Applied Surface Science 404 (2017) 334–341

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Highly sensitive, reproducible and stable SERS substrate based on reduced graphene oxide/silver nanoparticles coated weighing paper

Guina Xiao*, Yunxiang Li, Wangzhou Shi, Leo Shen, Qi Chen, Lei Huang*

Joint Lab with Wuhu Token for Graphene Electrical Materials and Application, Department of Physics, Shanghai Normal University, Guilin Road 100, Shanghai, 200234, PR China

ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 6 January 2017
Accepted 23 January 2017
Available online 25 January 2017

Keywords:
Surface-enhanced Raman scattering
Reduced graphene oxide
Silver nanoparticles
Printing
Weighing paper

ABSTRACT

Paper-based surface-enhanced Raman scattering (SERS) substrates receive a great deal of attention due to low cost and high flexibility. Herein, we developed an efficient SERS substrate by gravure printing of sulfonated reduced graphene-oxide (S-RGO) thin film and inkjet printing of silver nanoparticles (AgNPs) on weighing paper successively. Malachite green (MG) and rhodamine 6G (R6G) were chosen as probe molecules to evaluate the enhanced performance of the fabricated SERS-active substrates. It was found that the S-RGO/AgNPs composite structure possessed higher enhancement ability than the pure AgNPs. The Raman enhancement factor of S-RGO/AgNPs was calculated to be as large as 10^9. The minimum detection limit for MG and R6G was down to 10^{-7} M with good linear responses (R^2 = 0.9996, 0.9983) range from 10^{-4} M to 10^{-7} M. In addition, the S-RGO/AgNPs exhibited good uniformity with a relative standard deviation (RSD) of 7.90% measured by 572 points, excellent reproducibility with RSD smaller than 3.36%, and long-term stability with RSD less than 7.19%.

1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy is an advanced surface analysis technique that can enhance the Raman signals of probe molecules adsorbed on or near some roughened metal surfaces enormously [1,2]. Owing to its high sensitivity, good selectivity, non-destruction, and real-time response, SERS has been considered as one of the most powerful and promising tools for chemical analysis, biological detection, medical diagnosis, food safety inspection and environmental monitoring [3–7]. In general, there are two main enhancement mechanisms contributed to SERS effect: an electromagnetic enhancement that arises from huge local electric field due to surface plasmon resonance and a chemical enhancement due to charge transfer interaction between the substrate and the adsorbate [8–10]. However, one main obstacle of using SERS as a routine analytical tool is the fabrication of homogeneous, reproducible, and stable SERS-active substrate. In order to solve these difficulties, a variety of nanotechnologies have been developed, such as template method [11], self-assembly [12], nanosphere lithography [13], electron-beam lithography [14], nanoimprint lithography [15], DUV photolithography [16], and so on. Whereas, most of them are complicated, time-consuming and expensive.

Printing technique is an attractive candidate for rapid, facile, and economic fabrication of large-scale orderly arrays. Various printing techniques have been exploited to fabricate SERS-active substrates, including screen printing, gravure printing, as well as inkjet printing [17–22]. Paper-based SERS substrates have attracted considerable attention due to low cost and high flexibility [21–24]. For example, paper-based SERS substrates were developed by patterning silver nanoparticles on modified cellulose or chromatography papers with a consumer inkjet printer [21,22]. Although these substrates exhibited excellent SERS activities, the reproducibility and stability remain a great challenge owing to the porosity and roughness of paper in nature. It is reported that the graphene or its derivatives have a good contact with paper, and they are used to modify the surface of paper due to the flat plane of graphene [25,26]. Recently, graphene, graphene oxide (GO) or reduced graphene oxide (RGO) have been introduced to noble metal nanomaterials, to improve the sensitivity, stability, or reproducibility of SERS substrates [27–31]. There has been a lot of work reported on RGO based silver nanoparticles (RGO/AgNPs) hybrid composites both in solution phase and on solid substrates [32–35]. These RGO/AgNPs hybrids show great potential as SERS substrates because the charge transfer between adsorbate and RGO leads to chemical mechanism and the surface plasmon resonance of AgNPs results in electromag-

* Corresponding authors.
E-mail addresses: xiaoguina@shnu.edu.cn (G. Xiao), leihuang@shnu.edu.cn, elhuang68@yahoo.com.sg (L. Huang).

