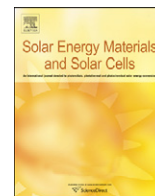




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Direct photocurrent generation from nitrogen doped TiO₂ electrodes in solid-state dye-sensitized solar cells: Towards optically-active metal oxides for photovoltaic applications

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ABSTRACT

Nitrogen-doped titanium dioxide (TiO₂) is considered as a promising photocatalytic material due to its optical absorption extended in the visible region compared to pure TiO₂. In the field of photovoltaic applications, dye-sensitized solar cells based on N-doped nanocrystalline titania electrodes have demonstrated improved performance due to the beneficial effects of nitrogen on the electronic and optical properties of TiO₂. In this context, we report on the influence of nitrogen doping on the performance of solid-state dye-sensitized solar cells, starting from TiO₂ and N-TiO₂ nanocrystals synthesized by laser pyrolysis. Using an integrated approach based on experimental and theoretical investigations, the relationship between the local electronic features of the starting metal oxide materials and device operation is described. We demonstrate that the short-circuit current density of the solar cells based on an N-doped TiO₂ electrode increases by more than 10% compared to that of pure anatase. This improvement is clearly associated with the extended absorption of the doped electrode, suggesting that alternative charge generation mechanisms occur in the cells in addition to the conventional dye absorption. Computer simulations on isolated nanoclusters, as well as electron paramagnetic resonance (EPR) experiments, confirm that nitrogen atoms in the presence of oxygen vacancies can explain the introduction of additional energy states near the valence band of TiO₂. Surface states associated with nitroxide radicals are also suggested to act as charge traps under illumination. These aspects confirm the strong potentialities of optically-active metal oxides for photovoltaic applications.

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1. Introduction

Dye-sensitized solar cells (DSSC) recently demonstrated power conversion efficiencies over 12% [1,2], placing them as a relevant low cost alternative to second generation solar cells such as inorganic thin film technologies. Whereas champion cells are mainly based on liquid electrolytes, solid-state DSSC that use solid electrolytes also appear as promising photovoltaic systems due to easy cell assembly and improved stability [2,3]. Efficiencies as high as 7%, and even up to 10%, have been recently demonstrated using respectively organic hole transporters such as spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene) [4] and inorganic compounds such as CsSnI₃ [5]. Many aspects have been, and

are still, considered to improve device performance, the main strategies focusing on: extending the light-harvesting region into the near infrared using new strongly-absorbing dyes; lowering the redox potential of the electrolyte to increase the open-circuit voltage (V_{OC}); replacing solid-state molecular glass electrolytes by light-absorbing π -conjugated polymers; modifying the TiO₂/dye/electrolyte interface; using light-trapping or co-sensitization strategies [2]. Moreover, important research efforts have also been paid to identify alternative metal oxides or alternative electrode architectures [6]. However, anatase TiO₂ processed from colloidal pastes remains the material of choice to achieve the best performance up to now. In the context of the nanocrystalline electrode, the demonstration of novel device concepts that may exploit additional charge generation mechanisms will be required in order to allow higher device efficiencies.

In this context, several studies demonstrated that doping metal oxides using metals [7–12] or non-metal elements [13–18] can be a

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fruitful strategy to improve photocurrent generation. In particular, Lindgren et al. demonstrated the appearance of additional states near the valence band of TiO₂ by the incorporation of nitrogen, leading to visible light absorption [19]. Although the energy states introduced by nitrogen in the gap can also act as recombination centers for the generated photo-carriers, the photo-electrochemical properties of the doped electrodes clearly indicated additional photocurrent generation in the blue part of the spectrum compared to un-doped electrodes. In 2005, Ma et al. demonstrated a liquid DSSC based on N-doped titania powders presenting an improved power conversion efficiency of 8% and an improved stability [13]. Again, an improved incident photon to current efficiency (IPCE) in the 400–532 nm region was observed, which was attributed to the influence of nitrogen on the optical band gap of the photo-electrode. Such benefits of doping by nitrogen were also evidenced in the field of photo-catalysis [20,21], starting to significantly raise the interest of researchers for metal oxide materials active in the visible. Since then, various strategies have been reported to reduce the optical band gap of TiO₂ for both photovoltaic applications [10,15,22–25] and photo-catalysis [26–30]. Among all these strategies, doping by nitrogen is probably one of the most reported [13,24,25,31]. Although improved solar cell performance is usually reported using N-doped TiO₂ electrodes, systematic studies have not yet been undertaken in order to clarify the exact charge transfer mechanisms occurring in the active layer. Especially, current generation resulting from the absorption of photons by the doped metal oxide electrode remains to be described, as well as the influence of nitrogen doping on solid-state DSSC operation.

