Highly electrocatalytic hybrid silver nanowire-graphene counter electrode for $\text{Co}^{3+/2+}$ redox mediator based dye-sensitized solar cells

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Abstract

Solution processed hybrid silver nanowire (AgNW)-graphene nanoplatelets (GNP) films were prepared and the electrocatalytic activity for the cobalt redox electrolyte in dye-sensitized solar cells (DSSCs) was examined. Cyclic voltammograms and Tafel polarization measurements confirmed the superior electrocatalytic activity of AgNW-GNP electrode than that of standard Pt counter electrode (CE). Electrochemical impedance spectroscopic (EIS) study also revealed the lower charge transfer resistance (R_{ct}) of AgNW-GNP compared to Pt based CE. However, the resistance of the electrolyte diffusion was higher for the AgNW-GNP based CE resulted from the porous structure of the hybrid CE. The photoconversion efficiencies of the DSSC prepared with AgNW-GNP based CE was found to be 2.44%, which was comparable to that of Pt based DSSC, 2.55%. This study proposed an alternative low-cost cathode material for the cobalt redox mediator based DSSCs.

Key words: Silver nanowire, Graphene platelet, Counter electrode, Cyclic voltammetry, Dye-sensitized solar cells

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Highlights:

- Highly efficient hybrid silver nanowire-graphene counter electrodes for dye-sensitized solar cells.
- Homogeneous electrocatalytic sites created by graphene platelets.
- Superior electrocatalytic properties of silver nanowire by graphene over coating in $\text{Co}^{3+}/\text{Co}^{2+}$ electrolyte.
- Low interfacial charge transfer resistance of silver nanowire-graphene based counter electrode.

1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be one of the most promising photovoltaic technologies owing to their high efficiency, low cost and ease of fabrication [1,2]. A typical DSSC consists of a mesoporous semiconductor film coated with light-harvesting dye molecules as a working electrode, a redox electrolyte and a catalytic cathode material coated on transparent conductive oxide (TCO) substrate as a counter electrode (CE) [3]. Among them, the CE performs two critical functions: it collects the electrons flowing from the external circuit and catalyzes the reduction of counter ion, thereby realizing the regeneration of the sensitizer [4]. Although Pt deposition on F-doped tin oxide (FTO) conductive glass is a conventional CE for DSSCs due to its high electrocatalytic property and resistance against most of the aggressive electrolytes but the limited availability and high cost of Pt is an obstacle for the commercialization of DSSCs [5]. Therefore, it is worthwhile to develop low-cost and efficient CEs using abundant materials.

Many attempts have been made to replace Pt by other materials for the CEs in DSSCs [6,7]. However, the corrosive nature of iodide based electrolyte limits the use of other metals such as silver, gold as a cathode material in DSSCs [8]. In this context, the development of cobalt based mediator system opened the door of using non-Pt metals as cathode materials [9]. Besides the non-corrosive nature, cobalt complex redox mediator has some other attractive features such as tunability of redox potential, large inner sphere reorganization energy, and non-Pt metals can also be a candidate as cathode material [10]. In particular; silver nanowires (AgNWs) are promising nano material for the energy sector due to their unique electrical and optical properties. Several papers recently have been reported on the application of AgNW in organic photovoltaics using PEDOT:PSS as a work function tuner to achieve reasonable catalytic property [11]. AgNW based counter electrode fabricated with organic hole conductor, 2,2,7,7- tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene

(spiro-OMeTAD), were also reported in the solid state DSSCs [12]. In addition, graphene and other carbon based materials also have attracted much attention as cathode materials for the DSSCs, due to their high surface area and excellent catalytic property [13,14].

In this work, we firstly applied the AgNW based CEs in DSSCs employing the cobalt bipyridyl redox electrolyte. In addition, AgNW based CE with graphene nanoplatelets (GNP) was also prepared and employed as a cathode material in cobalt electrolyte based DSSCs. The electrocatalytic and photovoltaic performances of four kinds of electrodes (AgNW, GNP, AgNW-GNP, Pt) were thoroughly examined and compared.

