



## Synthesis of graphene based noble metal composites for glucose biosensor



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### ABSTRACT

Graphene (GR) based noble metal composites such as Pt-GR and Au-GR were synthesized for sensitive glucose biosensors. Aerosol spray pyrolysis (ASP) was employed to synthesize the noble metal nanoparticles-GR composites using a colloidal mixture of GO and noble metal precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$ ). The morphology of noble metal-GR composites was generally the shape of a crumpled paper ball, and the average composite size was about 1  $\mu\text{m}$ . Crystalline Pt and Au nanoparticles less than 5 nm in diameter were uniformly deposited on the crumpled GR sheets, respectively. The characteristics of the as-prepared biosensors were tested through cyclic voltammetry measurements. All the biosensors based on the noble metal-crumpled GR composite exhibited a higher current flow as well as clear redox peaks, which resulted in a superior ability of the catalyst in terms of an electrochemical reaction. The amperometric response of the glucose biosensor based on the Pt-crumpled GR composite indicated the highest sensitivity as 62  $\mu\text{A}/\text{mM cm}^2$ .

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### 1. Introduction

Graphene (GR) is a single atom thick sheet of carbon atoms densely packed into a hexagonal two-dimensional (2D) nanosheet [1]. The unique structure of GR has been demonstrated to have a high specific surface area, high thermal conductivity, excellent mechanical stiffness, good biocompatibility, and fast electron transportation which results in promising applications in the fields of nanocomposites, solar cells and electrochemical sensors [2–4].

Many materials such as metal oxides, semiconductors and noble metals have been used widely to fabricate the functional GR composites. In case of noble metals, those provide a suitable microenvironment for biomolecules immobilization retaining their biological activity, and facilitate electron transfer between the immobilized proteins and electrode substrates [5,6]. Therefore, it is expected that a composite of noble metals and GR can exhibit improved sensitivity and selectivity as a glucose biosensor. But

only a few studies were reported about the glucose biosensor base on the noble metal-GR composite [7–9].

Lu et al. (2008) developed Pt-graphite nanoplatelets for a glucose biosensor, which showed a high sensitivity and selectivity [7]. The authors reported that graphite nanoplatelets incorporated into the biosensor interface increased the effective electrode surface area and served as an excellent support for Pt nanoparticles. Baby et al. (2010) reported a prominent electrochemical response to glucose with wide linear ranges and a high sensitivity using Au-GR [8]. Chen et al. (2011) also fabricated Au-GR composite for sensitive glucose biosensor [9]. Baby et al. (2010) and Chen et al. (2011) reported that the good electrocatalytic activity might be attributed to the synergistic effect of graphene and Au nanoparticles. These previous results indicated that noble metal nanoparticles provided a better environment for electrochemical reaction for glucose biosensing applications, and GR is expected to play an important role in improving the catalytic performance of biosensing applications.

In this paper, we introduce GR based noble metal composites synthesized by the aerosol spray pyrolysis (ASP) and their application to glucose biosensors. All the previous studies employed the liquid phase reaction including many time consuming stages such as filtering, washing, and drying in order to synthesize noble metal nanoparticles with GR. On the other hand, the ASP shows many advantages for the synthesis of GR from GO because it is a very

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fast, simple and continuous process to fabricate self assembled composites as a one-step method. It also takes a very short reaction time of several seconds and does not require any post heat treatment or purification [10–13]. Here, we synthesized the noble metal–GR composites from a noble metal precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and GO by the ASP. Then, the composites are characterized and tested for application as a glucose biosensor through cyclic voltammetry measurements.

## 2. Experimental

**Preparation of noble metal–GR composite and noble metal–GR/GOD electrode:** Colloidal graphene oxide (GO) was prepared by the oxidation of graphite powder (Alfa Aesar, 99.9%) using a modified Hummer's method [14–18].

