



Graphene cryogel-based counter electrode materials freeze-dried using different solution media for dye-sensitized solar cells



Jie Ma^{a,b}, Wei Shen^a, Cheng Li^a, Jie Zheng^{c,*}, Fei Yu^{a,b,*}

^a State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, PR China

^b College of Chemistry and Environmental Engineering, Shanghai Institute of Technology, Shanghai 2001418, PR China

^c Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325, USA

HIGHLIGHTS

- *t*-Butanol was selected as an excellent freeze-drying medium for freeze-drying.
- Higher SSA based on *t*-butanol medium than water was achieved.
- GCT-based counter electrodes exhibited excellent electrocatalytic activity.
- PCE increased to 8.70% from 7.05% under assisted by *t*-butanol as solvent.

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ABSTRACT

Cryogels are typically synthesized using a freeze-drying method based on hydrogels. However, we have found that the volume changes of water during the freeze-drying process can destroy the gel structure. In this paper, *t*-butanol was selected as an excellent freeze-drying medium because of its favorable properties and retention of the massive gel structure. The graphene/single-walled carbon nanotube (SWCNT) cryogel exhibited a higher specific surface area (SSA) using *t*-butanol as a solvent (GCT) compared with using water (GCW) in the hydrogel for freeze-drying. GCT retained the most porous structure with the highest SSA (402.19 m²·g⁻¹) after the freeze-drying process. Then, GCW and GCT were tested as counter electrode materials as a substitute for platinumized FTO in dye-sensitized solar cells (DSSCs). The DSSC based on the GCT counter electrode exhibited a remarkable photovoltaic conversion efficiency (8.70%) compared with the GCW-based CE (7.05%) and Pt (7.57%). Hence, our results demonstrate that graphene/SWCNT cryogels freeze-dried with *t*-butanol as the solvent are promising candidates for use in Pt-free DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been the subject of intense research as the third-generation solar cells because of their favorable properties, including remarkable power conversion efficiency (PCE) and economic feasibility [1–3]. In a conventional DSSC, the counter electrode (CE) plays a vital role in the regeneration of iodide and electron transfer at the interface between the electrode and the electrolyte for high-performance DSSCs. Platinum (Pt) is known as an excellent counter electrode material

because of its outstanding electrocatalytic activity, but its scarcity and high cost have restricted the commercial application of DSSCs [4,5]. Therefore, it is imperative to explore other materials with alternative, cost-effective and eco-friendly properties, such as carbonaceous materials [6], metal chalcogenides [7–9], conducting polymers [10–12], alloy [13–15] and carbides [16]. The combination of different carbon materials has been tested in the design of new CE materials as an alternative to Pt CEs and has exhibited excellent conductivity and catalytic properties in DSSCs [17–20].

Recently, to provide more vertical sites to react with the three-dimensional electrode, increasing attention has been paid to the design of materials with 3D structures, especially those based on cryogels, such as 3D nitrogen-doped graphene foam [21], graphene cryogels [22], and carbon nanotube/graphene cryogels [23]. Porous graphene hydrogels can be easily formed utilizing the self-assembling ability of graphene oxide (GO) under hydrothermal

* Corresponding authors at: Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio 44325, USA (J. Zheng). College of Chemistry and Environmental Engineering, Shanghai Institute of Technology, Shanghai 2001418, China (F. Yu).

E-mail addresses: jma@tongji.edu.cn (J. Ma), zhengj@uakron.edu (J. Zheng), fyu@vip.163.com (F. Yu).

conditions [24]. The freeze-drying method is widely used to fabricate cryogels from hydrogel [25,26].

Freeze-drying is a separation process based on sublimation with the advantages of removing moisture while maintaining the material structure. Water is the main liquid in the products. However, in the process of freeze-drying, the volume of water will change upon freezing, causing the gel structure to likely be destroyed [27,28]. Thus, nonaqueous solvents are added to accelerate the drying process and boost the sublimation rate [29,30]. *t*-Butanol is an outstanding nonaqueous solvent for freeze-drying because of its favorable properties, including high vapor pressure, low freezing point, fast sublimation rate during primary drying, and low toxicity [28,30], making it an excellent potential freeze-drying medium.

Herein, we synthesized a graphene/SWCNT cryogel (GCT) using *t*-butanol as a solvent to substitute for the water in the hydrogel for freeze-drying. In this method, the GCT cryogels remained the most porous structure with higher SSA ($402.19 \text{ m}^2 \cdot \text{g}^{-1}$) after the freeze-drying process. However, the graphene/SWCNT cryogel (GCW) obtained using water as the freeze-drying solvent had a smaller SSA ($291.06 \text{ m}^2 \cdot \text{g}^{-1}$). Then, GCW and GCT were utilized to prepare counter electrodes for dye-sensitized solar cells (DSSCs). The resulting GCT-based counter electrodes (CEs) exhibited a remarkably higher conversion efficiency (PCE) (8.70%) compared with the GCW-based CE (7.05%) and Pt (7.57%). Consequently, our results indicate that graphene/SWCNT cryogels using *t*-butanol as the freeze-drying solvent exhibit favorable characteristics for further application in Pt-free DSSCs.

