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Carbon Black Paste Combined with Conductivity-enhanced CuSCN for Improved Performance in Quasi-solid-state Dye-sensitized Solar Cells

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Vast improvement in the performance of a dye-sensitized solid-state solar cell of TiO_2/N719/modified CuSCN is observed when carbon paste is applied on CuSCN. AC-impedance analysis reveals the existence of the ionic nature of the modified CuSCN material, and it is further developed when carbon paste is applied on CuSCN in the solar cell. Voltage-transient spectra of decay analysis show the improvement of the lifetime of the photogenerated electrons and thus improve the voltage in the carbon-paste-applied solar cell.

Research on dye-sensitized solar cells (DSCs) have recently been shifted from those based on liquid electrolyte to solid-state or quasi-solid-state cells, due to liquid electrolyte devices suffering from problems associated with dye desorption, volatility of the solvent and the leachability, permeation of water and oxygen molecules into the electrolyte, the possible reactions of the sealant with the electrolyte, and especially the corrosive nature of iodine with counter electrode, which limit its durability and hence practical applications.[1]

Various approaches have been made to replace liquid electrolyte by materials such as ionic liquid electrolyte,[2] polymer electrolyte,[3] organic hole conductors,[4] and inorganic p-type semiconductors. Out of many inorganic p-type semiconductors investigated such as $CuAlO_2$,[5] NiO,[6] CuI,[7,8] and CuSCN,[9–12] the latter material CuSCN is of particular interest due to its unique chemical robustness and polymeric structure.[13,14]

Incomplete filling of solid electrolyte in the pores of TiO_2 and increase of recombination losses of photogenerated carriers are major drawbacks of solid-state devices compared to liquid-electrolyte-based DSC. As a preventative measure of recombination losses of photogenerated carriers, ultrathin layers of insulating metal oxide layer such as MgO[15] and Al_2O_3[16] have been utilized as coating layers of TiO_2. The solar cell as fabricated shows both improved conversion efficiency and stability. Pore-filling efforts have been studied with detailed descriptions by utilizing inorganic p-type semiconductor of CuI[7] and organic hole conductors.[17]

β-CuSCN which has a band gap of ca. 3.6 eV[18] possesses a three-dimensional polymer-like structure constituted by layers of close-packed CuSCN units.[19] The major drawback of CuSCN as p-type semiconductor in dye-sensitized solid-state solar cells (DSSCs) is its very poor hole conductivity ($10^{-2}\,S\,m^{-1}$)[9,12] and consequent slower rate of reduction of oxidized dye molecules, thus allowing the recombination of electrons injected to TiO_2 CB with the oxidized dye molecules.

In an attempt to increase p-type conductivity of CuSCN, we have introduced in our previous work a versatile method for synthesizing conductivity-enhanced CuSCN material, prepared by incorporating triethylamine-coordinated Cu(II) sites in its structure.[11] The maximum conductivity of $1.42\,S\,m^{-1}$ was reported compared to that of $10^{-2}\,S\,m^{-1}$ for pure CuSCN. The use of such conductivity-enhanced CuSCN in DSSCs gives a best energy conversion efficiency as 3.39% compared to that of 0.25% for pure CuSCN at 1 sun illumination.[11]

In this manuscript outstanding improvement of DSSC using the conductivity-enhanced CuSCN combined with carbon black paste as a hole conducting material is discussed. Results are discussed with the characterization methods of *I–V* characteristics, AC impedance analysis, and photogenerated carrier decay.

Mesoporous TiO_2 films were prepared by a procedure described elsewhere.[7] Then N719 [*cis*-bis(thiocyanato-*N*)bis-(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-κ^2N)ruthenium(II)] was adsorbed by dipping a TiO_2 film in N719 solution for 15 h at room temperature (4×10^{-4} M, in 1:1 volume ratio of acetonitrile and *t*-butanol). The structure-modified CuSCN was prepared as follows: CuSCN (0.5 g) was mixed with sufficient amount of triethylammonium thiocyanate (THT-0.3 g) to obtain a paste which was then stirred with 10.0 mL of propyl sulfide (PS) and allowed to stand still in the dark in a closed sample tube. The color of the mixture of solution changes to black after a few days of preparation. This black color solution (after 20 days of preparation) was spread on a preheated (100 °C) dye-coated TiO_2 film dropwise, allowing the solvent to evaporate. Thickness of the CuSCN film was ca. 3 μm from the top of the TiO_2 surface. Then *I–V* measurements were carried out by applying a carbon paste (Carbon nanopowder mixed with MPN) on top of the CuSCN films and having platinum-sputtered FTO glass plate as a counter electrode under simulated sunlight (AM 1.5, $100\,mW\,cm^{-2}$ - JASCO, CEP-25BX).