2. Experimental

Silver nanowires (AgNWs) having the diameter ranging from 30–80 nm with the aspect ratio of ~300 were synthesized by modified polyol method. The detailed synthetic procedures could be found elsewhere [15]. AgNWs in isopropyl alcohol (IPA) with the concentration of 10 mg mL⁻¹ were sonicated for 30 s and coated on oxygen plasma treated fluorine doped tin oxide (FTO) glass by doctor blade technique maintaining the wet thickness of ~20 μm. On the other hand, graphene nanoplatelets (xG Science, Grade C-750 m² g⁻¹) consist of several sheets of graphene with an overall thickness of ~2 nm (ranging from 1 to 15 nm) and the particle diameter less than 2 μm were dispersed in IPA to prepare the concentration of 3.0 mg mL⁻¹. The dispersion was centrifuged at 7000 rpm to remove the larger platelets, and the supernatant containing a few layer of graphene were collected which was reasonably stable without any marked sedimentation. The graphene dispersion was spin-coated on previously prepared AgNW film at 1000 rpm, and thermally annealed at 150 °C for 20 min. The mass loading of graphene platelets was 0.29 μg cm⁻².

Cobalt redox mediator, i.e., Co^{3+/2+} tris(4,4'-di-*tert*-butyl-2,2'-bipyridyl) {[Co(*t*-Bu₂bpy)₃]^{3+/2+}}, was synthesized according to the procedure reported in an our previous paper

[16]. The final electrolyte was composed of 0.22 M $[\text{Co}(t\text{-Bu}_2\text{bpy})_3]^{3+/2+}$, 0.20 M LiClO_4 (Aldrich, 99.99%), 0.20 M 4-*tert*-butylpyridine (Aldrich, 96%), and 0.02 M NOBF_4 (Aldrich, 95%), in acetonitrile.

TiO_2 (Ti-Nanoxide D, Solaronix SA) film with a thickness of $\sim 8\ \mu\text{m}$ was sensitized by ruthenium sensitizer (N719, Solaronix SA) and assembled with the predrilled counter electrode by using a Surlyn[®] spacer. Then few drops of cobalt electrolyte were injected into the cell. A Pt sputtered CEs were also prepared for comparison. Cyclic voltammograms (CVs) were recorded using Autolab PGSTAT12 (the Netherlands) in a three electrodes configuration. The applied voltage ranged from -0.40 to 0.60 V (with respect to a saturated Ag/AgCl reference electrode) at a scan rate of $100\ \text{mV s}^{-1}$. The diluted electrolyte for the CV measurement consisted of 2.2 mM Co^{3+} complex, 0.2 mM NOBF_4 and 0.1 M LiClO_4 in acetonitrile. A Pt wire was used as a counter electrode. Symmetric dummy cells, consisting of two identical FTO-glass coated with the catalytic materials, were used for the electrochemical impedance spectroscopic (EIS) and Tafel polarization study. EIS measurements were carried out with an impedance analyzer (CH Instruments, Inc., Austin, TX). The frequency range was 10^{-1} – 10^5 Hz and the perturbation amplitude was 10 mV. All measurements were performed at room temperature in the dark condition at 0 V. A ZView software (Scribner Associates Inc.) was used to fit the EIS data. The rest of the DSSC preparation procedure and characterization methods were described in the literature [17].

