Thin Solid Films 657 (2018) 24–31

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Rapid preparation of conductive transparent films via solution printing of graphene precursor

Ziwen Liu[a], Yifan Xie[a], Juan Zhao[b,*], Sijia Wu[a], Min Wen[a], Yi-Bing Cheng[a,c], Jie Zhong[a,*]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China
[b] School of automotive engineering, Wuhan University of Technology, Wuhan 430070, PR China
[c] Department of Materials Science and Engineering, Monash University, VIC 3800, Australia

ARTICLE INFO

*Keywords:*
Graphene
Solution printing
Large area
Rapid
Perovskite solar cell

ABSTRACT

We report convenient approaches to obtain large-area conductive graphene films via a solution printing method. Spray deposition and blade coating were used to prepare graphene films as the representative printing methods. Some parameters, such as the reduction temperatures, pre-treatments of precursor, printing speeds and etc., were investigated to optimize the conductivities of samples. The prepared graphene oxide (GO) and reduced graphene oxide (rGO) films were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, UV–vis spectroscopy and X-ray photoelectron spectroscopy. The results indicate that films prepared by spraying GO–hydrazine dispersion and blade coating GO solution possess good performance, including decent photoelectric property, crystal structure and a high carbon to oxygen ratio. Sheet resistances of 3.4 kΩ/sq. (spray coating) and 3.6 kΩ/sq. (blade coating) at around 75% transparency were obtained by measuring the printed conductive films. Moreover, the as-made rGO films were used as the transparent conductive layer for planar perovskite solar cells and achieved an efficiency of 3.38%.

## 1. Introduction

Transparent conductive films (TCFs) play an increasingly important role in the booming optoelectronic devices applications such as solar cells, organic light emitting diodes, liquid crystal display panels, touch screen panels and solid-state lighting [1–3]. The traditional material indium tin oxide (ITO) with high conductivity and transmittance as the transparent conductive film material has been successfully used in optoelectronics for more than fifty years. However, the scarcity of indium and the low flexibility of ITO cause an urgent demand for new developments of TCFs. Carbon nanotubes [4,5], conducting polymers [6,7], graphene [8–10] and metal nanowires [11,12], etc. have sprung up to fulfill this purpose.

Graphene, as a representative and marvelous 2D structure, with a special $sp^2$ honeycomb lattice carbon structure and numerous excellent properties, such as superior electrical, mechanical, optical, thermal and mechanical properties has been the focus of intense scientific research. Nowadays, a variety of methods have been developed to prepare graphene films, including micromechanical exfoliation [13,14], growth on silicon carbide surface [15], chemical vapor deposition (CVD) [16], liquid-phase exfoliation [17] and chemical reduction of graphene oxide (GO) [18]. Among these, CVD and solution-based chemical reduction of GO were used most widely in the research and development of graphene field. The CVD growth of graphene on metal substrates (such as Cu, Ni) has many unique advantages in terms of the production of uniform graphene. The produced graphene has a tunable film thickness and a large domain size [19]. Nevertheless, the route involves a complicated and tedious transferring process. After the deposition process, as-synthesized graphene needs to be transferred onto insulating target substrates, which frequently results in the generation of defects and thus inflects the integrity of graphene. Meanwhile, the metal substrates need to be heated at a high temperature. In consequence, the method leads to much energy consumption and of course increases the expenses [20]. On the contrary, the operation method of solution-based chemical reduction of GO is simple and great beneficial to cost effective upscaling. The preparation and reduction process of GO based solution printing are usually carried out at facile and easy conditions, with the merits of fast, low-temperature and low-cost fabrication, which is suitable for fabricating large-area graphene films. Although the photoelectric properties of reduced graphene oxide (rGO) films prepared by solution-based chemical reduction of GO can hardly comparable with CVD at present by reason of the current technical limitations and difference of preparation properties [3,21,22], so many aforementioned advantages are still enough to make it a principal method to prepare

* Corresponding authors.
*E-mail addresses:* juan.zhao@whut.edu.cn (J. Zhao), jie.zhong@whut.edu.cn (J. Zhong).

https://doi.org/10.1016/j.tsf.2018.05.005
Received 4 January 2018; Received in revised form 21 April 2018; Accepted 2 May 2018
Available online 03 May 2018
0040-6090/

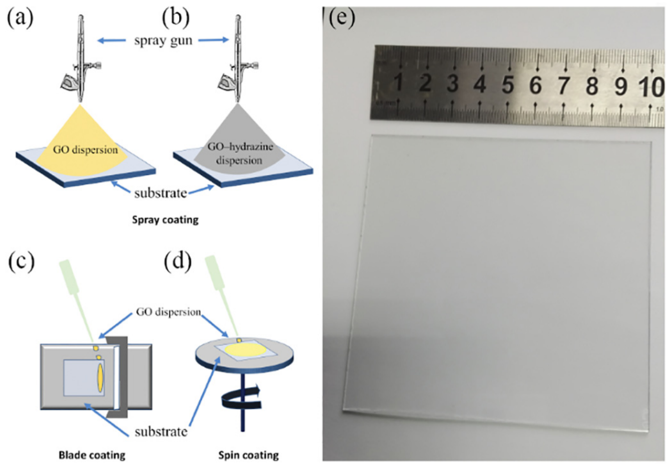


**Fig. 1.** Schematic illustration of (a) spraying GO solution, (b) spraying GO–hydrazine dispersion, (c) blade coating GO solution, and (d) spin coating GO solution. (e) Optical photographs of the large-area rGO film prepared by spraying GO–hydrazine dispersion premixed with hydrazine hydrate.

graphene films as TCFs.

