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Multi-functional energy conversion and storage electrodes using flower-like Zinc oxide nanostructures

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ABSTRACT

In the present paper we demonstrate the efficient use of shape controlled flower-like ZnO (Zinc oxide) nanostructured particles as multifunctional electrode for both energy conversion and storage applications, i.e. Dye-sensitized Solar Cells (DSCs) and lithium-ion batteries.

As regards DSC (Dye-sensitized Solar Cell) device, ZnO flower-like particles, prepared by a simple, low-cost and reliable hydrothermal method under mild reaction temperature, are efficiently used as photoanode in a microfluidic architectured cell in combination with NMBI (N-methylbenzimidazole), employed as additive of the electrolytic solution for the first time in a ZnO-based DSC. We obtain a remarkable sunlight conversion efficiency of 3.6%.

As regards storage applications, a stable long-term ambient temperature cycling behavior in lithium cell is demonstrated, even at increasingly higher currents. Remarkable charge-discharge efficiency and specific capacity are obtained up to 200 cycles, which is the highest number of cycles reported so far for similar systems. Noteworthy, such results are achieved without the addition of foreign additives, nor during the synthesis process neither during the electrode preparation, and also no carbon coating on ZnO surface is used.

The originality of the present paper consists not only in showing for the first time the efficient operation of such ZnO particles as anode in Li-ion batteries for prolonged cycling, but also in demonstrating the versatile and multifunctional use of the same material for two different energy related applications. The reported results enlighten indeed the promising prospects of the flower-like ZnO nanostructured material for the successful implementation as stable and long-term performing anodic material in the next generation of both energy conversion and storage devices.

1. Introduction

ZnO (Zinc oxide) is a well-known inorganic material and, due to its peculiar properties, was proposed for plenty of different applications. It is a wide band-gap semiconductor (3.37 eV), characterized by a high electronic mobility [1] and a low electron–hole recombination probability [2]. In addition, it is characterized by high transparency across the visible spectrum with an ultra-violet luminescence [3], tunable super-hydrophobicity or hydrophilicity [4,5], and piezoelectric behavior [6,7]. All these properties make ZnO suitable for being effectively used in the fabrication of different kinds of devices, such as Dye-sensitized Solar Cells (DSCs) [8], gas sensors [9], optical devices (e.g., light-emitting diodes) [10], piezoelectric nanogenerators [11], thermo-voltage generators [12], Li-based batteries [13], and thermoelectric power generators [14].

In particular, regarding the field of energy conversion and storage [15,16], ZnO has recently raised noticeable attention as an alternative material with respect to TiO_2 for DSC (Dye-sensitized Solar Cell) photoanodes [17]. Indeed, despite showing a similar band gap, ZnO theoretically presents higher electron mobility, significantly longer carrier lifetime and similar electron injection process from the light-excited dye molecules [18]. However, the photocurrent and the efficiency of the ZnO-based cells are still lower than those of TiO_2–based DSCs [19]. Long incubation times in the sensitizing solution have proven to induce the formation of aggregates between the dye molecules and the dissolved Zn^{2+} ions originating from the ZnO surface [20,21]. This phenomenon leads to a strong reduction of the electron injection in the semiconductor conduction band, thus resulting in a lower overall device efficiency. Sensitization procedure needs to be optimized in order to avoid

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ZnO surface damaging and molecular aggregate formation. In the framework of optimizing the photoanode architecture (i.e. porosity, specific surface area) to improve the DSCs performances [22], ZnO can be exploited to investigate the effect of the morphology on the charge collection efficiency [23], thanks to its capability of growing with a great variety of different shapes. For instance, ZnO nanowires are characterized by a very high electron transfer [24], but more complex 3-D architectures like branched nanowires [25] or coral-shaped nanostructures [26] can combine the effect of improved charge transfer properties with a high surface area available for the dye chemisorption.

In addition, like other transition metal (e.g., Cu, Fe, or Co) oxides [27], ZnO is now attracting considerable interest as anode material for the next generation of Li-ion batteries [28,29], conceived for both portable and/or automotive/aerospace applications [30–32]. It can offer indeed higher capacity and improved safety with respect to conventional graphite [13]. However, it is challenging at present to ensure the electrode integrity upon prolonged cycling [33,34], due to the typical conversion reaction leading to the metal-oxide structure dissolution and Li–Zn alloys formation [35,36]. Moreover, a passivation layer can be formed during cycling, preventing the fully reversible insertion of Li-ions into the structure [37]. It is therefore of paramount importance to optimize the material properties to improve the surface electrochemical reactivity, thus achieving higher performances.

Many papers report on the synthesis of ZnO micro and nanostructures by different techniques, exploiting both physical and chemical growth methods, such as sputtering [38,39], pulsed laser [40], atomic layer [41], electrochemical [42], chemical vapor [43,44] and metal-organic chemical vapor [45] depositions, or template-assisted sol–gel [46] and hydrothermal [7,44] growths. In the present paper, we report on a simple synthesis route to form shape-controlled ZnO particles, leading to nanostructured flower-like morphologies with nanosized petals. The advantages of using the hydrothermal method for the synthesis are numerous: low temperatures (usually below 90 °C) for obtaining a final single phase crystalline wurtzite structure, absence of catalysts, use of simple equipment, strict morphology control, low cost of the reagents which can be selected as environmentally friendly and less hazardous, high reproducibility and scale-up prospects [47].

