We report here on the fabrication and characterization of dye-sensitized solar cells with ZnO-based photoanodes with valuable efficiency. A simple, low cost and scalable method for the deposition of sponge-like mesoporous ZnO nanostructures was used. A nanostructured Zn film is grown on glass covered with fluorine-doped tin oxide by radio frequency magnetron sputtering technique and subsequently subjected to a thermal treatment in oxygen atmosphere. The structural characterization of the material shows the formation of a pure wurtzite crystalline structure, without metallic inclusions. A coral-like structured film is formed, showing the superimposition of small branches, with an almost isotropic growth in length. The size and spacing of the nanostructures are on the order of the exciton diffusion length, ensuring optimal electron collection efficiency. The optimization of the sensitization procedure using Ru-based dye was performed, and a photovoltaic conversion efficiency as high as 4.83% under AM1.5G illumination was demonstrated.

2. Experimental details

2.1. Materials and methods

Fluorine-doped tin oxide (FTO) coated glasses (7 Ω/sq. Solaronix) were used as substrates. They were cleaned with "piranha" solution (sulfuric acid and hydrogen peroxide in 3:1 volume ratio) and covered with a hard mask. The nanostructured Zn film was grown by rf magnetron sputtering starting from a pure (99.99%) Zn target, using Ar plasma. The chamber was evacuated down to a pressure of about 10\(^{-7}\) Torr, and no intentional heating was applied to the substrates. The Zn film was subsequently thermally oxidized at 380 °C for 60 min in ambient condition. Details of the growth procedure are reported elsewhere [8].

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Photoelectrodes were heated at 70°C and soaked into a 0.25 mM N719 dye solution (Ruthenizer 535bis-TBA, Solaronix) in ethanol for different times at room temperature and then rinsed in ethanol to remove the un-adsorbed dye molecules. The counter electrode was constituted by a glass/FTO sheet with a thin (5 nm) layer of Pt deposited on it by thermal evaporation.

DSCs were assembled using a microfluidic architecture [9, 10]. A liquid $I^-/I_3^-$ electrolyte (Iodolyte AN50, Solaronix) was used. All cells had an active area of 0.78 cm$^2$ and measurements were performed with a 0.22 cm$^2$ black rigid mask.

2.2. Characterizations

The morphology of the Zn and ZnO films was investigated by means of a ZEISS Supra 40 field-scanning electron microscope (FESEM). The topography was investigated both in top view and in cross view (electron energy 5 keV).

X-ray diffraction technique was used to determine the crystalline structure of the films (Panalytical PW1140-PW3020, Cu K$_\alpha$ X-ray source). The scans were performed in a parallel beam geometry with a fixed angle of incidence $\omega = 1.5^\circ$, in order to minimize the contribution of the substrate to the observed diffracted intensities.

The Brunauer-Emmett-Teller (BET) specific surface area of the ZnO sample was evaluated from N$_2$ sorption isotherms (Quantachrome Autosorb 1) by multipoint method within the relative pressure range of 0.1-0.3$P/P_0$.

$I-V$ electrical characterizations under AM1.5G illumination (1000 W/m$^2$) were carried out using a class A solar simulator (91195A, Newport) and a Keithley 2440 source measure unit. Electrochemical impedance spectra were collected under the same illumination using an electrochemical workstation (760D, CH Instruments) in the frequency range 10$^{-1}$-10$^5$ Hz at open circuit voltage. The amplitude of the AC signal was 10 mV.

3. Results and discussion

In Fig. 1a the morphology of the deposited film as evaluated by FESEM is presented. The Zn film shows a sponge-like structure, compatible with the results proposed by Baker et al. for Zn-Al coatings [11]. The nanostructuring of a metallic film in a sponge-like structure occurs for growth processes performed with a substrate temperature $T$ approximately equal to a half of the melting temperature $T_m$ (e.g. $T/T_m \approx 0.5$) [12]. Being the melting temperature for zinc particularly low, it is possible to synthesize a porous nanostructured layer for $T \sim T_{amb}$. Films with thicknesses up to 15 μm were deposited.

As depicted in Fig. 1b, no significant morphological variation can be noticed after the high temperature oxidation procedure, resulting only in a moderate volume expansion. Top view in Fig. 1c allows appreciating the porous morphology of the film and its similarity with the structure of natural coral. The specific exposed surface, as measured by BET, was equal to 14.1 m$^2$/g, in line with what was measured for mesoporous ZnO layers deposited with other techniques [2].

In the magnified FESEM picture in Fig. 1d it is possible to observe the 3-dimensional coral-like nanostructure, formed by the superimposition of small branches able to grow in length along basically every direction. The typical dimension of the particular is around 40 nm, with spacing between adjacent structures in the range 10-60 nm. Taking into account that the typical exciton length in ZnO is in the range 5-20 nm, such morphological feature presents all the desired characteristics for efficient dye loading and charge transport towards the electrode [13].