http://dx.doi.org/10.1016/j.apsusc.2017.01.231
0169-4332/

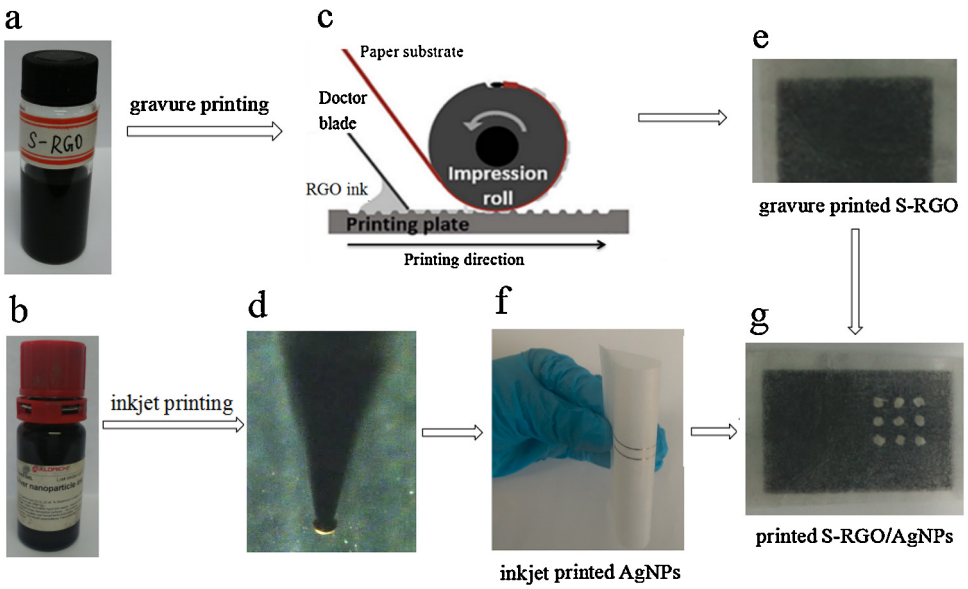

Fig. 1. (a, b) Photographs of S-RGO ink and Ag nanoparticle ink. (c) Schematic illustration of the gravure printing process. (d) Photograph of the inkjet printing process. (e, f) Photographs of gravure printed S-RGO thin film and inkjet printed AgNPs lines on flexible weighing paper. (g) Photograph of inkjet printed AgNPs spots array on S-RGO coated weighing paper.

netic mechanism. However, RGO/AgNPs with hierarchical structure on paper has not been reported.

In this work, highly efficient and flexible SERS substrates were developed by combining gravure-printed S-RGO thin film with inkjet-printed AgNPs directly on hydrophobic weighing paper. The SERS activities were investigated using malachite green (MG) and rhodamine 6G (R6G) as probe molecules. The SERS enhancement performance, uniformity, reproducibility, and stability of the printed S-RGO/AgNPs substrate were systematically investigated.

2. Experimental

2.1. Materials

Natural graphite flakes with 325 mesh was purchased from Alfa-Aesar. Sulfanilic acid, sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$), sodium nitrite ($NaNO_2$), hydrochloric acid (HCl), anhydrous ethanol (EtOH), malachite green (MG), rhodamine 6G (R6G), and weighing paper were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. The silver nanoparticle ink (20 wt%, dispersion in ethanol and ethanediol) was purchased from Sigma-Aldrich. The size distribution of Ag nanoparticle ink was analyzed both by dynamic light scattering measurement and transmission electron microscopy, as shown in Figs. S1 and S2 . MG and R6G solution were diluted to various concentrations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} M with distilled water. All the above chemicals were of analytical grade.

2.2. Preparation of S-RGO ink

Graphite oxide (GO) was synthesized from graphite powder by a modified Hummers method [36]. S-RGO was prepared from GO through aryl diazonium reaction of sulfanilic acid [37]. The detailed experimental process was reported in our previous paper [38]. Briefly, 300 mg of purified GO was dispersed in 300 mL distilled water by sonication for 30 min. A 5 wt% NaOH solution was added into the GO dispersion until its pH value was adjusted to 9. Then, 30 mL (40 g/L) $NaBH_4$ was added to the above GO dispersion at 80 °C under stirring for 1 h. The pre-reduced GO was achieved by centrifugation and redispersion in 300 mL distilled water for three times. Then, 368 mg sulfanilic acid and 144 mg $NaNO_2$ reacted with 80 mL HCl (0.05 M) to form the aryl diazonium salt in an ice bath. Subsequently, the diazonium salt was added to the pre-reduced RGO dispersion and kept at 0 °C for 2 h to obtain S-RGO. The S-RGO was further centrifuged and rinsed with distilled water for three times. Finally, the S-RGO ink was obtained by mixing S-RGO powders with 20 mL H_2O/EtOH (1:9, volume ratio). Fig. S3 shows the typical TEM image of the fabricated S-RGO ink, and the wrinkled and folded morphology of RGO nanosheets can be seen clearly.

2.3. Fabrication of fully-printed SERS substrates

The weighing paper was used without any processing. The SERS substrates were fabricated on flexible weighing paper by using a gravure printer (Schläfli Labratester, Switzerland) and an inkjet printer (Microplotter II, Sonoplot), as shown in Fig. 1. The S-RGO ink was patterned by gravure printing method at room temperature and dried at 80 °C for 30 min. The Ag nanoparticle ink was patterned by inkjet printing method and dried at 100 °C for 30 min to form spots or lines arrays as designed. For comparison, three structures with different combinations, including S-RGO, AgNPs, and S-RGO/AgNPs were fabricated.

2.4. Characterization

The surface morphology and microstructure were characterized by field emission scanning electron microscope (SEM, S4800, Hitachi) and high-resolution transmission electron microscopy (TEM, JEM-2010, JEOL). The surface morphology and surface roughness were obtained with an Asylum Research MFP-3D atomic force microscopy (AFM) operating in a tapping mode. Ultraviolet–visible (UV–VIS) absorption spectra were measured with a Varian Cary 5000 UV–VIS–NIR spectrophotometer.

2.5. SERS detections

Normal Raman scattering (NRS) and SERS spectra measurements were carried out on a Horiba Jobin-Yvon XploRA^{TM} Raman microscope equipped with multi-lasers of 532, 638, and 750 nm. An