For the synthesis of the noble metal–GR composite, a colloidal mixture solution as a precursor was prepared by the as-prepared GO colloid and noble metal precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ). The precursor was prepared with different weight ratios of noble metal/GR from 0.05 to 0.2 while the concentration of the GO was fixed at 0.5 wt% in the colloidal mixture. The experimental apparatus for the ASP process consisted of an ultrasonic atomizer, an electrical tubular furnace, and a filter sampler. The ultrasonic atomizer was used to generate micron-sized droplets of the noble metal–GO colloidal precursor. The droplets were then carried into the furnace by 1.0 l/min of argon. The evaporation of water, thermal reduction of GO and noble metal precursor, and the self-assembly between GR and noble metal nanoparticles were carried out in series in a tubular furnace. The fabricated noble metal–GR composites were then collected by a Teflon membrane filter. The operating temperature was 800 °C. The schematic diagram for synthesizing the noble metal–GR composites is shown in Fig. 1.

1 mg of the as-prepared noble metal–GR composite was dispersed in a 1 ml of 10 mg/ml GOD solution (Sigma-Aldrich, *Aspergillus niger*, 200 units/mg). For the cyclic voltammetry measurement, 5  $\mu\text{l}$  of noble metal–GR/GOD colloid was dropped onto the surface of a glassy carbon electrode (GCE). Then, 10  $\mu\text{l}$  of 0.05 wt% Nafion (Sigma-Aldrich) solution was additionally cast on the surface of the modified GCE for fixing the noble metal–GR composite. A D-(+)-glucose (Sigma-Aldrich, 0–8 mM) was used as the reaction solution for glucose biosensor.

**Analysis:** The particle morphology and size of the noble metal–GR composite were characterized by a field emission scanning electron microscope and a transmission electron microscope (FE-SEM, FEI, Sirion, TEM, Philips, CM 12). The crystallinity of the composite was analyzed by X-ray diffractometry (XRD, Rigaku, RTP 300 RC). Raman spectra were collected from 600 to 2000  $\text{cm}^{-1}$  with 532 nm laser excitation (Lambda Ray, LSI Dimension P1). The electrochemical properties of the glucose biosensor were measured by a cyclic voltammetry (CV) method using an electrochemical interface instrument (Bio-Logics, VSP). A conventional

three-electrode cell was used, including a glassy carbon electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum foil as the counter electrode.

## 3. Result and discussion

**Synthesis of noble metal–GR composites:** The Raman spectrum of the as-prepared GO showed a G band at 1600  $\text{cm}^{-1}$  and D band at 1337  $\text{cm}^{-1}$ . The G band of GO broadened compared to graphite, mainly due to the extensive oxidation (Fig. S1) [19]. Our previous study proved the characteristics of GO by XRD and XPS analyses [18]. These results confirmed that GO was successfully synthesized from graphite and matched well with previous results [19,20].

In Fig. 2, FE-SEM analysis reveals that the morphology of the noble metal–GR composites was generally the shape of a crumpled paper ball, and the average composite size was about 1  $\mu\text{m}$ . Unlike the two-dimensional GR sheets, the crumpled GR have both high free volume and high compressive strength, and can tightly pack without significantly reducing the area of accessible surface. It can also deliver much higher specific capacitance and better rate performance [12,22]. Then, the highly sensitive electrocatalytic activity of glucose biosensors by the composites are expected. TEM images of Fig. 2 also reveal that noble metal nanoparticles are deposited on the surface of the GR crumples. In particular, Fig. 2 shows that Pt and Au nanoparticles of 3 and 5 nm in diameter are uniformly deposited on GR sheets, respectively.

Fig. 3 shows the diffraction patterns of the noble metal–GR composites according to the XRD analysis. The crystallinity each of the as-prepared composites at synthesized 800 °C indicates the same peaks as those of the noble metal reference. The peak detected at around 25° exhibits GR. The crystallite sizes which were calculated by the Scherrer equation were 3.3 and 5.5 nm in Pt and Au, respectively.