The macroscopic appearance of the deposited film before and after the oxidation treatment drastically changes, moving from a black to a transparent feature, as shown in Fig. 2a. In Fig. 2b, the XRD characterization of the film before and after the oxidation procedure is reported. The diffraction pattern after the thermal treatment witnesses a complete oxidation of the film, without the formation of Zn residuals, which could be detrimental for charge transport in DSC photoelectrodes.

Photovoltaic characterizations were performed using a microfluidic architecture, which is an advantageous tool for the optimization of the process, being the assembly procedure simple and fast in a controlled and reproducible way [14]. A picture of the final device is shown in Fig. 2c. The sensitization procedure is known to be critical for ZnO electrodes [15], since it is necessary to avoid the partial ZnO dissolution in the dye solution. In Fig. 3 the $I-V$ curves and the evaluation of photovoltaic conversion efficiency (PCE) as a function of dye incubation time are reported. PCE was evaluated starting from the $I-V$ curves as

![Fig. 1. FESEM characterization: (a) Zn film, cross view; (b) ZnO film, cross view; (c) ZnO film, top view, and (inset) visual comparison with a natural coral; (d) magnified image of the coral-like morphology, where the branched structure is evidenced.](image-url)
The efficiency increase for short incubation times is related with the slow kinetic of dye adsorption on the surface of the semiconductor. When the number of chemisorbed dye molecules on the surface of ZnO is low, the PCE is reduced both because of the small number of photogenerated charges injected in the semiconductor and because of the higher recombination rate with the electrolyte, occurring at the semiconductor unoccupied sites. When the optimal incubation time is exceeded, the formation of molecular aggregates between dissolved Zn^{2+} ions and dye molecules occurs [17]. The aggregates are inactive in terms of charge generation and act as filters for the impinging light, decreasing the overall efficiency of the device.

\[ \text{PCE} = \frac{FFV_{oc}J_{sc}}{P_{in}}. \]

\( V_{oc} \) is the open circuit voltage, \( J_{sc} \) is the short circuit current density, \( P_{in} \) is the input power density, and \( FF \) is the fill factor, defined as \( (V_{max}/J_{max})/(V_{oc}J_{sc}) \), where \( V_{max} \) and \( J_{max} \) are the voltage and current density at maximum power output, respectively.

![Fig. 2. (a) Picture of the photoanode, before (left) and after (right) the oxidation treatment; (b) XRD characterization, before and after the oxidation treatment (JCPDS cards: Zn 87-0713, ZnO 89-1397); (c) picture of the microfluidic cell.](image)

![Fig. 3. Evaluation of the photovoltaic conversion efficiency in microfluidic cells for different sensitization times, starting from \( I-V \) curves (inset). The thickness of the ZnO film is 15 μm.](image)

Photoanodes with a ZnO film thickness equal to 15 μm were used. Several devices were tested and the relative error between different samples was within the 5%, meaning a very high reproducibility. An incubation time of two hours was found to be optimal for the sensitization of this material, in line with previously reported data [10] and for materials synthesized with other techniques [16]. In particular, an evident increase in \( J_{sc} \) is noticed, while \( FF \) is almost independent of the sensitization procedure.

With the optimized sensitization time of two hours, the photovoltaic behavior of the device as a function of the ZnO film thickness was tested. The results of the \( I-V \) characterization and the Bode representation of the electrochemical impedance spectroscopy (EIS) phase are reported in Fig. 4. The increase in photoanode thickness from 12.5 μm to 15 μm in the microfluidic architecture allowed obtaining a slightly higher efficiency, with an increase on the short circuit current, while the \( FF \) value remained unaffected.

![Fig. 4. \( I-V \) and EIS (Bode plot, inset) characterization of ZnO-based DSCs fabricated with different photoanode thicknesses, 12.5 μm (black) and 15 μm (red). The sensitization time was 2 h.](image)
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The dependence of electron lifetime on the photoanode thickness is probably related with the contribution of the back transfer of electrons at the FTO-electrolyte interface [19]. For thicker photoanodes, this parasitic effect loses importance, giving as a macroscopic result a higher overall carrier lifetime, as reported previously for mesoporous TiO$_2$ films [20].

4. Conclusions

The fabrication and characterization of DSCs made with a coral-shaped ZnO photoanodes is reported. A simple and scalable method for the synthesis of sponge-like Zn structure was presented. The Zn nanostructures were oxidized with a simple thermal treatment in air, obtaining a porous ZnO film with a 3D coral-like morphology. XRD characterization showed the complete oxidation of the film.

The solar energy conversion efficiency of DSCs based on ZnO films sensitized with Ru-based dyes was evaluated. The sensitization procedure was refined, being the optimal sensitization time equal to 2 h. Using a 15 µm thick photoanode assembled in a microfluidic architecture, a noticeable photovoltaic conversion efficiency of 4.83% was evaluated, with a charge carrier lifetime at open circuit voltage equal to 48 ms.

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References