In general, GO sheets contain masses of oxygen-containing functional groups such as epoxy, hydroxyl, ketone and ether. These groups make GO sheets hydrophilic and lead to the high solubility of GO in aqueous solution. However, for the same reason, GO sheets are insulating in nature. To obtain a rGO thin film, the deoxygenating process must be carried out in the subsequent process [23]. The most common chemical reductants for GO contain hydrazine [24], hydriodic acid [25,26] and sodium borohydride [27]. There are also some other relatively green reductants, like vitamin C [28], alcohols [29], or even *Lycium barbarum* extract [30].

In this work, we present novel and convenient approaches to obtain large-area graphene films on insulating soda-lime glass substrate via solution printing method. Spray coating and blade coating are two of the most important solution printing methods. We compared the performance difference of graphene films fabricated by these two methods with spin coating. Meanwhile, we regulated solution preparing parameters in order to get optimum performance. The results show that the photoelectric properties of obtained graphene films through the former are much better. The transmittances at 550 nm are both 75% for these two samples obtained by spraying GO–hydrazine dispersion and blade coating GO solution with sheet resistances of 3.4 kΩ/sq. and 3.6 kΩ/sq., respectively. This demonstrates the superiority of solution printing method. Moreover, these rGO films were applied to planar perovskite solar cells as transparent conductive layer and the efficiency can reach up to 3.38%.

## 2. Experimental

### 2.1. Materials

GO was produced using a modified Hummers method reported elsewhere [31]. The 85% hydrazine hydrate was purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium diisopropoxide (bis-2,4-

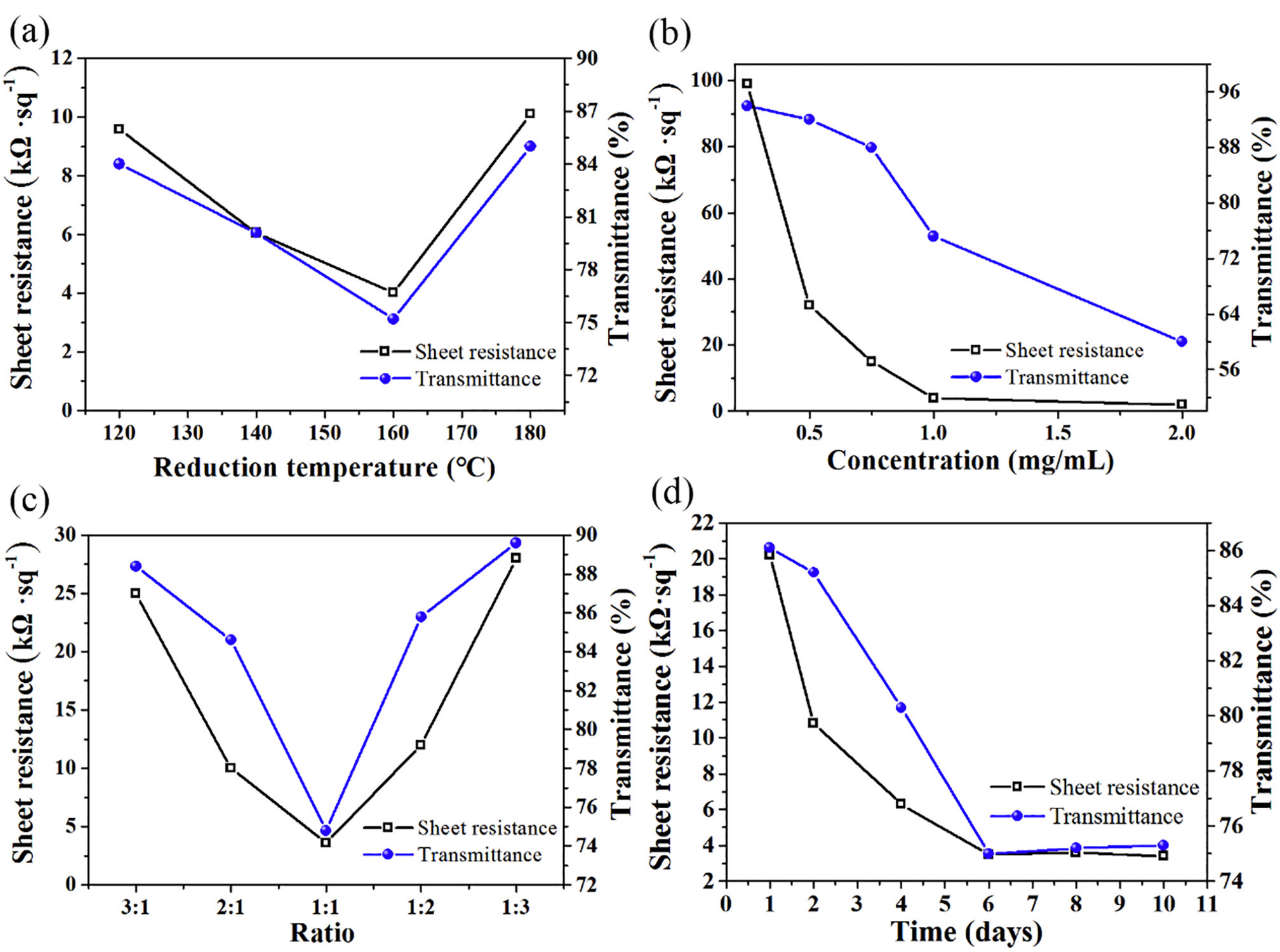


**Fig. 2.** Sheet resistance and transmittances at 550 nm wavelength of rGO as a function of (a) reduction temperature, (b) the concentration of GO solution, (c) the premixed ratio between GO solution and hydrazine hydrate, and (d) the storage time of the GO–hydrazine dispersion.