Conductivity improvement of CuCrO₂ nanoparticles by Zn doping and their application in solid-state dye-sensitized solar cells

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Abstract

Undoped and Zn-doped CuCrO₂ nanoparticles were synthesized by sol-gel method as promising wide band gap p-type semiconductor materials for solid-state dye-sensitized solar cells (DSSCs). We studied the influence of Zn dopant concentration on structural, electrical and optical properties of CuCrO₂ nanoparticles. The X-ray diffraction data indicated that the delafossite-to-spinel ferrite phase transition occurs by increasing the amount of Zn doping. The average nanoparticle size was determined about 40 nm. A minimum value of electrical resistivity of 5.7 Ωcm was obtained for doping concentration of 5%. Having optimized the Zn-doped CuCrO₂ nanoparticles, solid-state DSSCs were fabricated using undoped and Zn-doped CuCrO₂ (5%) as solid electrolytes. As the photoanode layer, the vertically aligned TiO₂ nanorod arrays were grown on FTO glass using a hydrothermal method. Compared with undoped CuCrO₂, the Zn-doped nanoparticles exhibited an improvement in photovoltaic properties. The overall efficiency enhancement of 39% was obtained for the dopant concentration of 5%. The improved power conversion efficiency is attributed to the lowered electrical resistivity and enlarged work function of Zn-doped CuCrO₂ nanoparticles.

Keywords: A. Sol-gel processes; A. Powders: chemical preparation; C. Electrical conductivity; Zn-doped CuCrO₂ nanoparticles; Solid-state dye-sensitized solar cells

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Introduction

P-type semiconductors are one of the most interesting materials for dye-sensitized solar cells (DSSCs). They have been used as photocathode in p-type DSSCs (p-DSSCs) [1] and as solid-state electrolyte (hole-transport material) in n-type DSSCs (n-DSSCs) [2]. Though there are many reports concerning n-DSSCs (for instance, different structures of TiO_2 and ZnO have been studied) [3-5], DSSCs based on sensitization of p-type semiconductors are moderately new and their efficiency is still much lower than that of n-DSSCs [6-9]. Generally, the lower efficiency of the p-DSSCs is due to poor light absorption in thin mesoporous films, low carrier mobility in p-type semiconductors and energy-level mismatch with sensitizers and electrolytes [10].

Recently, the idea of tandem-DSSCs (t-DSSCs) with a photoanode constructed from a conventional n-type semiconductor and a photocathode created by a p-type semiconductor (such as NiO), which both being dye-sensitized but by two different dyes, have been presented [11]. The goal of the construction of the t-DSSCs is to achieve higher open-circuit voltage (V_{oc}) and broader light absorption in the solar spectrum [12, 13]. Theoretical calculations have shown that photon to energy conversion efficiency (PCE) of t-DSSCs can rise up to about 43% [14]. The construction of t-DSSCs with higher efficiency in the conversion of sunlight into the electrical power requires efficient p-DSSCs. On the other hand, although solid-state inorganic semiconductors do not have many disadvantages of liquid electrolytes such as toxicity, leakage and solvent evaporation [15, 16], the efficiency of solid-state DSSCs is still limited by this kind of semiconductors [17]. For instance, the low efficiency of the solid-state DSSC employing CuAlO_2 as a solid electrolyte has been attributed to large size of the CuAlO_2 nanoparticles which could not penetrate enough into the TiO_2 network and also low p-type conductivity of CuAlO_2 nanoparticles [2]. Therefore, as well as the case of p- and t-DSSCs, improvement of p-type conductivity is strongly demanded for construction of solid-state DSSCs.

