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Full Length Article

Microwave-assisted synthesis of C-doped TiO_2 and ZnO hybrid nanostructured materials as quantum-dots sensitized solar cells

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ABSTRACT

The microwave-assisted solvothermal synthesis of C-doped TiO_2 and ZnO hybrid materials was performed. Saccharose, titanium isopropoxide and zinc acetate were used as organic and inorganic sources for the synthesis. The influence of temperature and reaction time on the textural and optoelectronic properties of the hybrid materials was verified. Carbon quantum-dots of TiO_2 and ZnO nanostructured spheres were obtained in a second pot by controlled calcination steps of the precursor hybrid materials. A carefully characterization by adsorption-desorption N_2 isotherms, XRD, XPS, SEM, UV–vis/DR and electro- and photo-electrochemistry properties of the carbon quantum-dots TiO_2 and ZnO spheres was performed. The photoelectrochemical activity of TiO_2-C and ZnO-C films proved to be dependent on the conditions of synthesis. It was found a red-shift in the energy band gap of the semiconductors with values of 3.02 eV and 3.13 eV for the TiO_2-C and ZnO-C, respectively, clearly lower than those on bare semiconductors, which is associated with the C-doping effect. From the photo-electrochemistry characterization of C-doped TiO_2 and ZnO films can be concluded that the present materials have potential applications as photoelectrodes for quantum-dots sensitized solar cells.

1. Introduction

Climate change, associated with global warming is the result of excessive use of fossil fuels. This has led us to evaluate renewable energy sources such as solar or photovoltaic cells. Sunlight is an attractive energy source, clean, and renewable. It has been estimated that by only covering 1% of the earth's surface, photovoltaic energy will supply the global demand on energy [1], nowadays around 20 TW. An exponential growth in the installed capacity of thermo-solar and photovoltaic energy from 1400 MW in 2007 to more than 136,000 MW at 2014 [2] has been registered. This growth is linked to the price of electric energy produced from solar energy that has fallen and will continue to fall in the following years due to an increased production of photovoltaic systems with high efficiency with more solar thin-film domiciliary facilities.

Photovoltaic (PV) cell technology can be classified in first, second and third generation. The former occupies 85% of the market and is based on single or multiple crystals of silicon with a conversion efficiency from solar to electric energy between 15 and 30%. However, silicon solar cells have some disadvantages such as high manufacturing cost and the emission of environmentally harmful chemicals during manufacture [3]. The second and third generation are based on thin layers of multiple inorganic oxides or in rare-earth's such as lanthanides-based materials which commercially have an efficiency less than 15% and beside of the high cost, some components of these solar cells such as CdTe or GaAs have a high degree of toxicity [4]. In short, 2nd and 3rd generation commercial solar cells have some general disadvantages such as a high fabrication cost and emission of environmentally unfriendly chemicals during fabrication. In addition, these commercial solar cells have also an important limitation in one of the most important parameters as is the light harvesting efficiency (LHE) because the low scattering of light [5,6].

It can be said that the report on a dye-sensitized solar cell (DSSC) in 1991 by O'Regan and Grätzel [7] is the starting point of the last generation' solar cells. The photosensitization effect of a dye adsorbed on nanocrystalline Titania or the co-sensitization by inorganic compounds have been studied extensively because of their high-power conversion efficiency (>10%) and low produc-

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tion costs reported in several works [8–21]. The photosensitization of semiconductors such as TiO_2 and ZnO requires a visible light-induced electron or hole injection into conduction band or valence band, respectively [16] which is strongly affected by the energy band gap (E_{bg}) of the semiconductor and by the chemical environment due to the presence of doping agents in the framework of TiO_2 or ZnO [21–36]. For example, it has been reported that carbon- or nitrogen-doped semiconductors induced a red-shift in the E_{bg} and accordingly an increase in the photoefficiency of TiO_2-based photoelectrodes for solar cells [17,22,25–30]. It has been also reported [29] an enhancement in the photocurrent density of TiO_2-based photoelectrodes in presence of CdS and PbS nanoparticles. More recently, an increase in the photoelectrochemical response of TiO_2 nanowires decorated with Ag nanoparticles due to the surface plasmon-driven of the noble metal has been also reported [30]. In addition, remarkably effects of CdS, graphene, and Cu_2O upon the optical properties of ZnO-bases thin films have been reported for CdS/ZnO/graphene composites [31], and ZnO/Cu_2O thin films [32]. The influences of the water content and solvent as well as the addition of ammonia during the solvothermal synthesis upon the optical properties and photocurrent response of ZnO-based thin films have been also reported [33,34].