2. Experimental section

2.1. Materials and reagents

Tertiary butanol (TBA), ethanediol, ethanol, polyvinylpyrrolidone with an average molecular weight of 4000 (PVP-k30), and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai, China. Deionized water was used to prepare the solutions in our work. All chemicals were of analytical grade and utilized without any further purification. SWCNTs were synthesized using floating catalytic chemical vapor deposition [31] and purified using a nondestructive approach [32]. Graphite oxide was prepared using the improved Hummer's method [33–35].

2.2. Preparation of cryogels

GO and GO/SWCNT solutions were prepared by dispersing 100 mg of graphene oxide in 100 ml of deionized water and adding 400 mg of SWCNTs to 200 ml of the GO solution ($1 \text{ mg} \cdot \text{mL}^{-1}$), respectively. Then, 200 mg of glutathione was dissolved in the above solutions to reduce the GO, after which they were placed in an 85°C water bath for 12 h to synthesize the rGO and rGO/SWCNT hydrogels via self-assembly. The hydrogel was dipped in *t*-butanol as a substitute for the water in the hydrogel. The water or *t*-butanol was removed during the freeze-drying process over 48 h and then the cryogel was obtained. After removing *t*-butanol, the rGO and rGO/SWCNT cryogels were designated as GT and GCT, respectively. The GO/SWCNT cryogel was designated as GCW by removing the water from the hydrogel without dipping in *t*-butanol. Finally, the cryogel was annealed at 800°C for 2 h in an Ar atmosphere.

2.3. Preparation of counter electrodes

Graphene or graphene/SWCNT cryogel powders were mixed with PVPk30 at a weight ratio of 2:1. The above paste of mixtures was synthesized utilizing ethylene glycol as the solvent and

subsequently dropped onto a square of FTO glass with dimensions of $7 \times 7 \text{ mm}$. Then, the coated FTO glass squares were dried at 80°C for 24 h under vacuum conditions. Finally, the CEs were incubated at 400°C under flowing argon for 1 h. Pt counter electrode were purchased from Dalian HeptaChroma SolarTech Co., Ltd. As for Pt counter electrode, it is fabricated by means of screen printing methods. The FTO with loading Pt paste at the specific location was inside a vacuum oven, which maintain a vacuum for 4–5 h. Then, the dry Pt CE was annealed at 400°C for 1 h.

2.4. Fabrication of dummy cells

The dye solution was prepared by blending N719 dye in ethanol ($3 \text{ mmol} \cdot \text{L}^{-1}$) and TiO_2 photoanodes were subsequently immersed in the dye solution for 20 h at 60°C . The solar cell was assembled and fixed using two binder clips with a $25 \mu\text{m}$ -thick Surlyn film placed between the photoanode and the CE to separate them. The iodide electrolyte consisted of 0.6 M 1-methyl propyl imidazolium iodide, 0.1 M lithium iodide, 0.05 M iodine, and 0.5 M *tert*-butyl pyridine in acetonitrile. A symmetric dummy cell was manufactured by placing two symmetric CEs together face to face using the same process.

2.5. Characterizations and measurements

The chemical properties of GT, GCW and GCT cryogels were determined using X-ray photoelectron spectroscopy (XPS). The microstructures and morphologies of the materials were characterized using transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM). Additionally, the specific surface area (SSA) and pore size distribution of the samples were measured using the multi-point BET and Barrett-Joyner-Halenda (BJH) methods. Measurements of micro-Raman spectra were performed using a Raman Scope system (LabRam, 1B) with a 532 nm wavelength incident laser light and 20 mW power. Then, I-V measurements were performed under simulated AM 1.5 G illumination (Model 69911, Newport, USA).

All of the electrochemical tests were conducted on an electrochemical workstation (CHI Instruments 660D). The cyclic voltammetry (CV) was measured in a three-electrode system in which Pt foil and Ag/AgCl served as the counter and reference electrodes, respectively, in an acetonitrile solution containing 10 mM LiI, 1 mM I_2 , and 0.1 M LiClO_4 . EIS spectra were measured using simulating open-circuit at ambient atmosphere with an applied bias voltage and AC amplitude set to 0 V and 10 mV, respectively, at a frequency varying from 100 kHz to 0.1 Hz. Tafel curves were collected at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ between $\pm 1.0 \text{ V}$.

3. Results and discussion

3.1. Compositions and structural characterization

As shown in Fig. 1a, the same GO/SWCNT hydrogels were set in different solution media, *t*-butanol (left) and water (right). After freeze-drying, there was a significant difference between the two cryogels (Fig. 1b). The GCT cryogel almost retained the original shape of the hydrogel. However, the GCW cryogel collapsed because of the volume change of the residual water during the freeze-drying process.

The SEM and TEM images of GT, GCW, and GCT cryogels are shown in Figs. 2 and 3, respectively. Fig. 2 shows that all the cryogels possess a large area with a highly wrinkled and porous structure. In addition, the HR-TEM and SEAD of GT (Fig. S1) reveal a thin layer structure on the local scale. Both the TEM and SEM results in Figs. 2 and 3 shows that the SWCNTs were inserted into the

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