3. Results and discussion

Fig. 1 shows Field Emission Scanning Electron Microscope (FE-SEM) images of silver nanowire (AgNW) and AgNW-graphene nanoplatelets (AgNW-GNP) hybrid film on FTO glass. The diameter of AgNW was ca. 30–80 nm (Fig. 1d), and the sparse coverage and cross-linked network of AgNW on FTO surface showed uncovered areas of as large as $10\ \mu\text{m}$

shown in Fig. 1a. After GNPs were over-coating on AgNW film (Fig. 1b), the surface was shown to have homogeneous coverage of FTO surface. The over stacking of graphene platelets assumed to be appeared as black spot on AgNW film in Fig. 1b. It was speculated that during the spin coating, only a few layer graphene platelets covered the open areas and the thick platelets were removed by the centrifugal force. In Fig. 1c, the cross-sectional view indicated the close contact between FTO and AgNW and the thickness of AgNW film corresponds to roughly 2-4 nanowires.

Fig. 2a represents the optical transmittance spectra of Pt, AgNW, GNP and AgNW-GNP films deposited on FTO glass. The AgNW film showed 17.16% higher transmittance compared to Pt film. AgNW-GNP hybrid film displayed similar transmittance to Pt. The transmittance difference between AgNW and AgNW-GNP hybrid film at 550 nm was ~12.2 % which implies that about 5 layered of graphene sheet was over-coated on the AgNW film, consistent with the result obtained for graphene platelet film only [18].

Cyclic voltammetric (CV) measurements were conducted for different types of cathode materials on FTO-glass and presented in Fig. 2b. A pair of well-defined redox peak for Pt, GNP and AgNW-GNP based electrodes was observed, whereas, a pair of broad peak with smaller current was obtained for AgNW film. The experimental results are listed in Table 1. The AgNW exhibited the lower magnitude of cathodic current density, ca. 0.18 mA cm^{-2} compared to that of AgNW-GNP ca. 0.69 mA cm^{-2} for the cobalt bipyridal complex. However, the GNP exhibited little higher electrocatalytic activity compared to Pt which might be related to the higher surface-to-volume ratio of GNP, consistent with the literature [19]. On the other hand, the highest catalytic activity of the AgNW-GNP electrode may be attributed to the individual contribution of slightly electro-active AgNW and moderate electro-active GNP. It is also believed that the compact layer of GNP on the highly porous AgNW film as shown in Fig. 1b would provide relatively higher interfacial surface area

contacted with cobalt redox electrolyte as a result of the creation of active catalytic sites encountered by GNP. The ratio of the J_{pa} to J_{pc} was near 1, which resembled the quasi reversibility of electrochemical conversion [20].

To investigate the peak current density related to the resistance variation of different electrodes, Tafel polarization measurements were carried out and presented in Fig. 2c. The exchange current density (J_o) was calculated and presented in Table 1. The variation of J_o is closely associated with charge transfer resistance (R_{ct}) according to the eqn (1) [7]. AgNW-GNP electrode displayed 2.76 mA cm⁻² more exchange current density than the standard Pt which indicates the higher electrocatalytic activity compared to Pt.

$$J_o = \frac{RT}{nFR_{ct}} \quad (1)$$

Electrochemical impedance spectra (EIS) of symmetric dummy cells prepared by different cathode materials were fitted by an equivalent circuit analogue (Fig. 3a) and plotted in Fig. 3b. The semicircle in high frequency regime is related with the charge transfer resistance (R_{ct}) between CE and cobalt redox mediator. The semicircle in low frequency range indicated the resistance of electrolyte diffusion (W) [16]. The R_{ct} value of GNP (1.81 Ω cm²) was found to be lower than standard Pt (16.47 Ω cm²) based electrode which was also observed by other report [21,22]. But a significant decrease in the magnitude of R_{ct} of AgNW-GNP, even lower than that of GNP was observed. AgNW-GNP exhibited an R_{ct} value of 1.42 Ω -cm² which is quite smaller than 6299.19 Ω -cm² of AgNW only as shown in Fig. S1. It is also worthwhile to mention that the tendency of R_{ct} variation in Table 1 with J_o of different electrodes is in good agreement with the relation in eqn (1) along with the peaks observed in CV analysis (Fig. 2b). It is also known that the limiting current density, J_{lim} , in Tafel polarization curve (Fig. 2c) has a positive relation with the diffusion coefficient and the diffusion coefficient is also correlated negatively with the diffusion impedance, W [7]. The

