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Impact of Electrocatalytic Activities of Doping Surfactants on Polyaniline as Pt-free Counter Electrode in DSSCs

Kezhong Wu, Qiongwei Zhao, Lei Chen, Bei Ruan, Mingxing Wu[*]

Key Laboratory of Inorganic Nano-materials of Hebei Province, Department of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, 050024, P.R. China
[*]E-mail: wukzh688@163.com

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A series of composite counter electrodes were chemically synthesized by doping surfactants with, Ganodermalucidum Polysaccharide (GLP), Sodium dodecyl sulfate (SDS) and Ethylenediaminetetraacetic acid (EDTA) disodium salt on polyaniline (PANI) for Dye-sensitized solar cells (DSSCs). Surfactants can reduce the surface tension of the liquid, along with changing the conductivity and morphology of PANI. Scanning electron microscopy (SEM) results showed that PANI electrode morphology was strongly influenced by the surfactant. The electrochemical activity of surfactant-doping PANI was investigated by cyclic voltammetry (CV) curve, electrochemical impedance spectroscopy (EIS), Tafel polarization curve and current density–voltage curves (*J*-*V*). The power conversion efficiency (PCE) of PANI-doped CEs with additions of SDS, GLP and EDTA disodium salt (4.25%, 2.69% and 2.51%) were higher than 2.29% for PANI CE without doping. These results indicate a potential application of surfactants doped polyaniline as counter electrode in cost-effective DSSCs.

Keywords: Dye-sensitized solar cells; Counter electrode; Polyaniline; Surfactant; Power conversion efficiency

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs), as electrochemical devices that can convert solar energy into electrical energy, have many advantages such as low price, easy manufacturing, zero emission and high efficiency. Most of the DSSCs are mainly composed of an electrolyte, a counter electrode(CE) and a dye-sensitized photoanode [1-3]. CE is mainly composed of a conductive substrate and a catalytic material. The conductive substrate is used to collect the electrons of the external circuit, and the catalytic material serves to catalyze the mutual conversion of the redox electrons in the electrolyte to ensure the reduction and regeneration of the dye [4-8]. Pt has excellent catalytic activity and conductivity as CE material. However, Pt can be slightly corroded due to reaction with I_3^-/I^- electrolyte, resulting in a decrease in battery life. In addition, the expense for Pt increases the production cost of DSSCs which is not suitable for industrial production [9-13]. In order to reduce the costs, people began to search for low-cost electrode materials, such as alloy CE materials [14], metal oxides materials [15], carbon materials [16] and conductive polymer materials [17].

In many organic conductive polymers, Polyaniline (PANI) has the advantages of being low cost, simply synthesized, and having higher conductivity [18]. Due to the networked porous structure and high specific surface area of PANI, it is more conducive to the diffusion of the electrolyte and easily improves the electrocatalysis of I_3^-/I^- [19-24]. Although PANI is a promising CE catalytic material, its catalytic performance is further improved by surfactants. Surfactants can reduce the liquid's surface tension, change the PANI morphology and improve its conductivity [25-28]. In this work, three surfactant-doped PANI composite electrodes were synthesized by chemical oxidation using Ganodermalucidum Polysaccharide (GLP), Sodium dodecyl sulfate (SDS) and Ethylenediaminetetraacetic acid (EDTA) disodium salt. The electrocatalytic performance was evaluated by CV, EIS and Tafel polarization curves. Finally, the photovoltaic performance of the PANI composite electrode was evaluated by a *J-V* curve.

2. EXPERIMENTAL

2.1 Preparation of working electrode

1 mol aniline and 0.01mol surfactants (GLP/SDS/ EDTA disodium salt) were first dissolved in 20 ml of 2 $mol \cdot L^{-1}$ HCl solution, to which, another 30 ml of 2$mol \cdot L^{-1}$ HCl containing 0.6 mol potassium dichromate was added slowly. The mixture was stirred for 5 h. To remove the excess potassium dichromate, surfactants and byproducts, the as-prepared PANI nanofibers were washed with 2 $mol \cdot L^{-1}$ HCl solution 3 times and collected by centrifugation Finally, PANI-doped composites were dried under vacuum at 30^0C for 24 hours. Pure polyaniline is prepared by the same method, excluding the surfactant.