In this study, the influence of zinc dopant concentration on structural, electrical and optical properties of CuCrO_2 nanoparticles has been investigated. The p-type semiconductor CuCrO_2 has lower electrical resistivity in comparison with CuAlO_2 and CuGaO_2 delafossite structures. CuCrO_2 nanopowder has been previously synthesized by Miclau et al. using hydrothermal method [18]. Furthermore, in a recent work, we have also produced its single-crystal nanoparticles with a narrow size distribution by sol-gel method [19]. Carrier diffusion length could be increased by decreasing carrier scattering from grain boundaries in small nanoparticles. However, a major influence on the physical and electrical properties of these nanoparticles can be achieved by substitution of divalent dopants on the trivalent metal site. For example, the solubility of Mg^{2+} at Cr^{3+} site has been studied by Maignan et al. [20]. They realized that the holes, created by the Mg^{2+} substitution, are responsible for the transport properties of these compounds. Recently, the effect of zinc doping on the structural and magnetic properties of polycrystalline CuCrO_2 bulk samples, synthesized by solid-state reaction method, has also been investigated [21]. Nevertheless, there is not any report on characterization of Zn-doped CuCrO_2 nanoparticles. In this work, the sol-gel method has been employed in order to synthesize the Zn-doped CuCrO_2 nanoparticles. Then, their application in the solid-state DSSCs can be expected. To assemble the DSSCs we utilized an aligned TiO_2 nanorod array as the photoanode grown on FTO glass. The TiO_2 nanorods have been created using hydrothermal method. Using TiO_2 nanorods instead of nanoparticles can improve the contact area of TiO_2 photoanode and CuCrO_2 nanoparticles.

Experimental methods

In this research, the sol-gel method was employed for synthesis of CuCrO_2 nanoparticles. We used copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Merck, with purity of >98%) and chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Merck, with purity of >99%) as starting materials, and 2-methoxyethanol ($\text{CH}_3(\text{CH}_2)_2\text{OOH}$, Merck, with purity of >99.5%) as a solvent. Furthermore, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Merck, with purity of >99%) was used as a dopant source. The CuCrO_2 precursor solution was prepared by dissolving copper acetate monohydrate and chromium nitrate nonahydrate in 2-methoxyethanol at temperature 60 °C. Zinc acetate dihydrate with various concentrations was added to the precursor solution as the Zn source under stirring. The molar ratio of copper acetate and chromium nitrate was fixed at 1:1. The concentration of copper acetate in the solution was maintained to be 0.7 M and the concentration of Zn as a dopant was 0, 2.5, 5 and 7.5 at % with respect to Cr in the initial solution. The resultant solution was stirred in a magnetic stirrer at 60 °C for

3 hour to obtain a deep green, transparent and homogenous solution. The obtained solution was dried at 110 °C for 3 h. Finally, the dried powders were annealed in air at 900 °C for one hour.

Subsequent to characterization of CuCrO₂:Zn nanoparticles, we constructed the solid-state DSSCs using the prepared nanoparticles. In this stage, the TiO₂ nanorod array was prepared on FTO glass using a hydrothermal method. In a typical synthesis, 15 ml of deionized water, 0.5 ml of titanium tetraisopropoxide (TTIP, Samchun Chemical Co.) and 15 ml hydrochloric acid (HCl, Amertat Shimi Co.) were mixed in a magnetic stirrer [22]. After stirring for 10 min, the mixed solution was transferred into a 100 ml capacity Teflon-lined stainless steel autoclave. The cleaned FTO substrates were immersed in the solution and the autoclave was placed in a furnace at temperature of 160 °C for 12 h. After cooling, the FTO substrates were taken out, washed with deionized water and ethanol, and then dried in air at 160 °C for 30 min. Subsequently, they were immersed in 0.5 mM N719 dye solution for 24 h, and then, the photoelectrodes were rinsed with ethanol. To create CuCrO₂:Zn nanoparticles coating as a solid-state electrolyte, a few drops of CuCrO₂:Zn suspension in ethanol were placed on dyed TiO₂ film and spin-coated at 1000 rpm for 30 s. Subsequently, a platinum counter electrode was clipped onto the top of the FTO/TiO₂/N719/CuCrO₂:Zn structure to form a solid-state DSSC. The active area of the resulting cells exposed to light was around 0.25 cm² (0.5 × 0.5 cm²).

