

LOW-TEMPERATURE HYDROGEN PLASMA REDUCTION OF GRAPHENE OXIDE COUNTER ELECTRODES FOR PRINTED DYE-SENSITIZED SOLAR CELLS

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Abstract

In this work, solution-processable graphene oxide (GO) dispersions were used for the simple preparation of thin GO layers (50 nm thickness), which were reduced by low-temperature hydrogen plasma. Hydrogen plasma reduction (ideal treatment time 8 sec) led to a decrease of oxygen-containing groups and consequently, in the transformation of sp³-carbon oxidized domains to preferable sp²-carbon aromatic domains in rGO layers (XPS). GO and rGO layers were used as counter-electrodes (CEs) in printed dye-sensitized solar cells (DSSCs). DSSCs with rGO CEs reached an increased conversion efficiency of $\eta = 0.9\%$ compared to DSSCs based on GO CEs with $\eta = 0.4\%$. This can be attributed to the higher catalytic activity of plasma reduced rGO CEs in the presence of iodine electrolyte and also lower sheet resistance ($<100\text{ M}\Omega/\square$) compared to GO CEs.

Keywords: Graphene oxide, plasma reduction, dye-sensitized solar cell, counter electrode, printed electronics

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) belongs to the promising 3rd photovoltaic generation which has several benefits compared conventional silicon-based solar cells such as transparency (possibility for both side illumination), reasonable efficiency at artificial light conditions, use of low-cost materials and the possibility of printing production (roll-to-roll) on a various flexible substrate [1-2]. The standard DSSCs structure consists of three main components: mesoscopic metal nano-oxide photoanode (TiO₂, ZnO) sensitized with dye (ruthenium, porphyrin and various organic dyes), iodide liquid electrolyte and Pt counter electrode (CE).

The counter electrode has a key role in electron collection from the external circuit to the electrolyte, where iodide ions are reduced. Therefore, CE should meet several important properties: high conductivity, high catalytic activity and stability, transparency in the UV-Vis region and mechanical stability [3]. For its excellent catalytic activity in the presence of iodide electrolyte and high transparency, the Pt is often used as the standard and reference CE. However, the high cost of Pt, its corrosion caused by liquid electrolyte and requirement of the high-temperature treatment of Pt CEs for the high DSSCs conversion efficiency are serious drawbacks for its large-scale preparation by printing and coating techniques. As the alternative and printable materials for CEs, carbon-based materials (graphene, graphene oxide, CNT, MWCNT, graphite, carbon black) reached a lot of research attention [4].

Graphene (G) and graphene oxide (GO) are two-dimensional materials with carbon atoms arranged in a hexagonal lattice structure. G has several unique properties, such as high electrical and thermal conductivity, high optical transmittance, large surface area thanks to which it is often studied as an alternative CE [5-6]. In contrast to G, the GO (functionalized graphene with peroxide, hydroxyl and carboxyl groups) is electrically

insulating material. This is due to the change in GO conjugated system of bonds where sp^2 hybridization of functionalized C-C bonds is changed to sp^3 hybridization. However, compared to G, the GO is hydrophilic material and thus can be prepared in the form of stable water or organic solvent-based coating and printing inks. Moreover, different techniques (thermal, chemical, UV light, plasma) enable the reduction of oxygen-containing groups in GO which leads to partially restored electrical properties of reduced graphene oxide (rGO) and its application as CE in DSSCs [7-8]. Among these reduction techniques, plasma treatment has great benefits of short reduction time (several seconds), low-temperature (up to 70 °C), no need of toxic chemicals and can be directly incorporated in the roll-to-roll process [9].

Here, we report on a simple and large-scale applicable preparation process of rGO CEs for DSSCs. Low-viscosity water-based GO dispersions were spin-coated onto FTO glass substrates (fluorine-doped SnO_2) without any further drying. Prepared GO layers were afterward reduced by low-temperature dielectric discharge barrier hydrogen plasma (DCSBD) at atmospheric pressure. The positive effect of plasma treatment on the rGO chemical structure was studied by X-ray photoelectron spectroscopy (XPS). rGO was used as CEs in printed DSSCs. DSSCs with rGO CEs reached a double increase in conversion efficiency compared to GO CEs. However, the very high electrical resistivity of rGO have a significant effect on overall low electrochemical performance of rGO (cyclic voltammetry) and subsequently on the lower photovoltaic performance of DSSCs (I-V characteristic).