2.2 Cell fabrication

The excellent optical transparency of FTO was pretreated using an ultrasonic bath in detergent, ethanol, double-distilled water and isopropyl alcohol for 30 min. 0.1250g of PANI-doped with blank (a), GLP (b), SDS (c), and EDTA disodium salt (d) respectively, were dissolved in 6 mL of isopropanol. The solution was then ultrasonically dispersed for 1 h to achieve the spray paste. The prepared paste was then painted on FTO glass with a spray gun and finally the PANI-doped CEs were dried under vacuum.

The active area of the DSSC was 0.16 cm^2. Symmetrical cell was fabricated with two identical CE clipping the electrolyte. The cells were sealed with a hot-melt surlyn film. The photoanode used in this work was an 8 μm thick TiO_2 film sensitized with N719 dye. The electrolyte contains 0.1M of LiI, 0.6M 1-propyl-3-methylimidazolium iodide, 0.07M I_2, 0.5M 4-tert-butyl pyridine, and 0.1M guanidinium thiocyanate in 3-methoxypropionitrile (MPN).

3. RESULTS AND DISCUSSION

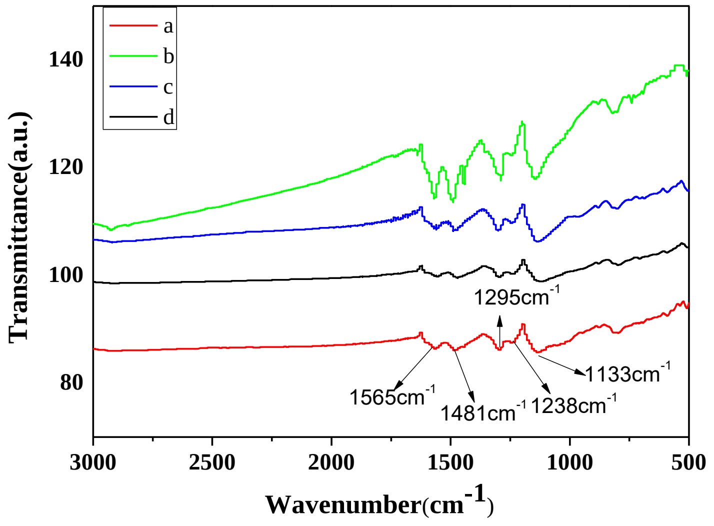

Figure 1. FTIR curves of chemically synthesized (a) PANI, (b) GLP PANI-doped, (c) SDS PANI-doped and (d) EDTA disodium salt PANI-doped counter electrode.

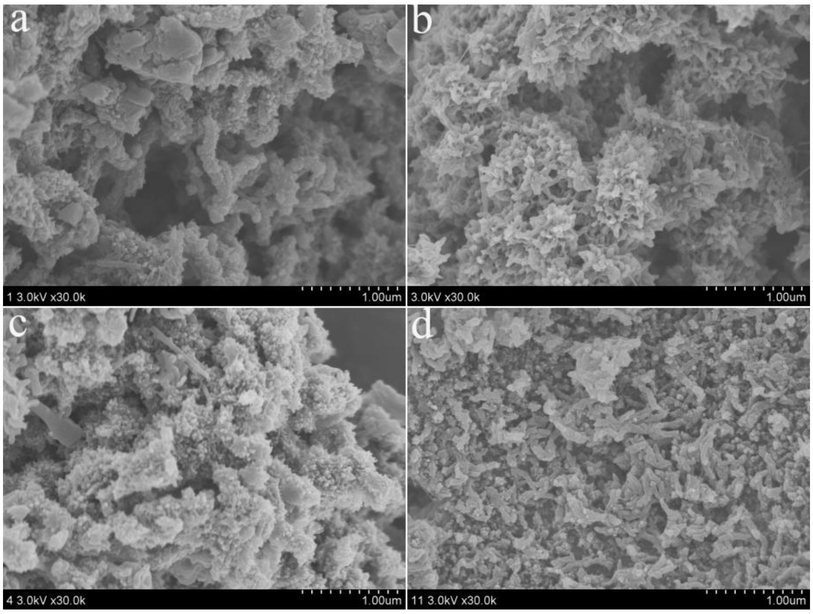

Figure 2. SEM images of the synthesized (a) PANI, (b) EDTA disodium salt PANI-doped, (c) GLP PANI-doped, (d) SDS PANI-doped.