The crystallinity of the prepared powders and TiO₂ nanorods was investigated by X-ray diffraction (XRD) with a PANalytical's X-ray diffractometer, using CuK α =1.5406 Å radiation and then crystallite sizes were determined. To find out the size and morphology of the nanoparticles, field emission scanning electron microscopy (FESEM, TESCAN mira 3 xmu) was used. Moreover, a Hitachi S-4160 scanning electron microscope (SEM) was utilized to characterize the morphology of the TiO₂ nanorods. The transmission electron microscopy (TEM) measurements of the prepared nanoparticles were carried out by using a Zeiss EM 900 transmission electron microscope operating at 80 kV. The electrical properties were determined by hot-probe, Hall effect and resistivity measurements, employing the van der Pauw configuration. The magnetic field in Hall effect measurements was fixed at 400 mT. The optical absorption spectrum was also investigated by 3648 UV-Vis Avantes spectrophotometer in the range of 280–600 nm and the optical band gap was estimated from optical absorption spectrum. The current -voltage characteristics (I-V) of DSSCs were measured using a four-probe setup by applying voltage and measuring the current. The current-voltage measurements were scanned from 0 mV (short circuit condition) to 150 mV (beyond open circuit voltage), with a step of 10 mV under a light intensity of 100 mWcm⁻² at AM1.5G provided by a solar light simulator (Sharif Solar, SIM-1000).

Results and discussion

Addition of Zn ion marginally changes the color of CuCrO₂ nanoparticles from green to dark green. However, the shape of particles remains the same. The FESEM images of the prepared CuCrO₂ nanoparticles with different zinc doping concentrations are exhibited in Fig. 1. Though, the average particle size is around 40 nm, it can be seen that the size of Zn-doped nanoparticles (2.5%) is slightly larger than that of undoped ones and with increasing of Zn dopant concentration they become smaller. Doping of CuCrO₂ nanoparticles with zinc also affects the structural properties of the nanoparticles. In order to study the effect of zinc concentration on the crystalline structure of CuCrO₂ nanoparticles, different dopant concentrations were examined. X-ray diffraction spectrum for undoped CuCrO₂ and Zn-doped CuCrO₂ nanoparticles are depicted in Fig. 2. Diffraction peaks of the samples are precisely indexed to a delafossite structure of CuCrO₂ (space group: R-3m (166)), which matched the JCPDS Card (No. is 01-089-6744). As can be seen in Fig. 2, the intensity of the diffraction peaks decreases with Zn concentration indicating that Zn-doping can lead to reduction in the crystalline quality of CuCrO₂ nanopowder. In addition, the full-width at half-maximum (FWHM) of the XRD peaks gradually increases with the increase of Zn content and the peaks for the doped CuCrO₂ nanoparticles slightly shift toward lower angles. The decrease in crystal quality may be due to the appearance of stress because of the difference in ion size between Cr ($r_{Cr^{3+}} = 0.063$ nm) and Zn ($r_{Zn^{2+}} = 0.074$ nm). On the other hand, for Zn concentrations higher than 5%, diffraction peaks of CuCr₂O₄ and ZnO structures also appear, an indication showing that the delafossite-to-spinel ferrite phase transformation occurs by Zn doping. The deviation in crystalline quality can be quantified by the crystallite size. By considering (006) direction and using the Debye-Scherrer formula, the

crystallite size was obtained as 39.8, 38.7, 36.3 and 34.6 nm for the prepared CuCrO₂ nanoparticles at the Zn content of 0, 2.5, 5 and 7.5 at %, respectively.