**Evaluation of the electrocatalytic activity of glucose biosensors:** The noble metal–crumpled GR composites were explored for their application as glucose biosensors through cyclic voltammetry (CV) measurements. The characterizations of the glucose biosensors prepared with crumpled GR, and the noble metal–crumpled GR composites were done with 2 mM of glucose solution in each case.

Fig. 4 shows the cyclic voltammetry result of a glucose biosensor prepared by the composites at a 0.2 weight ratio of noble metal/GR. The current flow of the biosensor prepared by the Pt–GR was higher than another composite. Also, the redox peak of the electrochemical reaction by the Pt/GR was the strongest at –0.07 and –0.25 V. As we can see in Fig. 2(a), many of the Pt nanoparticles of 3 nm in diameter are uniformly deposited on the surface of GR in comparison with the Au–GR composites. This result demonstrated that biosensor performance is significantly affected by metal loading, particle size, and distribution [9]. In other words, the noble metal–crumpled GR composite covered with uniformly distributed noble metal nanoparticles had higher electrochemical activity since noble metals can enhance the electron transfer between the enzyme and the electrode.

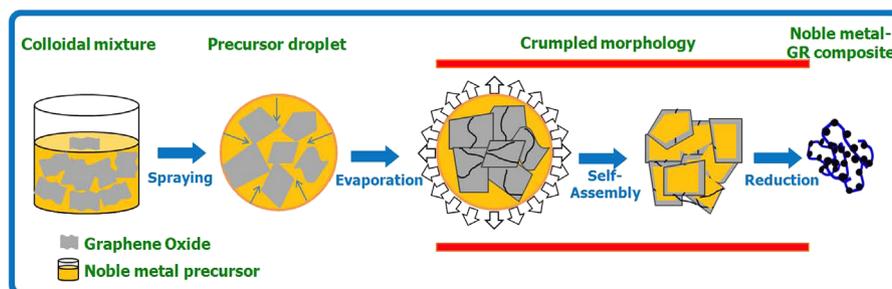
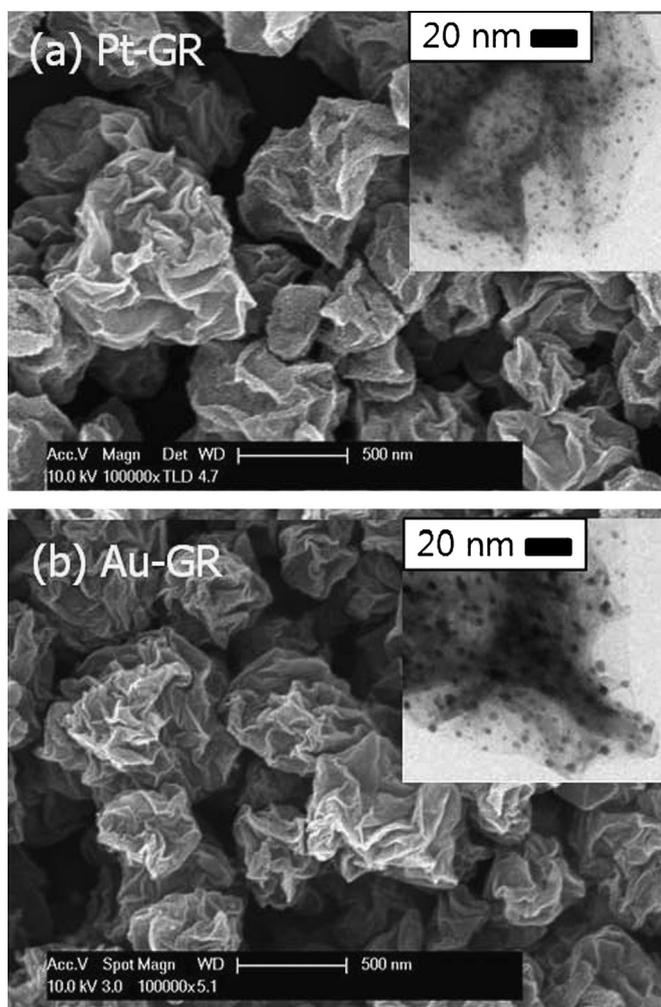
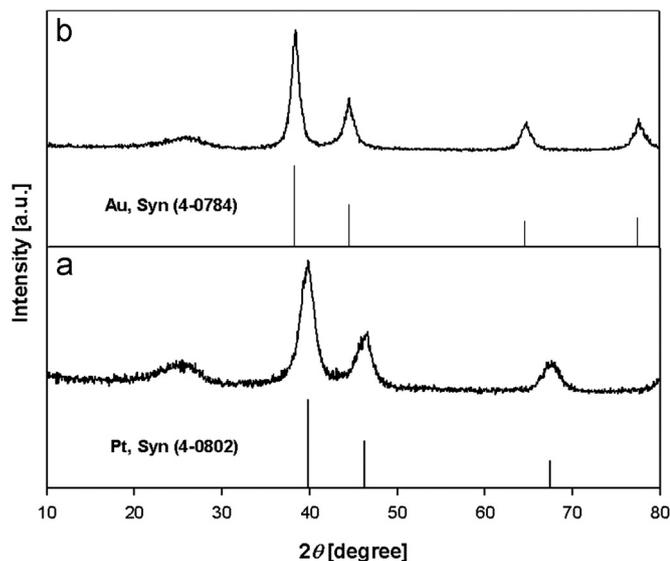