The chemically synthesized PANI and PANI-doped composites were characterized by FTIR spectroscopy as shown in Fig.1. The infrared absorption showed characteristic peaks of PANI present near the wavenumbers of 1565 cm^{-1}, the C=C stretching vibration of PANI at 1481 cm^{-1}, the C-N stretching vibration of in PANI at 1295 cm^{-1}, C-N stretching vibration of quinone ring units at 1238 cm^{-1} and in-plane bending vibration of the aromatic ring C-H at 1133 cm^{-1}. The vibrational absorption peaks of PANI-doped composites are similar to those of pure PANI. The results showed that the addition of these three surfactants did not alter the framework structure of PANI, suggesting the characteristic absorption peaks of PANI-doped hybrids to be same as PANI, but in the presence of surfactants the peaks are slightly shifted.

Fig.2 shows a SEM image containing PANI(a), GLP doped PANI(b), SDS doped PANI(c) and EDTA disodium salt doped PANI(d) electrode materials. It can be seen from Figure 2-a, that chemically synthesized PANI has a rod-like structure with small surface-dense particles. Figure 2-b shows that the surface of GLP doped PANI is clustered together in the form of more and denser particles, and GLP doped PANI surface particles are more dense than pure PANI-surface particles. As can be seen in Figure 2-c, SDS-doped PANI is composed of rods of uniform size and smooth surface. The SEM images clearly demonstrate the effect of addition of three surfactants on the transformation of the original PANI morphology. Figure 2-d shows that EDTA disodium salt doped PANI microstructure is coral and uniform in size.

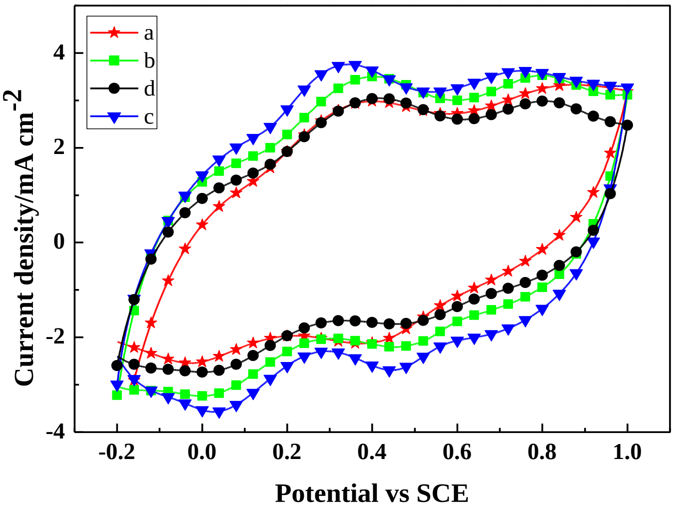

Figure 3. CV curves of (a) PANI, (b) GLP PANI-doped, (c) SDS PANI-doped (d) EDTA disodium salt PANI-doped

Fig.3 shows the CV curve of chemically synthesized PANI(a), GLP doped PANI(b) , SDS doped PANI(c) and EDTA disodium salt doped PANI(d) counter electrode. The redox potentials of PANI, GLPs, SDS doped PANI and EDTA disodium salt were found to be 431, 407, 318, and 417 mV respectively. The above data shows that the addition of surfactants reduces the redox potential difference to some extent and increases the adhesion of PANI to the substrate. The peak current densities of PANI, EDTA disodium salt doped PANI, GLPs doped PANI and SDS doped PANI at low potential were found to be 2.546, 2.735, 3.239 and 3.573 mAcm^{-2} respectively. Addition surfactants enhanced the electrochemical performance of PANI.

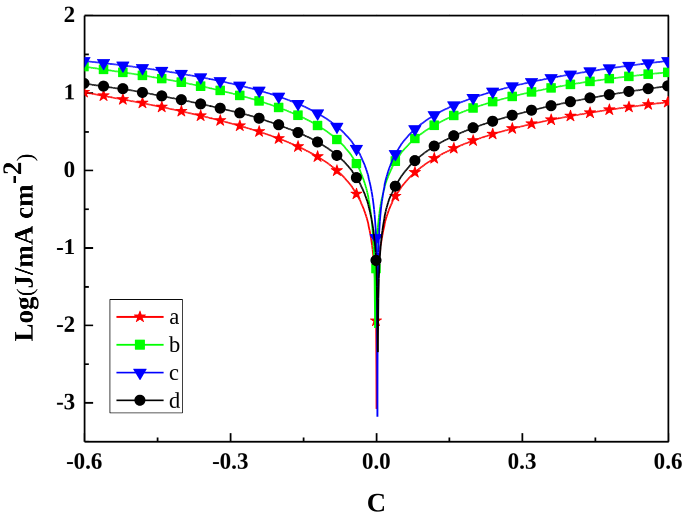

Figure 4. Polarization curves of (a) PANI, (b) GLP PANI-doped, (c) SDS PANI-doped and (d) EDTA disodium salt PANI-doped