When CuCrO₂ nanoparticles are doped with Zn atoms, they occupy the site of Cr atoms. On the other hand, since the ionic radius of Zn is larger than that of Cr, some Zn atoms prefer to locate in or near the crystallite boundary regions [23]. These Zn atoms can prevent crystallite growth and induce lattice distortion [24]. Furthermore, the segregation of the dopant in the crystallite boundaries may occur for high doping concentrations [25]. Therefore, the crystallite size decreases as the concentration of Zn in the nanoparticles increases. In a similar research, Gao et al. have reported that the lattice constants and unit cell volume of Fe-doped CuCrO₂ linearly increase with Fe concentration and the deterioration of the crystallinity is observed because of stresses arising from the larger ionic radius of Fe³⁺ (0.065 nm) [26]. The deterioration of the crystallinity of the doped CuCrO₂ nanoparticles can be explained by the energy formation of the prepared nanoparticles. In order to study the structural instability of the doped delafossites, Liu et al. calculated the formation energies of the CuAlO₂ with different concentrations of sulfur dopant [27]. Their calculations showed that the formation energy of the S-doped CuAlO₂ is negative and increases with S doping concentration. For this reason, the observed deterioration of the crystallinity of the Zn-doped CuCrO₂ nanoparticles can be attributed to the increase in the formation energy.

In order to gain an insight into the impact of Zn-doping on the electrical properties of CuCrO₂ nanoparticles, the nanopowders annealed at 900 °C were pressed into cylindrical pellets of 1 mm thickness and 10 mm in diameter at a pressure of 25 MPa using a hydraulic press [28]. Hot probe measurements established the conductivity of CuCr_{1-x}Zn_xO₂ powders as p type. The origin of p-type conductivity in CuCrO₂ delafossite structure is attributed to the copper vacancies and oxygen interstitials [29]. The increase in p-type conductivity in delafossite CuCr_{1-x}Zn_xO₂ is mainly due to the divalent cation (Zn²⁺) doping on the trivalent site (Cr³⁺). This substitution leads to Cu¹⁺/Cu²⁺ hole hopping mechanism. The hole hopping mechanism can be expressed with the equation:

where Zn_{Cr}²⁺ indicates the Zn²⁺ cation on the Cr³⁺ position and *h* stands for a hole carrier with positive charge. Existence of both Cu¹⁺ and Cu²⁺ in CuCrO₂ doped with a divalent cation has been verified by X-ray photoelectron spectroscopy measurement carried out by Zheng et al. [30]. The presence of Cu²⁺ is due to the charge compensating process which introduces excess positive charge carrier [31, 32].

As mentioned above, the electrical resistivity of Zn-doped CuCrO₂ is primarily related to copper vacancies, oxygen interstitials and dopant concentrations. Moreover, the resistivity depends on the crystallinity of nanoparticles [33]. As can be seen from Table 1, the resistivity is initially found to decrease with incorporation of zinc. When a small amount of Zn is introduced into the CuCrO₂ delafossite structure, the Zn placed in Cr³⁺ site is ionized into Zn²⁺ and subsequently one free hole is created from each substituted zinc atom. Carrier concentration increases with zinc content up to 5 at % but by further growth of zinc concentration, the resistivity of the CuCrO₂ nanoparticles increases. The growing of resistivity is attributed to the solubility of zinc atoms inside CuCrO₂ structure. Because of the limited solubility of Zn inside CuCrO₂ structure at higher doping concentrations (>5 at %), most zinc atoms cannot occupy the correct places inside CuCrO₂ lattice and produce extra phases such as CuCr₂O₄ and dopant oxide (ZnO) which degrade the crystal structure of CuCrO₂ nanoparticles. Subsequently, the increase of zinc dopant concentration does not produce more charge carrier. This explanation is supported with results obtained from the XRD analysis and also consonant with other literature on Mg-doped CuCrO₂ thin films [33, 34]. A minimum value of electrical resistivity of 5.7 Ωcm was obtained for doping concentration of 5 at %.