2. EXPERIMENTAL

2.1. DSSCs preparation

Mesoscopic TiO_2 electrodes (photoanode - PA) were prepared from screen-printable TiO_2 highly viscous inks. The detailed preparation process of TiO_2 ink and the screen-printing process is described in our previous work [2]. TiO_2 electrodes were printed onto cleaned and UV treated FTO glass slides (covered with $TiCl_4$ blocking layer). Then, electrodes with a controlled final thickness of 10 μm were sensitized for 24 h in 0.4 mM ethanol solution of N719 ruthenium dye (Solaronix, Switzerland). GO counter electrodes were prepared by spin-coating of 5 mg/ml water-isopropyl alcohol GO dispersion (1-5 μm particle size, Ossila, England). The dispersion was spin-coated onto cleaned and UV treated FTO glass slides. GO layers were afterward treated for 8 s by DCSBD plasma (100 W/cm^3 , ROPLASS s.r.o., Czech Republic) in H_2 reduction gas. DSSCs were assembled as sandwich-type cells by the addition of 16 μl of liquid electrolyte (Iodolyte AN-50, Solaronix, Switzerland) between the PA and CE. Electrodes were afterward connected by bonding polymeric film (Meltonix 1170, Solaronix, Switzerland).

2.2. Measurement and characterization

The plasma for the reduction was generated by diffuse coplanar surface barrier discharge (DCSBD, Roplass s.r.o., Czech Rep.). The DCSBD generated thin, high power-density plasma in H_2 gas with power density 100 W/cm^3 . The effect of plasma reduction on the chemical composition of rGO electrodes and nontreated GO electrodes was investigated by XPS measurement (Al $K\alpha$ ESCALAB 250Xi, ThermoFisher Scientific). The morphology of prepared GO layers was analyzed by AFM (Ntegra Prima (NT-MDT)). Cyclic voltammetry (CV) measurements were performed in a three-electrode electrochemical cell in a supporting electrolyte acetonitrile solution containing 0.1M $LiClO_4$, $10 \cdot 10^{-3}$ M LiI and $1 \cdot 10^{-3}$ M I_2 using a sample of CE as the working electrode, a Pt wire as the auxiliary electrode and $Ag/AgCl/3 \text{ mol } L^{-1} \text{ KCl}$ as the reference electrode, respectively. The photovoltaic performances of DSSCs (I-V characteristic) were characterized under simulated light irradiation of 100 $mW \text{ cm}^{-2}$.

3. RESULTS AND DISCUSSION

Topography and thickness of spin-coated GO layers were evaluated by AFM and profilometry measurements. Analyzed GO layers consisted of particles with size from hundreds of nm up to 3 μm (**Figure 1** - left). The average layer thickness of one time spin-coated (2000 rpm) 5 mg/ml GO dispersion was approx. 50 nm (**Figure 1** - right). Profilometry analyses show (**Figure 1** - right) that spin-coated GO layers have high roughness with the lowest thickness locality ≈ 10 nm up to the highest points ≈ 160 nm. Because of plasma treatment is efficient only at the material surface, the high layer roughness is beneficial for large surface area reduction.