In this work, we investigate the use of nitrogen-doped TiO₂ electrodes based on nanocrystals synthesized by laser pyrolysis for solid-state dye-sensitized solar cells. These nanocrystals, which have been recently demonstrated to be a relevant alternative to commercial pastes [32], take benefit from a versatile synthesis method that allows easy doping procedures [33]. Device performance is discussed with regard to the influence of nitrogen on the nanocrystal local structure using both electron paramagnetic resonance analysis and numerical simulations. It is worth noting that these simulations are for the first time performed using density functional theory (DFT) based on quantum chemistry codes on isolated TiO₂ clusters with and without nitrogen. The improved photo-current generation observed in the presence of nitrogen confirms that optically-active metal oxides are of particular interest in the field of hybrid photovoltaics.

2. Experimental procedure

2.1. Synthesis of TiO₂ and N-TiO₂ nanocrystals

Laser pyrolysis of liquid titanium tetraisopropoxide (TTIP) was used to produce both pure and nitrogen-doped titanium oxide nanocrystals [33]. A TTIP aerosol was produced using an ultrasonic spraying process (Pyrosol) and carried in the reaction zone by a carrier gas where it crossed the CO₂ laser beam (1 kW). Some amount of C₂H₄ was introduced in the reactant mixture due to the poor absorption of the infrared laser radiation by TTIP. The decomposition of precursors in the laser beam is followed by particle growth which is rapidly stopped when the mixture exits the reaction zone, leading to the formation of nanoparticles which are collected downstream on collection filters. N-doped particles were formed in a similar manner, except that gaseous ammonia (NH₃) was used as source of N atoms within the reactant mixture, and no C₂H₄ was required in this case. After the synthesis, the nanopowders are annealed in air at 400 °C for 3 h in order to remove free carbon atoms that result from the decomposition of TTIP and/or C₂H₄.

The morphology of the particles was studied by transmission electron microscopy (TEM) with a Philips CM12 (120 kV) instrument. Diffuse reflectance spectra of the powders were measured on a UV–vis–NIR spectrophotometer (Jasco V-570), which was equipped with an integrating sphere assembly. A given amount of nanopowder was uniformly pressed in a powder holder (Jasco) and placed in the sample holder on an integrated sphere for the reflectance measurements. The absorption coefficient, as well as the optical energy gap of the samples was deduced from the absorption data using the Kubelka-Munk equation [34].

2.2. Solar cells assembly and testing

Porous TiO₂ and N-TiO₂ electrodes were deposited by spin-coating on fluorinated tin oxide (FTO) substrates in ambient conditions from ethanol dispersions (nanopowders content 10 wt%) containing ethyl-cellulose (EC), as already reported [32]. After film deposition, a gradual sintering step up to 450 °C in air was performed, as well as a conventional TiCl₄ treatment, leading to 2 μm thick porous layers. A dense TiO₂ layer of approximately 150–300 nm was initially deposited by spray pyrolysis on the FTO substrate. The porous electrodes were then immersed at 80 °C overnight in a diluted solution of the commercial indoline dye D102 (Mitsubishi Paper Mills, Japan) dissolved in an acetonitrile:tert-butanol (1:1 volume ratio) mixture. The obtained dye-sensitized electrodes were rinsed and infiltrated by the molecular hole conductor spiro-OMeTAD (Merck KGaA, Germany) by spin-coating, using conventional recipes with lithium salt and tert-butylpyridine as additives. Gold top contacts were finally evaporated under vacuum at 10⁻⁶ mbar using shadow masks that defined two active areas per substrate (0.18 cm² each).

Scanning electron microscopy (SEM) was performed on bare and infiltrated dye-sensitized porous TiO₂ and N-TiO₂ layers using a JEOL MEB-FEG 7400F. UV-visible optical absorption spectra were recorded by a SAFAS DES 200 spectrometer used in transmission mode. Current density–voltage (J–V) characteristics were recorded in air using a calibrated Keithley 2400 source-measure unit, in the dark and under simulated solar emission (Atlas Solarconstant 575PV). The spectral mismatch between the emission of the solar simulator and the global AM1.5G (ASTM G173-03) solar spectrum was taken into account using standard procedures [35] and the solar simulator irradiance was corrected accordingly to match 100 mW cm⁻² on the tested cell. The incident photon-to-current efficiency (IPCE) was measured using a monochromated 75 W Xenon lamp (Newport) and a calibrated picoammeter (Keithley 485) used in static regime in order to ensure full collection of all photo-generated charge carriers. The calibration was performed using a calibrated silicon photo-detector of known spectral response (Newport).

2.3. Computer simulations of TiO₂ and N-TiO₂

The electronic properties of nanostructured (TiO₂)_n and (TiO_{2-x}N_x)_n were calculated using the density functional theory (DFT) formalism following a cluster approach. The clusters were constructed by removing Ti and O atoms, from a large cluster obtained by expansion of the anatase crystal structure unit cell in all three dimensions. The anatase nanostructures were modeled with hydrogen saturation atoms, without full geometry optimization. The single point calculations were performed using GAMESS program package [36] applying effective core potential basis set named Stevens-Basch-Krauss-Jasien-Cundari (SBKJ) [37–39]. Our previous computational works proved that to reproduce the HOMO–LUMO energy gap splitting of the anatase structure, it is appropriate to use long range correlated LC-BLYP hybrid functional with generalized gradient approximation (GGA)

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