The presence of the dopant also influences the Hall mobility of carriers. According to Table 1, the mobility gradually decreases with the dopant content. In typical semiconductor materials, the decrease in Hall mobility is mainly due to different scattering mechanisms such as optical and acoustic phonon scattering mechanisms (also called lattice scattering), ionized and neutral impurity scattering, grain boundary scattering and defect scattering [35]. In our study, the characterization of all samples has been carried out at room temperature in the same

conditions. Thus, the phonon scattering does not contribute to the reduction of the Hall mobility. As mentioned above, with increasing Zn dopant content, the crystallinity of CuCrO_2 structure is deteriorated and excess phases are formed (see Fig. 2). Therefore, the defect scattering and deterioration of the crystallinity of CuCrO_2 structure and formation of excess phases such as CuCr_2O_4 and ZnO are the main sources of the Hall mobility reduction.

For measuring the UV-Vis spectrum, the nanoparticles were suspended in ethanol to form a microemulsion system. A quartz cell of 1 cm thick was used as the solution container. The optical characteristic of the samples was investigated from the absorption measurements in the wavelength range of 280-600 nm. Fig. 3 shows the UV-Vis absorption spectra of CuCrO_2 and $\text{CuCrO}_2\text{:Zn}$ nanoparticles dispersed in ethanol solution. The rapid decrease of absorption at a particular wavelength, corresponding to the optical band gap, reveals that the particles are almost homogeneously dispersed in the sample. From the absorption spectrum the band gap energy can be calculated using Tauc's relation. The optical band gap of CuCrO_2 nanoparticles was obtained from the inset of Fig. 3. The band gap of the undoped CuCrO_2 nanoparticles was determined around 4.04 eV. After doping with 5% of Zn the band gap of the nanoparticles was slightly reduced to about 3.97 eV. Similar results have also been reported in other literatures. For example, Herraiz-Cardona et al. have observed similar optical band gap red shift in Mg-doped CuGaO_2 nanoparticles [36]. In our case, the observed red shift in the band gap is attributed to the quantum size effect. In fact, because of the quantum size effect, the optical band gap is proportional to the inverse size of the nanoparticles [19, 37]. Our results on the band gap are in consonant with SEM images. For more clarity, the TEM images of undoped and 5% Zn-doped CuCrO_2 nanoparticles are shown in Fig. 4. According to this figure, the size distribution verifies a slightly increase in the size of the nanoparticles by Zn doping. From the histograms the average size of the CuCrO_2 nanoparticles is around 36.5 nm and that of the 5% Zn-doped CuCrO_2 nanoparticles is about 39 nm.

Fig. 5 shows the XRD pattern of TiO_2 nanorods deposited on the FTO conducting glass substrate. Obviously, the SnO_2 peaks were detected for all samples, which clarifies that the TiO_2 nanorods have been constructed on the FTO substrates. The diffraction peaks of the TiO_2 nanorod arrays are consistent with the rutile phase (JCPDS card No.00-001-1292). The density of the TiO_2 nanorods on the surface of an FTO substrate and the diameter of the nanorods can be varied by changing the initial titanium tetraisopropoxide concentration in the liquid solution [22]. The top view of the TiO_2 nanorods is seen in Fig. 6, and as can be seen both of them increase with initial TTIP concentration. Nanorods with the diameter of 60-150 nm were obtained for the value of 0.8 ml TTIP and about 75-160 nm-thick nanorods were achieved for 0.9 ml of TTIP. Furthermore, the diameters of the nanorods for 1.0 and 1.1 ml of TTIP in the growth solution are about 90-160 and 150-180 nm, respectively. In general, larger diameter TiO_2 nanorods are created at higher concentration of TTIP. Moreover, at higher concentrations of the TTIP, the grown TiO_2 nanorods are more uniform, dense and vertically aligned on the FTO substrate whereas, the obtained nanorods at low TTIP concentration in liquid solution have a broad size distribution and stand at different directions. Fig. 6 (e) shows the SEM cross-section of nanorods fabricated from the solution with 1.1 ml TTIP concentration. The average length of the nanorods made using different TTIP concentrations looks almost the same around 2 μm .