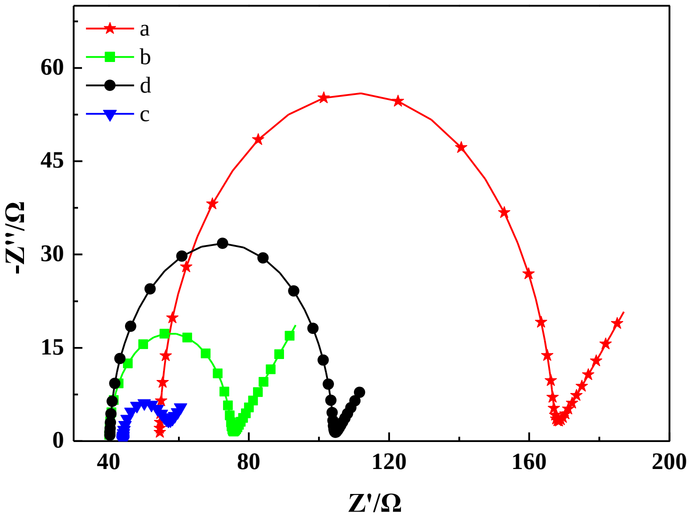

Figure 5. Nyquist curves of (a) PANI, (b) GLP PANI-doped, (c) SDS PANI-doped and (d) EDTA disodium salt PANI-doped

Fig.4 shows the Tafel curve of chemically synthesized PANI(a), GLP doped PANI(b) , SDS doped PANI(c) and EDTA disodium salt doped PANI(d). As can be seen from the figure, J_0 of surfactants doped PANI are greater than that of pure PANI. Hence, the electrochemical activity of PANI doped with all three surfactants was concluded to be stronger than that of pure PANI.

Fig.5 shows the Nyquist curves of PANI(a), GLP doped PANI(b) , SDS doped PANI(c) and EDTA disodium salt doped PANI(d). The R_s value of PANI, GLP doped PANI, SDS doped PANI, and EDTA disodium salt doped PANI were 54.6 Ω, 40.16 Ω, 44.08 Ω, and 40.35 Ω, respectively. The R_s

values of the three surfactant-doped PANI composite electrodes were found to be approximately equal, indicating that they have similar binding ability to the substrate and are stronger than the binding ability of PANI to the substrate. The R_{ct} value of PANI, EDTA disodium salt doped PANI, GLP doped PANI and SDS doped PANI were 111.7 Ω, 63.47 Ω, 34.56 Ω and 11.55 Ω respectively. The smaller the R_{ct} value, the faster the electrons are delivered at the electrode-electrolyte interface and the more electrochemically active the electrode.

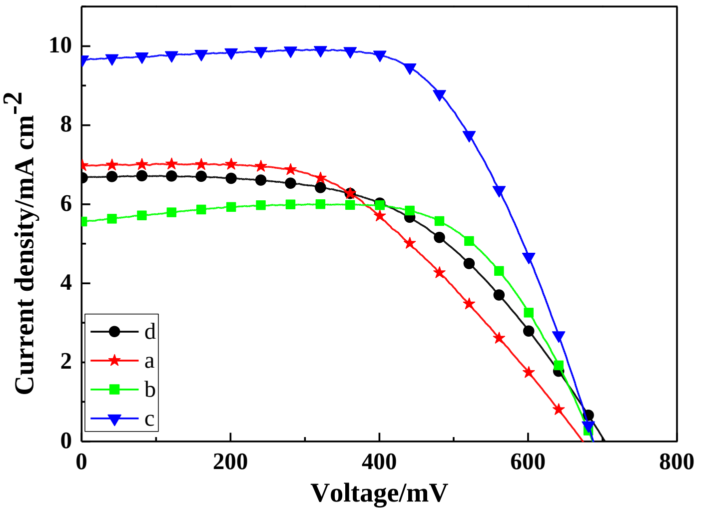

Figure 6. *J-V* curves of (a)PANI, (b) GLP PANI-doped, (c) SDS PANI-doped and (d) EDTA disodium salt PANI-doped

Table 1. Photovoltaic parameters of chemically synthesized PANI, GLP PANI-doped, EDTA disodium salt PANI-doped, SDS PANI-doped, counter electrode *J-V* curve.