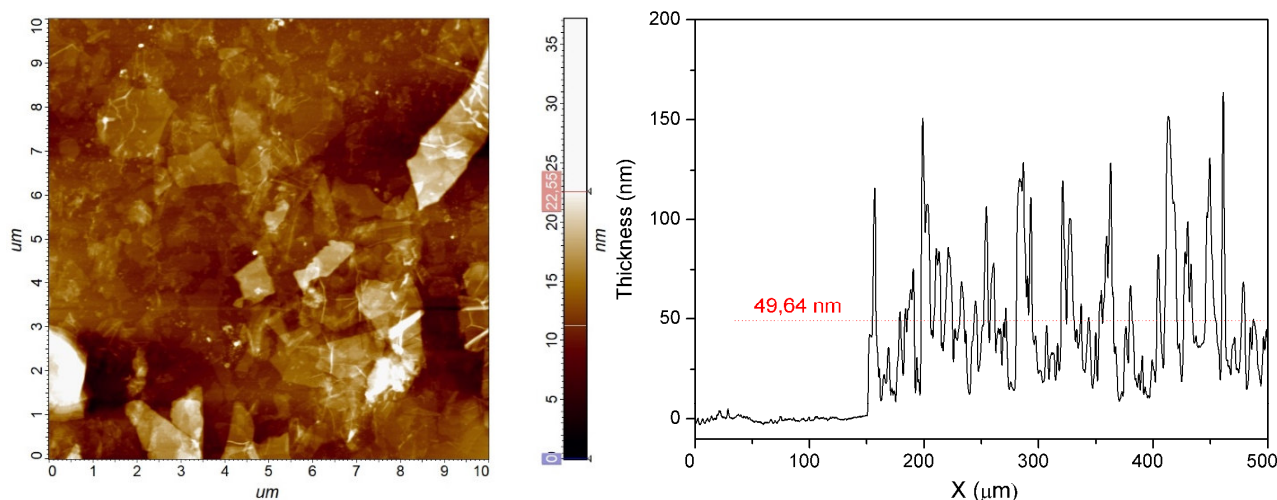


Figure 1 Topography (AFM, left) and profilometry (right) of spin-coated GO layer

The chemical surface composition of the prepared GO and plasma reduced rGO samples were analyzed by XPS. **Figure 2** shows C1s peaks of GO before (GO) and after hydrogen plasma reduction for 8s (rGO). GO C1s peak at 286 eV corresponding to C-C bonds in sp^2 and sp^3 hybridization state. After plasma treatment (rGO) is this peak shifted towards lower binding energies which can be contributed to the decrease of sp^3 - bonded carbon (**Figure 2** - right). The second peak at 288 eV can be attributed to carbon-oxygen bonding. After plasma treatment, the quantitative decrease of carbon-oxygen bonds is evident and is also plotted in **Figure 2** -right.

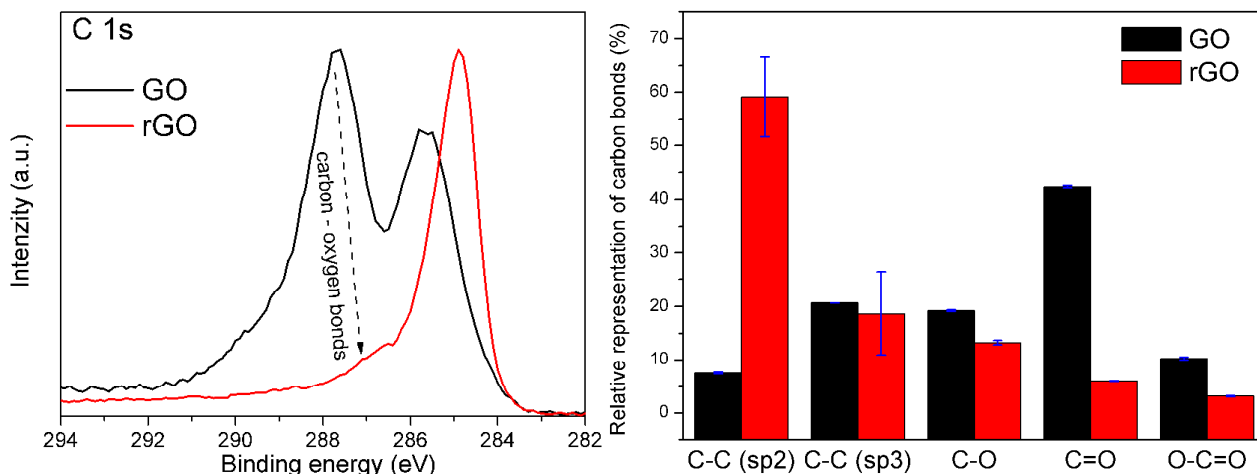


Figure 2 XPS C1s spectra of GO and rGO (reduced in hydrogen plasma for 8 s) chemical composition (left) and relative representation of carbon bonds in GO and rGO (right)

Figure 3 shows I-V characteristics with inserted calculated photovoltaic properties (V_{oc} - open-circuit voltage, J_{sc} - short-current density, FF - fill factor, η - conversion efficiency) of prepared DSSCs with GO and rGO CEs. DSSCs with rGO CEs reached increased overall photovoltaic properties with $\eta = 0.89\%$ compared to $\eta = 0.44\%$ evaluated for GO CEs. The non-standard shape I-V curves measured for GO and also for rGO can be assigned mainly to the high series resistance (low electrical sheet resistance of rGO $R_{sh} \approx 100 \text{ M}\Omega/\square$) of the DSSCs with low $FF_{GO} = 0.27$ and $FF_{rGO} = 0.29$.

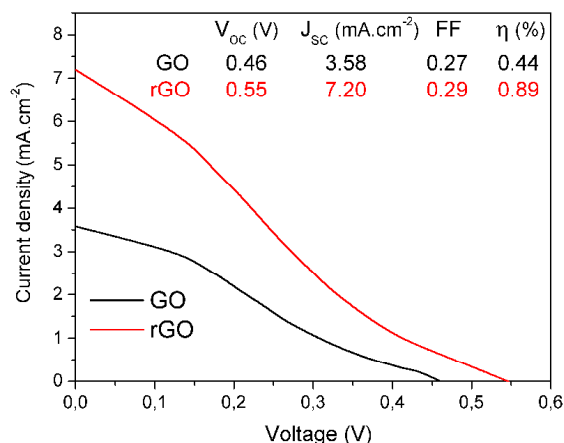


Figure 3 I-V characteristics of DSSCs assembled with GO and rGO CEs under 100 mW cm^{-2} irradiation, with inserted calculated photovoltaic parameters

