuit potential,  $V_{OC}$ , modulating the frequency of the superimposed sinusoidal potential wave (amplitude = 20 mV).

The Raman images of mixed-phase TiO<sub>2</sub> electrodes were registered using an Alpha WITec confocal Raman microscope equipped with a 532 nm laser (WITec, maximum power =  $100 \text{ mW cm}^{-2}$ ) and a piezo-driven xyz table. The 517 and 448 cm<sup>-1</sup> bands were selected for Raman imaging of anatase and rutile phase domains, respectively.



**Fig. 1.** Confocal Raman image showing micrometric sized rutile rich (green) and anatase rich (red) areas in a 50%:50% anatase/rutile mesoporous film, as well as their typical spectrum (B and C) registered in the indicated areas. The image was registered setting the laser power (532 nm) to  $39.5 \text{ mW} \cdot \text{cm}^{-2}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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