diffusion resistance, W , of GNP and AgNW-GNP was higher than that of standard Pt. Due to the porous surface of GNP and AgNW-GNP, cobalt complex suffer from weaker penetration-take out difficulties which lead to increase of diffusion resistance. On the other hand, Pt CE has a flat surface and the bulky cobalt complex might not face any restricted diffusion except its intrinsic slower mobility compare to traditional iodine based electrolyte. After performing the comprehensive analysis of CV, Tafel polarization and EIS results, we can conclude that the AgNW-GNP based hybrid cathode material exhibited the highest electrocatalytic activity compare to the AgNW, GNP and Pt electrodes.

Fig. 4 shows the $J-V$ characteristic curves of the DSSCs prepared by Pt, AgNW, GNP and AgNW-GNP CEs. The open circuit voltage (V_{oc}) and short circuit current (J_{sc}) were somewhat closer for all samples as listed in Table 2. The difference among the conversion efficiencies was relied on the corresponding fill factors (FF) which affected the photoconversion efficiency (PCE) significantly. Both of R_{ct} and W has serious impact on FF . The trend of catalytic activity and R_{ct} among AgNW, GNP and AgNW-GNP was also consistent with that of the FF s and PCEs as well. Among AgNW, GNP and AgNW-GNP, the AgNW-GNP had the highest catalytic activity and had the lowest R_{ct} , resulted in the highest FF and PCE. Due to the lower R_{ct} values of GNP and AgNW-GNP, it was expected that these devices should show higher PCE compare to Pt. But practically it was not observed because of the higher diffusion resistance which limits the faster regeneration of cobalt species. The slightly higher PCE for Pt based DSSC with inferior electrocatalytic property might be related to the light trapping by internal reflection during illumination [23]. On the other hand, the diffused reflectance of AgNW was countervailed by graphene platelet over-coated on AgNW film. The as prepared AgNW-GNP hybrid CEs based DSSCs showed 95.69% relative PCE compared to the DSSCs made of sputter Pt CEs.

The possible reasons behind the significant electrochemical performance enhancement of the AgNW-GNP based hybrid CEs is due to the compensation of irrational catalytic sites related by GNP over-coating as schematically illustrated in Fig. 5. The GNP eased the accessibility of larger catalytic sites for effective $\text{Co}^{3+}/\text{Co}^{2+}$ conversion. It is important to mention that the DSSCs under the combination of N719 (Ruthenizer 535-bisTBA) sensitizer and cobalt bipyridal complex ($[\text{Co}(\text{t-Bu}_2\text{bpy})_3]^{n+}$) as a redox couple exhibited relatively lower photoconversion efficiency compared to conventional I_3^-/I^- based electrolyte [16,24]. Particularly, the bulkier size of the cobalt bipyridal complex leads to insufficient mass transport of the oxidized species through the mesoporous electrode which limit the photocurrent and hereby lower the photovoltaic performances in DSSCs [25]. Thus with suitable engineering in the photoelectrode and sensitizer would expect to improve the absolute PCE values. However, this study showed the potentiality of using metal nanowire with graphene as a hybrid CE for cobalt electrolyte based DSSCs which may be an efficient alternative to conventionally expensive Pt CE.

4. Conclusions

In this study, four different types of CEs (Pt, AgNW, GNP and AgNW-GNP) were prepared for the cobalt redox electrolyte based DSSCs. Both AgNW and GNP showed inferior catalytic activity for the cobalt redox electrolyte. However, hybrid AgNW-GNP exhibited a synergistic enhancement of electrocatalytic activity for cobalt species. The electrocatalytic performances were thoroughly studied by cyclic voltammetry, Tafel polarization and electrochemical impedance spectroscopic techniques. Owing to the lower R_{ct} , AgNW-GNP based DSSC showed comparable photoconversion efficiency to that of Pt based counter electrode (CE) in spite of the higher resistance of electrolyte diffusion. These results may provide an insight into the development of low-cost and efficient hybrid type AgNW-GNP CE for the cobalt redox electrolyte.