Having prepared the CuCrO_2 nanoparticles and TiO_2 nanorods, we have studied the effect of the TiO_2 nanorods density on the photovoltaic properties of the solid-state DSSCs. The current density-voltage (J-V) curves of the DSSCs using the TiO_2 nanorod arrays (as the working electrodes) prepared with different TTIP concentrations and CuCrO_2 nanoparticles as a solid-state electrolyte are compared in Fig. 7. The obtained results show that the efficiency of the DSSCs increases with growing the density and the diameter of the TiO_2 nanorods. At higher density of nanorods, the constructed photoanodes have larger surface area for anchoring dye molecules and thus enhance the efficiency. The conversion efficiency of solid-state DSSCs increases from 0.032% to 0.039%, 0.048% and 0.054% with increasing the TTIP concentration in growth solution for fabrication of TiO_2 nanorods. For this reason, in the following we concentrate on the TiO_2 nanorod photoanode made from the solution with 1.1 ml TTIP concentration to study the effect of Zn-doped CuCrO_2 nanoparticles on the photovoltaic properties of the solid-state DSSCs.

The photovoltaic current density-voltage (J-V) characteristic curves for the solid-state DSSCs made from the TiO_2 nanorod photoanode fabricated from the solution with 1.1 ml TTIP concentration and CuCrO_2 and Zn-

doped CuCrO₂ nanoparticles as solid-state electrolytes, under an AM1.5G solar simulator irradiation (100 mW/cm²) are shown in Fig. 8. The photovoltaic parameters as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (η) of the DSSCs have been summarized in Table 2. The data show that Zn doping in CuCrO₂ nanoparticles gives a clear improvement in J_{SC} and V_{OC} resulting in a device with higher η . The overall efficiency improvement in 5% Zn-doped CuCrO₂ is about 39%. Compared with undoped CuCrO₂ nanoparticles, the 5% Zn-doped CuCrO₂ nanoparticles exhibit a considerably increased V_{OC} by about 21%. This increase of V_{OC} may be explained by the difference in the work function of Zn-doped CuCrO₂ and that of undoped one. The CuCrO₂ nanoparticles with Zn doping have a larger work function resulting from a larger hole carrier concentration (see Table 1). With addition of acceptor dopant (Zn), the Fermi level (E_f) moves toward the valence-band edge. In this case, the work function $\phi = E_{\infty} - E_f$ (where E_{∞} is the vacuum energy), is increased [38, 39]. On the other hand, the increase of J_{SC} (about 27%) seems to be primarily due to the growth of carrier concentration with Zn doping. The power conversion efficiencies of cells are mainly limited by the series and shunt resistances which are mainly due to the resistivity of the nanoparticles (limited charge transport) and the poor coverage of FTO substrate by TiO₂ nanorods (increased recombination and shunting), respectively. Zou et al. have reported similar results for FTO/TiO₂/CdTe/C structure with energy conversion efficiency of about 0.07% under AM1.5G illumination (J_{SC} , V_{OC} , and FF are 0.67 mA/cm², 0.65 V and 0.17, respectively) [40]. Recently, Pavan and et al. prepared the TiO₂/Cu₂O all-oxide heterojunction solar cells by spray pyrolysis method onto FTO glass substrates with short-circuit current density of 0.4 mA/cm² and open circuit voltage about 350 mV [41]. Furthermore, Yuhas et al. [42] have observed photovoltaic properties in FTO/ZnO nanowire/Cu₂O nanoparticles structure with energy conversion efficiency of about 0.053% by using a TiO₂ blocking layer.