I–V characteristics of the DSSC (FTO/TiO_2/N719/CuSCN/Pt-FTO) prepared from modified CuSCN as hole conducting materil are shown in Figure 1, and their corresponding *I–V* parametes are given in Table 1. Solar cell (a) was prepared by applying carbon paste on top of the modified CuSCN while solar cell (b) was prepared by applying graphite on top of the modified CuSCN, and solar cell (c) was prepared using pure CuSCN and applying graphite on top of it.

Since pure CuSCN has very low conductivity, the *I–V* performance of DSSC fabricated from it is extremely low as shown in Figure 1c. When aging the reaction mixture of CuSCN mixed with THT in propyl sulfide, the p-type conductivity of CuSCN prepared from that solution enhances, and consequently short-circuit current density (J_{SC}) and the overall conversion efficiency (η) of DSSC show increment as shown in Figure 1b. The current enhanced is mainly caused by the improved conductivity of CuSCN.[11] Dramatic improvement of current and voltage and hence energy conversion efficiency of solar cell

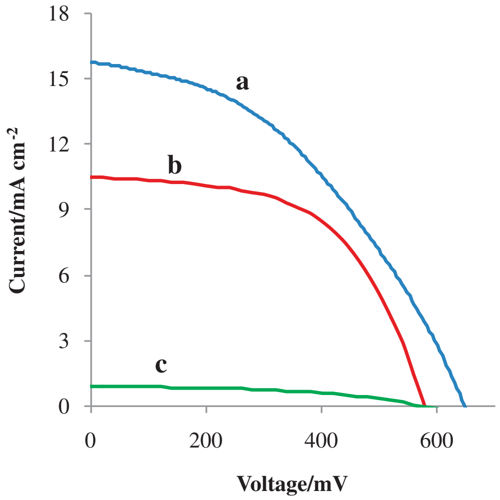


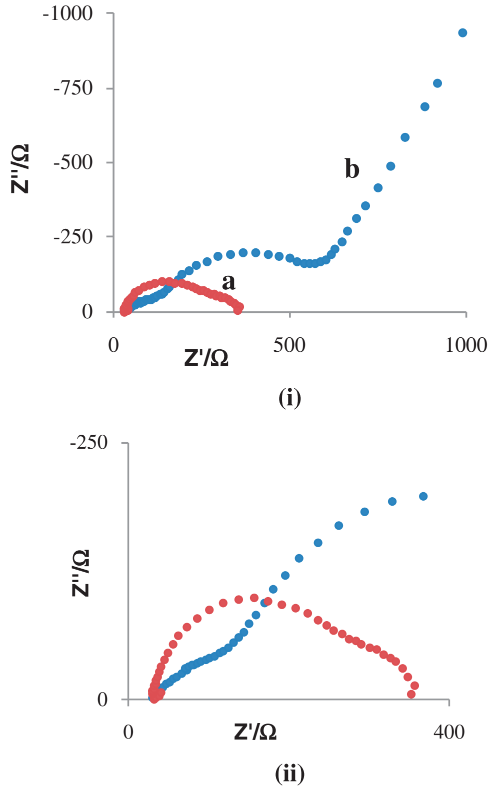
Figure 1. *I–V* characteristic of the solar cell: (a) TiO_2/N719/modified CuSCN/carbon paste, (b) TiO_2/N719/modified-CuSCN/graphite, and (c) TiO_2/N719/pure CuSCN/graphite; cell area: 0.25 cm^{-2}; 1 sun illumination.

Table 1. *I–V* parameters of the solar cells: (a) TiO_2/N719/modified CuSCN/carbon paste, (b) TiO_2/N719/modified CuSCN/graphite, and (c) TiO_2/N719/pure CuSCN/graphite

Cell	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η/%
a	15.76	647	0.416	4.24
b	10.52	578	0.556	3.39
c	0.90	576	0.477	0.25

(a) which is made by applying carbon paste on modified CuSCN, is discussed with AC-impedance and voltage-transient spectra as described bellow.