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References

- [1] B. O'Regan, M. Gratzel, *Nature*. 353 (1991) 737-740.
- [2] M.D. McGehee, *Science*. 334 (2011) 607-608.
- [3] M.K. Parvez, I. In, J.M. Park, S.H. Lee, S.R. Kim, *Solar Energy Mater. Solar Cells*. 95 (2011) 318-322.
- [4] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, *Chem. Commun.* (2009) 2198-2200.
- [5] T.N. Murakami, M. Grätzel, *Inorg. Chim. Acta*. 361 (2008) 572-580.
- [6] M. Al-Mamun, J. Lim, Y. Sung, S. Kim, *Chem. Lett.* 42 (2013) 31-33.
- [7] M. Wu, X. Lin, Y. Wang, L. Wang, W. Guo, D. Qi, X. Peng, A. Hagfeldt, M. Gratzel, T. Ma, *J. Am. Chem. Soc.* 134 (2012) 3419-3428.
- [8] M. Wang, N. Chamberland, L. Breau, J. Moser, R. Humphry-Baker, B. Marsan, S.M. Zakeeruddin, M. Gratzel, *Nat Chem*. 2 (2010) 385-389.
- [9] A. Yella, H. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W. Diau, C. Yeh, S.M. Zakeeruddin, M. Grätzel, *Science*. 334 (2011) 629-634.
- [10] T.W. Hamann, *Dalton Trans.* 41 (2012) 3111-3115.
- [11] W. Gaynor, G.F. Burkhard, M.D. McGehee, P. Peumans, *Adv Mater*. 23 (2011) 2905-2910.

- [12] B.E. Hardin, W. Gaynor, I. Ding, S. Rim, P. Peumans, M.D. McGehee, *Organic Electronics*. 12 (2011) 875-879.
- [13] L. Kavan, J. Yum, M.K. Nazeeruddin, M. Gratzel, *ACS Nano*. 5 (2011) 9171-9178.
- [14] R. Bajpai, S. Roy, P. Kumar, P. Bajpai, N. Kulshrestha, J. Rafiee, N. Koratkar, D.S. Misra, *ACS Appl. Mater. Interfaces*. 3 (2011) 3884-3889.
- [15] L. Hu, H.S. Kim, J. Lee, P. Peumans, Y. Cui, *ACS Nano*. 4 (2010) 2955-2963.
- [16] J. Kim, K.J. Lee, S.H. Kang, J. Shin, Y. Sung, *J. Phys. Chem. C*. 115 (2011) 19979-19985.
- [17] S. Kim, M. Al-Mamun, Y. Ko, *Chemical Physics Letters*. 538 (2012) 77-81.
- [18] S. Bae, H. Kim, Y. Lee, X. Xu, J. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y.I. Song, Y. Kim, K.S. Kim, B. Ozyilmaz, J. Ahn, B.H. Hong, S. Iijima, *Nat Nano*. 5 (2010) 574-578.
- [19] L. Kavan, J. Yum, M. Grätzel, *Nano Lett*. 11 (2011) 5501-5506.
- [20] L. Wan, S. Wang, X. Wang, B. Dong, Z. Xu, X. Zhang, B. Yang, S. Peng, J. Wang, C. Xu, *Solid State Sciences*. 13 (2011) 468-475.
- [21] L. Wang, E.W. Diau, M. Wu, H. Lu, T. Ma, *Chem. Commun*. 48 (2012) 2600-2602.
- [22] M. Al-Mamun, J.-Y. Kim, Y.-E. Sung, J.-J. Lee, S.-R. Kim, *Chemical Physics Letters*. 561–562 (2013) 115-119.