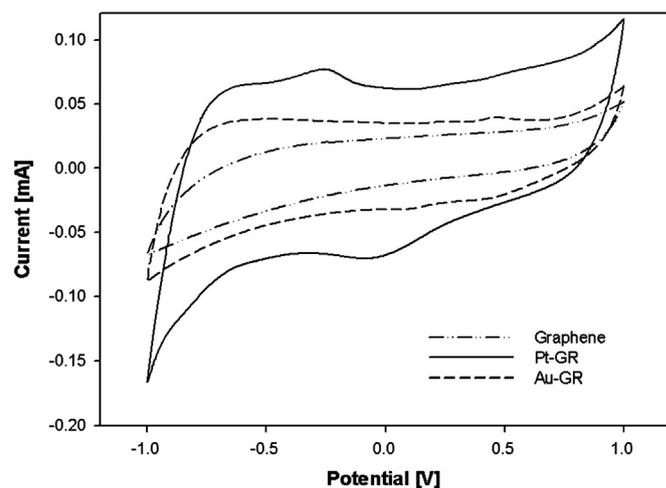
Fig. 1. Schematic illustration of the formation of noble metal–crumpled GR composite from colloidal mixture of noble metal precursor and GO via aerosol spray pyrolysis.



**Fig. 2.** FE-SEM and TEM images of the as-prepared noble metal-crumpled GR composites ((a) Pt-GR and (b) Au-GR) prepared at the fixed experimental condition (weight ratio of noble metal/GR: 0.2, GO: 0.5 wt%, temperature: 800 °C, and carrier gas flowrate: 1 l/min).



**Fig. 3.** The X-ray diffraction of patterns of the as-prepared noble metal-GR composites ((a) Pt-GR and (b) Au-GR) prepared at the fixed experimental condition (weight ratio of noble metal/GR: 0.2, GO: 0.5 wt%, temperature: 800 °C, and carrier gas flowrate: 1 l/min).



**Fig. 4.** Cyclic voltammograms of the glucose biosensor prepared by noble metal-GR (Pt-GR and Au-GR) at the fixed experimental condition (weight ratio of noble metal/GR: 0.2, GO: 0.5 wt%, glucose concentration: 2 mM, potential range: -1.0–1.0 V, and scan rate: 50 mV/s).

On the other hand, as we mentioned earlier, the higher electrochemical activity could be originated by the crumpled GR that can tightly pack without significantly reducing the area of accessible surface and can also deliver much higher specific capacitance and better rate performance [22].