Figure 2 shows the Nyquist plot of a complete solar cell, TiO_2/Dye/modified CuSCN, applied (a) carbon paste and (b) graphite on modified CuSCN under dark and 0.5 V forward bias voltage. Curve (b) has a small deformed arc at high frequency, a moderate arc at moderate frequency and Warburg characteristic at lower frequency. The deformed arc at high frequencies may correspond to the overlap behavior of hole diffusion in the bulk CuSCN and charge transfer at CuSCN/Graphite interface. The second arc may correspond to the charge-transfer mechanism (or recombination) at TiO_2/CuSCN interface. The straight line at lower frequency region is a characteristic behavior of Warburg impedance due to mass transportation.[11] Here we forcus only on characteristic behavior at very low frequencies, where ion difussion has taken place. This Warburg pattern at lower frequencies indicates the presence of ionic conductivity of the modified CuSCN. Curve (a) is relevant to the cell of TiO_2/Dye/modified CuSCN/C paste. It has a very small deformed arc at high frequencies (CuSCN/Carbon paste interface), a moderate arc at moderate frequency (TiO_2/CuSCN interface) and a small arc at low frequency (ion diffusion).[11] Due to the presence of wetting condition by adding carbon paste on the modified CuSCN materal in the DSSC the ion diffusion or mass transportation has improved, and that chracteristic behavior can be seen as a small arc at low-frequency region as in the liquid-electrolyte-based solar cell, Figure 2(ii).[20] This improvement of ionic behavior of the solar cell may be one of the factors for the improved efficiency of the solar cell (a).



(i)

(ii)

Figure 2. (i) Nyquist plots for the solar cells of TiO_2/N719/modified CuSCN, (a) carbon paste and (b) graphite applied on the modified CuSCN in the solar cell. (ii) Enlargement of the high-frequency region.

Even if small ionic conductivity is present in the modified CuSCN, its effect on an all-solid-state solar cell is negligible due to very high impedance in the solid phase. But in the presence of carbon paste this ionic conductivity becomes effective, and it contributes to increasing current density of the solar cell as shown in the Figure 1a. Other possible factors for the improvement of the final efficiency of cells fabricated with carbon paste are the improvement of the interface of CuSCN/counter electrode due to lowering the charge-transfer resistance and the extension of reactive area of the counter electrode.

Figure 3 shows the voltage-transient spectra of solar cell prepared (b) by applying graphite on modified CuSCN and (a) by applying carbon paste on modified CuSCN. It can be clearly seen that all-solid-state solar cell (curve b) has fast decay of photogenerated electrons while cabon-paste-based solar cell (curve a) has very slow decay as shown in Figure 3. This slow decay of photogenerated electrons indicates the enhancement of the lifetime of electrons, primarily due to surpressed back electron transfer for recombination in the carbon-paste-based solar cell and hence improves the voltage of the system as shown in the *I–V* curve (Figure 1a).

As far as the shape of the electron decay process is concerned, curve (b) shows single exponential decay while curve (a) shows visibly two exponential decays which may

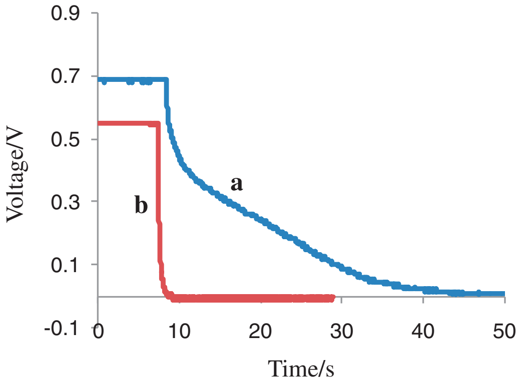


Figure 3. Photovoltage transient of the solar cell TiO_2/N719/modified CuSCN, (a) carbon paste and (b) graphite applied on the modified CuSCN in the solar cell.

correspond to the mainly two recombination process as shown in Figure 3. It is interesting to note this two exponential decay process which cannot be observed in the solid-state solar cell and the liquid-electrolyte-based solar cell.[21,22] Two exponential decay process is mainly attributed to the recombination of electrons in TiO_2 with the holes in CuSCN and with the chemical component such as $(SCN)_2$ present in the cell (assuming that the dye regeneration is very fast as in the liquid-electrolyte-based DSC). Since ionic behavior is present in the modified CuSCN material as explained in the AC impedance analysis above, existence of a small amount of redox species such as $(SCN)_2/SCN^-$ in the hole transportation layer is probable. We have revealed in our recent paper the possibility of exiting trapped SCN^- and $(SCN)_2$ in the modified CuSCN material.[11] Therefore, in the wetting condition by applying carbon paste on the modified CuSCN, the redox species $((SCN)_2/SCN^-)$ effectively affect to the efficiency of the solar cell.

Even though the ionic nature of modified CuSCN is improved due to wetting by applying carbon paste, the solar cell mainly works under hole-conduction mechanism under illumination. It is noteworthy for further study of this iodine-free thiocyanate-based quasi-solid-state dye-sensitized solar cell (in cooperation with lithium ion) for stable and long lasting application in the future.

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