- [23] T. Battumur, S.H. Mujawar, Q.T. Truong, S.B. Ambade, D.S. Lee, W. Lee, S. Han, S. Lee, *Current Applied Physics*. 12, Supplement 1 (2012) e49-e53.
- [24] S.A. Sapp, C.M. Elliott, C. Contado, S. Caramori, C.A. Bignozzi, *J. Am. Chem. Soc.* 124 (2002) 11215-11222.
- [25] B.M. Klahr, T.W. Hamann, *J. Phys. Chem. C*. 113 (2009) 14040-14045.

Figure Captions:

Fig. 1. FE-SEM images (a, b and d) top-view and (c) cross sectional view of AgNW and AgNW-GNP film on FTO-glass.

Fig. 2. (a) Optical transmittance spectra (b) cyclic voltammograms and (c) Tafel polarization curves of Pt, AgNW, GNP and AgNW-GNP based electrode in $\text{Co}(\text{t-Bu}_2\text{bpy})_3]^{3+/2+}$ electrolyte.

Fig. 3. (a) Equivalent circuit diagram for fitting the electrochemical impedance spectral data of half cells made of Pt, AgNW, GNP and AgNW-GNP and (b) Nyquist plots (inset shows the comparison of GNP and AgNW-GNP only) of Pt, GNP and AgNW-GNP respectively. Full symbols represent the experimental data and solid lines represent the model fitting (Fig. 3a).

Fig. 4. Comparison of $J-V$ characteristic curves of DSSCs fabricated with Pt, AgNW, GNP and AgNW-GNP based counter electrodes.

Fig. 5. Schematic illustration and mechanism of over coated graphene nanoplatelets on the open areas of AgNW network for enhanced catalytic property.

Table 1
Cathodic peak current density, electrochemical impedance parameters and exchange current density of different types of counter electrodes.

CEs	J_{pc}	R_s	R_{ct}	CPE:B	W	J_o
	(mA cm ⁻²)	(Ω)	(Ω cm ²)	(μF cm ⁻²)	(Ω cm ²)	(mA cm ⁻²)
Pt ^a	0.30	15.37 ^a	16.47 ^a	138.78 ^a	17.91 ^a	21.52
AgNW	0.18	13.89	6299.19	3.11	15246.84	1.76
GNP	0.41	15.77	1.81	368.49	53.26	2.09
AgNW-GNP	0.69	14.79	1.42	759.43	47.15	24.28

^aThe data was collected from reference [22].

Table 2

Transmittance and photovoltaic performances of DSSCs with Pt, AgNW, GNP and AgNW-GNP counter electrodes.

CEs	$\% T$ (550 nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η (%)
Pt	69.9	0.62	6.77	0.61	2.55
AgNW	81.8	0.62	6.20	0.30	1.16
GNP	88.8	0.58	6.69	0.40	1.57
AgNW-GNP	69.6	0.61	6.88	0.59	2.44

Figure 1
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Appendix A: Supplementary Information

Highly electrocatalytic hybrid silver nanowire-graphene counter electrode for $\text{Co}^{3+/2+}$ redox mediator based dye-sensitized solar cells

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Fig. S1: Nyquist plot of AgNW based symmetrical cell with the active area of 0.49 cm^2 . Inset shows the equivalent circuit diagram for fitting the electrochemical impedance spectral data. Open symbols represent the experimental data and solid line represents the model fitting.

References:

- [1] S. Huang, H. Sun, X. Huang, Q. Zhang, D. Li, Y. Luo, Q. Meng, *Nanoscale Res. Lett.* 7 (2012) 1-7.
- [2] L. Kavan, J. Yum, M. K. Nazeeruddin, M. Grätzel, *ACS Nano*. 5 (2011) 9171-9178.