Counter electrodes	V_{oc}/V	J_{sc}/mAcm^{-2}	*FF*	η/%
PANI- (a)	0.674	7.00	0.49	2.29
PANI-doped(d)	0.704	6.69	0.53	2.51
PANI-doped(b)	0.688	5.56	0.70	2.69
PANI-doped(c)	0.688	9.69	0.64	4.25

Fig.6 shows the *J-V* curve of PANI(a), GLP doped PANI(b) , SDS doped PANI(c) and EDTA disodium salt doped PANI(d) counter electrode. The power conversion efficiency (PCE) of PANI, EDTA disodium salt doped PANI, GLP doped PANI and SDS doped PANI were 2.29%, 2.51%, 2.69% and 4.25% respectively. Our results were found to display efficiency of the system, on comparison with previous studies. Bora [29] successfully synthesized a novel cost-effective mesoporous carbon black/polyaniline nanotube composite which was fabricated as a potential CE material by in-situ chemical oxidation polymerization of aniline. The composite CE contributed towards achieving a high performing DSSCs having PCE of 6.62% in liquid electrolyte for I_3^- to I^- reduction. Benlin [30] synthesized PANI-MoS_2 complex is an efficient material for designing transparent and cost-effective CE of bifacial DSSCs. The DSSCs employing PANI-(6wt%)MoS_2 complex CE achieve a recorded PCE of 9.71%, which is superior to the performance of the cell using

PANI CE. The enhanced catalytic activity may be due to massive changes in active catalytic sites and their microscopic morphology [31-32].

PANI combined with high surface-active anionic surfactants, decreased the surface tension of the solution, resulting in the change of the structure and morphology of the composite. Qiu [33] electropolymerized aniline in the presence of SDS to synthesize SDS-doped PANI as the counter electrode material for DSSCs. The experimental results show that in the presence of SDS, the microstructure of PANI can be changed. The PCE of SDS-doped PANI is 7.0%, which is close to 7.4% of the PCE of platinum. Thuy [34] prepared surfactant doped PPy composite electrodes with SDS as a surfactant. The PPy/MWCNT CEs prepared with anionic surfactant possessed more catalytic activity and lower charge transfer resistance in comparison with PPy-based CE. This resulted in a better PCE of 5.88% for PPy/MWCNT-based DSSCs. Shin [35] synthesized DBNTs with 2-5 nm PEDOT layer by emulsion polymerization technique using DBSA as a surfactant. The synthesized CNT/PEDOT core/shell nanostructures exhibited higher PCE than pure PEDOT at rates up to 4.62%. In this work, The PCE of all the three surfactant-doped PANI composite electrodes were higher than that of pure PANI. Surfactant-doped PANI composites have a higher reduction ratio for I_3^- than pure PANI because surfactant-doping affected the particle size of PANI, thereby increasing the current efficiency of the electrode and reducing the electrode polarization. The PCE of SDS-doped PANI greatly increased, which could be related to the microstructure of SDS doped PANI electrode. Indicating that loose and porous rod-like structure is conducive to electrolytic transport. These results indicate that the composite film with high catalytic properties for I_3^- reduction can potentially be used as the CE in a high-performance DSSC.

4. CONCLUSION

To improve the catalytic activity of CE in DSSC system, PANI doped in three surfactants (GLPs, SDS and EDTA disodium salt) were used as non-Pt materials for CE of DSSCs. An active PANI-doped CE could be formed through the appropriate composition of PANI-doped CE, which had a mammoth impact on the reduction of electrolyte and thereby boosting up the overall efficiency. The PCE of PANI-doped CEs with doping in SDS, GLP and EDTA disodium salt (4.25%, 2.69% and 2.51%) were higher than 2.29% for PANI CE without doping. The combination of PANI and surfactants can increase the rate of electron transfer and the number of active sites. The imposing electronic features of PANI-doped counter electrode can inflate the comprehensive performance of DSSCs to a greater level.

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