The photovoltaic performance of DSSCs can be further correlated with the electrochemical performance of GO and rGO CEs evaluated by cyclic voltammetry (CV) in iodide electrolyte. **Figure 4** - left shows cyclic voltammograms of GO and rGO electrodes in supporting iodide electrolyte. For both samples, the intensive reduction peaks at GO = -0.9 V and rGO = -0.75 V are evident. These anodic peaks can be ascribed to the particular reduction of I_3^-/I^- which have the key role in electrolyte ions reduction at CEs surface. Plasma reduced rGO CEs reached significantly higher catalytic activity compared to GO CEs. However, the evaluated electrochemical stability of rGO CEs in the presence of iodide electrolyte was low (**Figure 4** - right) and just at first repeated cycles reduction peak decreased. This phenomenon will be the subject of further study. Low stability of GO and rGO has a great impact on the non-standard shape of measured I-V and low values of η .

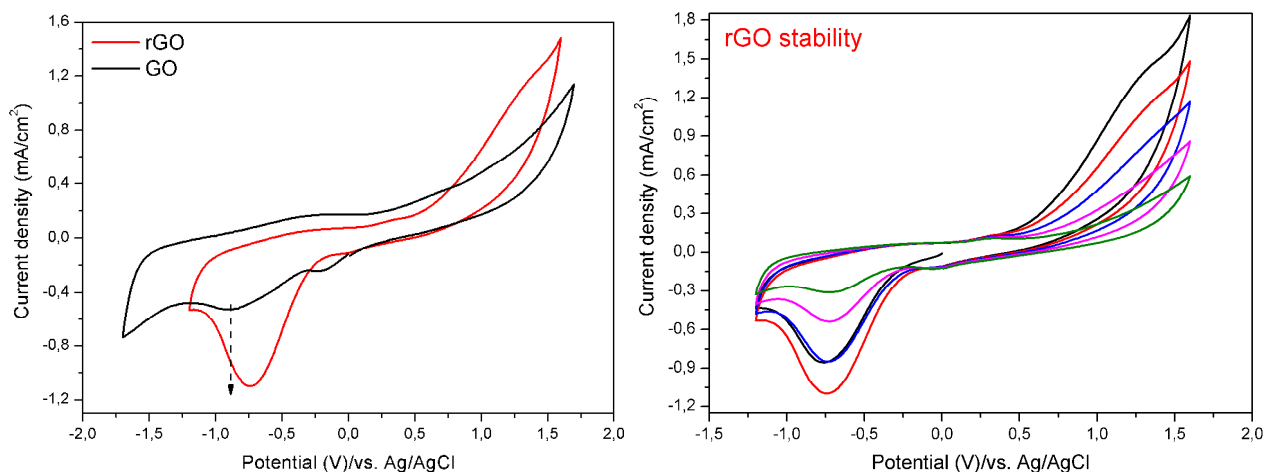


Figure 4 Cyclic voltammograms of GO and rGO CEs (left) and electrochemical stability of rGO CEs (right) in supporting electrolyte (acetonitrile solution 0.1 M LiClO_4 , $10 \cdot 10^{-3} \text{ M LiI}$ and $1 \cdot 10^{-3} \text{ M I}_2$)

4. CONCLUSION

Based on the results obtained in this work we can conclude that DCSBD hydrogen plasma reduction (treatment time = 8 sec) significantly reduced the presence of carbon-oxygen bonds and subsequently the presence of sp^3 hybridization domains in rGO layers (XPS) prepared by simply spin-coating of water-based GO dispersion. Plasma reduction also led to a decrease in rGO electrodes electrical sheet resistance. rGO electrodes were used as counter electrodes in printed dye-sensitized solar cells. Although the DSSC with rGO CE reached an increased conversion efficiency compared to DSSC with GO CE, the overall low photovoltaic performance of both GO and rGO CE can be ascribed to the low conductivity of both CEs. Moreover, the evaluated non-standard shape of the I-V characteristic of GO and rGO CE can be attributed to the low catalytic stability of the CEs in the presence of liquid iodide electrolyte. This phenomenon should be the subject of further study. Here we can conclude that the deeper study of various ink components, GO particle size and studying the effect of the GO layer thickness can increase the effect of hydrogen plasma reduction on rGO electrical properties as well as on the photovoltaic performance of DSSC.

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