The light harvesting efficiency (LHE) is the driven force for an enhanced performance of a solar cell. However, mainly due to the enormous difficulty of synthesizing simultaneously microspheres composed by SiO_2 or Lanthanides-based solar cells with mesoporous texture, another promising candidate of solar energy-responsive materials concerns to C-doped TiO_2 hollow spheres because these materials have proved to enhance the LHE [17–21]. Our group have reported [17,24] the synthesis of C-doped TiO_2 hollow spheres with mesoporous texture and with a TiO_2 crystalline framework mainly consisted of anatase phase. The C composition was tailored between 1.2 up to 1.5 wt% by a controlled calcination of the biomass-derived carbon source. These hybrid C-doped TiO_2 spheres showed a high photoactivity in the visible range for the degradation of methylene blue [17], attributed to a red-shift in the energy band gap of TiO_2 (lower than commercial TiO_2-P25, ca. 3.22 eV), consequence of the carbon doping. This material can be considered as a carbon quantum-dot sensitized solar cell (QDSSC) [24]. In addition, a greater absorption of photons in visible light (approximately 420 nm) has been reported [23] up to 23% in comparison with TiO2-P25, indicating that the control of the internal space (texture of the mesopores) of the C-doped TiO_2 spheres plays an important role upon the scattering of light and therefore on the LHE of the photoelectrode. This phenomenon has been also reported by other groups [18,20].

In this sense, the design of novel nanomaterials and composites plays a major role in the future of the photovoltaic (PV) cell technology. Despite many works have reported important enhancements in the optoelectronic response of photoactive semiconductors, many of these materials have been prepared by using expensive or non-commercial methodologies such as electron beam evaporation [28], pulsed laser deposition [14], vapor deposition [15], high temperature annealing [37], among others. In contrast, few studies have aimed at verifying the influence of quantum carbon points on solar cells based on TiO_2 using economical and environmentally friendly synthesis methods such as sol-gel, hydro/solvothermal [22,24,36] and even very few papers have reported on microwave-assisted hydrothermal synthesis to obtain C-doped TiO_2-based mesoporous materials [23]. Microwave-assisted processes permit to reduce the time of reaction and more importantly a better control of the morphology and texture of the spheres because the uniformity of energy supplied compared to a conventional convection heat in an oven.

In this sense, a systematic study of the influence of the temperature and time of reaction in the microwave-assisted solvothermal synthesis of C-doped TiO_2 and ZnO hybrid spheres was performed. Saccharose was used as the carbon source because is a mainly component of many biomass residues. Quantum-dots sensitized TiO_2 and ZnO spheres were obtained by controlled the calcination steps of the precursor hybrid materials. The texture, the crystalline framework, and the surface chemistry of the C-doped TiO_2 and ZnO spheres were correlated with their optical (UV–vis spectra) and electrochemistry properties.

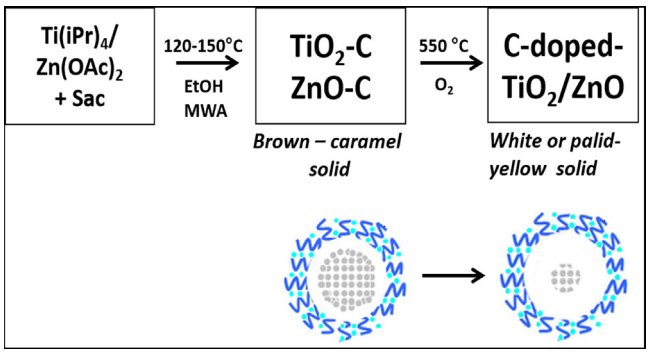

Fig. 1. Scheme for the microwave-assisted (MWA) synthesis of C-doped TiO_2 and ZnO.

2. Materials and methods

2.1. Materials

Titanium (IV) isopropoxide (97%), saccharose (BioXtra 99.5%) and zinc acetate (99.99%) were purchased from Sigma-Aldrich and absolute ethanol (99.99%) from Fermont. All reagents were analytical grade and used without further purification. Commercial TiO_2 P25 from Evonik (ex-Degussa) and ZnO from Degussa, were used for comparative purposes.

2.2. Synthesis of C-doped TiO_2 and ZnO

The C-doped materials were synthetized using a microwave oven (Monowave 400-Anton Paar). Fig. 1 shows the schematic steps of the microwave-assisted synthesis (MWA). In a typical synthesis, 0.5 g of titanium(IV) isopropoxide and 0.5 g of saccharose were dissolved in 9 mL of absolute ethanol. The resulting solution was poured into a borosilicate glass vial and exposed to microwave irradiation at a selected reaction temperature (120, 135 and 150 °C) during a specified time (30 and 150 min for each temperature) with a magnetic stirring rate of 600 rpm. Then, the solution was fast cooled to 55 °C using an air compressor. The resulting solid was filtered and washed several times with ethanol and the final powder was dried at 80 °C for 4 h in an oven, followed by a calcination process at 550 °C for 5 h.

All samples were denoted as TiO_2-C followed with the assigned temperature and time, ca. TiO_2-C-120-30 means C-doped TiO_2 material prepared at 120 °C by 30 min and submitted to calcination at 550 °C for 5 h.

For the synthesis of C-doped ZnO-based materials, 0.5 g of saccharose and 0.5 g of zinc acetate were dissolved in 9 mL of ethanol. The synthesis procedure was the same as for TiO_2-C. In short, the samples were exposed to microwave irradiation, then filtered, dried and finally calcined at 550 °C for 5 h. The temperature and time of synthesis were the same as those chosen for TiO_2-C samples. Each sample was denoted in the same way as TiO_2-C with the initial name ZnO-C. The reaction progress for both synthesis was visually followed by color changes with a standard integrated camera attached to the Monowave 400 microwave oven.