The aim of this work is to provide a simple and fast way of synthesizing nanostructured high surface area ZnO, demonstrating here for the first time its efficient electrochemical characteristics to be effectively used as multifunctional anode material in both DSCs and Li-ion batteries. In particular, the originality of the present paper consists not only in showing for the first time the efficient operation of flower-like ZnO nanostructured particles as anode in Li-ion batteries, but also to demonstrate the versatile and multifunctional use of the same material for two different applications, i.e. both dye-sensitized solar and lithium-ion cells.

2. Experimental

2.1. Synthesis procedure

To prepare the flower-like ZnO particles, 2.8 g potassium hydroxide (KOH, 1 M, Merck) and 7.4 g zinc nitrate hexahydrate ($ZnNO_3 \cdot 6H_2O$, 0.5 M, Sigma) were dissolved separately in 50 mL bidistilled water (from Direct-Q System, Millipore). The zinc nitrate solution was dropped into KOH under vigorous stirring, thus the total volume was 100 mL. The obtained white gel was transferred in a closed Teflon bottle at 70 °C for 4 h. At the end of this time, ZnO particles were separated from the solution by filtration, washed repetitively with deionized water until the pH neutralization, and dried at 60 °C overnight in air.

2.2. Characterization techniques

Powder XRD (X-ray diffraction) analysis was performed on a X'Pert diffractometer with Cu K_α X-ray radiation source ($\lambda \approx 1.54$ Å).

Morphologies of the as-obtained products were observed on a FESEM (Field Emission Scanning Electron Microscope, Dual Beam Auriga from Carl Zeiss, operating at 5 keV).

The BET (Brunauer–Emmett–Teller) specific surface area was evaluated by using nitrogen sorption isotherms measured at 77 K on a Quadrasorb instrument from Quantachrome by multipoint method within the relative pressure range of 0.1–0.3 p/p_0. Pore size distribution was derived from the desorption branch using DFT (Density Functional Theory) model.

2.3. Dye-sensitized solar cell assembly and characterization

A ZnO paste, obtained dispersing as-prepared flower-like particles in acetic acid-based solution [48], was preliminarily deposited onto cleaned FTO (Fluorine-doped Tin Oxide)-covered glasses, used as conductive substrates (7 Ω/sq, Solaronix), by doctor-blade technique. The coated films were initially baked at 90 °C for 30 min and subsequently thermally treated at 450 °C for 10 min in air, thus obtaining a ~14 μm-thick ZnO layer. Photoelectrodes were then heated at 70 °C for 5 min, soaked for 6.5 h into a 0.4 mM N719 (Ruthenizer 535bis-TBA, Solaronix) ethanol-based sensitizing solution having a pH of 10.7 at ambient temperature. Finally the photoelectrodes were rinsed in pure ethanol to remove the non-adsorbed dye molecules. A commercial liquid electrolyte solution (Iodolyte AN 50, Solaronix) with the addition of 0.5 M N-methylbenzimidazole was employed. The counter electrode fabrication, the cell assembly procedure and the electrolyte filling process were already detailed in a previously published work [49]. The active area of the cells was 0.78 cm^2 and the electrical characterization was performed with a 0.22 cm^2 black rigid mask. Photocurrent–voltage (I–V) measurements were carried out using a source measure unit (model 2440, Keithley) and a solar simulator (provided by a Newport 91195A class A solar simulator) under AM1.5G irradiation, with power output (100 mW cm^{-2}) calibrated by a Si reference solar cell. In addition, I–V characteristics were also acquired at different light intensities in the range between 0.2 and 1 sun, by using neutral density filters purchased from Newport. EIS (Electrochemical impedance spectroscopy) measurements were performed in dark conditions through an electrochemical workstation (760D, CH Instruments) in the frequency range 100 mHz–10 kHz at various applied bias voltages, with an AC signal amplitude of 10 mV. The experimental data were fitted through an equivalent circuit [22] in order to obtain information about the transport properties. From the fitting parameters R_T and R_{CT}, the diffusion length values L_n were calculated through the following Equation (E1):

$$L_n = d \cdot (R_{CT}/RT)^{1/2} \tag{E1}$$

where d is the photoanode thickness.

2.4. Lithium cell assembly and electrochemical characterization

The electrochemical properties of the as-obtained ZnO flower-like materials were investigated using a three-electrode T-cell configuration at ambient temperature with liquid electrolyte. The working electrodes were fabricated by drop casting a solution of ZnO flower-like particle on stainless steel discs without the addition of any electronic conductivity enhancer and/or binder. In a typical preparation, a 0.5 mg mL^{-1} suspension of the synthesized