Conclusion

We studied the influence of Zn doping on the operation of solid-state DSSCs made from TiO₂ nanorod photoanodes and CuCrO₂ nanoparticles as solid state electrolyte. The average size of the CuCrO₂ nanoparticles was found about 40 nm using FESEM. The Zn doping led to a considerable enhancement in the energy conversion efficiency of the DSSCs. Within the CuCrO₂:Zn nanoparticles prepared with different Zn concentrations, the nanoparticles with 5% Zn exhibited the lowest electrical resistivity. The device made from these particles revealed an overall efficiency improvement of 39%. The efficiency improvement is attributed to lower resistivity and larger work function of Zn-doped CuCrO₂ nanoparticles relative to those of the undoped ones.

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Fig. 1. FESEM images of delafossite structure of (a) undoped CuCrO_2 , (b) Zn-doped CuCrO_2 (2.5%) and (c) Zn-doped CuCrO_2 (5%).

Fig. 2. XRD patterns of the nanoparticles. Peaks labeled as * and # are attributed to the CuCr_2O_4 and ZnO structures, respectively. The solid lines are guide for the eyes.

Table 1. Structural, electrical and optical properties of $\text{CuCrO}_2\text{:Zn}$ nanoparticles.

Sample	CuCrO_2	$\text{CuCrO}_2\text{:Zn (2.5\%)}$	$\text{CuCrO}_2\text{:Zn (5\%)}$	$\text{CuCrO}_2\text{:Zn (7.5\%)}$
Crystallite size in (006) direction (nm)	39.8	38.7	36.3	34.6
Charge carriers concentration (cm^{-3})	5.0×10^{16}	8.3×10^{16}	4.6×10^{17}	9.5×10^{16}
Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	2.7	2.5	2.4	2.3
Resistivity (Ωcm)	46.3	30.1	5.7	28.6
Band gap (eV)	4.04	3.96	3.97	3.98

Fig. 3. Optical absorption spectra of CuCrO₂:Zn (0, 2.5, 5, 7.5%) nanoparticles. The inset shows $(\alpha h\nu)^2$ versus photon energy.

Fig. 4. TEM images of (a) undoped and (b) Zn-doped CuCrO₂ nanoparticles (5 %). (c) and (d) show the size distribution of the undoped and 5 % Zn-doped CuCrO₂ nanoparticles, respectively.

Fig. 5. XRD patterns of TiO₂ nanorods grown on the FTO glass substrates with different TTIP concentrations.

Fig. 6. SEM images of top view of the TiO₂ nanorods array grown on FTO glass substrates with a) 0.8 ml, b) 0.9 ml, c) 1.0 ml and d) 1.1 ml TTIP concentration in growth solution. e) SEM cross-section of nanorods fabricated from 1.1 ml TTIP concentration in liquid solution.

Fig. 7. The current density-voltage curves of the solid-state DSSCs based on TiO_2 nanorod photoanodes fabricated with different TTIP concentrations in growth solution (0.8, 0.9, 1.0 and 1.1 ml) and CuCrO_2 nanoparticles measured under an AM1.5G solar irradiation of 100 mW/cm^2 .

Fig. 8. The current density-voltage (J-V) curves of solid-state DSSCs made from the fabricated TiO₂ nanorods photoanode with 1.1 ml TTIP concentration, undoped CuCrO₂ and Zn-doped CuCrO₂ as solid-state electrolytes.

Table 2. Photovoltaic parameters of solid-state DSSCs made from the fabricated TiO₂ nanorods photoanode with 1.1 ml TTIP concentration, undoped CuCrO₂ and Zn-doped CuCrO₂ as solid-state electrolytes under AM1.5G illumination.

Device	J _{sc} (μAcm ⁻²)	V _{oc} (mV)	FF	η (%)
0 %	430	234	43	0.054
2.5 %	476	280	41	0.065
5 %	544	283	42	0.075
7.5 %	513	274	43	0.068