The amperometric responses by the glucose biosensors based on the Pt-GR and Au-GR composite were linear against the concentration of glucose ranging from 0 to 8 mM at -0.25 and 0.47, respectively. The sensitivity indicated 62 and 15  $\mu\text{A}/\text{mM cm}^2$  for the Pt-GR and Au-GR composites, respectively (Fig. S2). Although both noble metal-GR biosensors indicate good sensitivity and electrochemical activity, higher sensitivity was obtained from the Pt-GR composite. The as-obtained sensitivity of the Pt-GR and Au-GR electrodes in this study was higher than that of the Pt-graphite and Au-GR electrode in the previous studies, respectively [7,8]. It should be noted that aerosol process could prepare the noble metal-crumpled GR composite that could exhibit highly sensitive glucose biosensor much faster than previous methods.

#### 4. Conclusions

Sensitive glucose biosensors were successfully prepared with noble metals-crumpled graphene (Pt-GR and Au-GR) composites, which were synthesized via the aerosol spray pyrolysis (ASP). The morphology of the composites was crumpled and the noble metal nanoparticles were well dispersed on the surface of the crumpled GR. The biosensors prepared by the noble metal-crumpled GR composite exhibited higher current flow as well as a clear redox peak. This result shows that loading of noble metal nanoparticles such as Pt and Au less than 5 nm in diameter on the surface of crumpled GR demonstrate superior ability as catalyst in terms of the electrochemical reaction. The highest amperometric response of the glucose biosensor was prepared by the Pt-crumpled GR composite, which indicated the sensitivity at about 62  $\mu\text{A}/\text{mM cm}^2$ . The noble metal-crumpled GR composites show prospective materials as the enhanced glucose biosensor.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2013.05.033>.

#### References

- [1] Zhou K, Zhu Y, Yang X, Luo J, Li C, Luan S. *Electrochim Acta* 2010;55:3055–60.
- [2] Li D, Muller B, Gilje S, Kaner RB, Wallace GG. *Nat Nanotechnol* 2008;3:101–5.
- [3] Liu S, Tian J, Wang L, Luo Y, Lu W, Sun X. *Biosens Bioelectron* 2011;26:4491–6.
- [4] Miller JR, Outlaw RA, Holloway BC. *Science* 2010;329:1637–9.
- [5] Shan C, Yang H, Han D, Zhang Q, Ivaska A, Niu L. *Biosens Bioelectron* 2010;25:1070–4.
- [6] Jia F, Shan CS, Li FH, Niu L. *Biosens Bioelectron* 2008;24:945–50.
- [7] Lu J, Do I, Drzal LT, Worde RM, Le I. *ACS Nano* 2008;2:1825–32.
- [8] Baby TT, Aravind SSJ, Arockiadoss T, Rakhi RB, Ramaprabhu S. *Sens Actuators B* 2010;145:71–7.
- [9] Chen Y, Li Y, Sun D, Tian D, Zhang J, Zhu JJ. *J Mater Chem* 2011;21:7604–10.
- [10] Jang HD, Kim SK, Chang H, Choi JW, Luo J, Huang J. *Aerosol Sci Technol* 2013;47:93–8.
- [11] Luo J, Zhao X, Wu J, Jang HD, Kung HH, Huang J. *J Phys Chem Lett* 2012;3:1824–9.
- [12] Luo J, Jang HD, Sun T, Xiao L, He Z, Katsoulidis AP, Kanatzidis MG, Gibson JM, Huang J. *ACS Nano* 2011;5:8943–9.
- [13] Shon K, Na YJ, Chang H, Roh KM, Jang HD, Huang J. *Chem Commun* 2012;48:5968–70.
- [14] Cote LJ, Silva RC, Huang J. *J Am Chem Soc* 2009;131:11027–32.
- [15] Cote LJ, Kim F, Huang J. *J Am Chem Soc* 2009;131:1043–9.
- [16] Hummers WS, Offeman RE. *J Am Chem Soc* 1958;80:1339.
- [17] Kim F, Luo J, Silva RC, Cote LJ, Sohn K, Huang J. *Adv Funct Mater* 2010;20:2867–73.
- [18] Jang HD, Kim SK, Chang H, Roh KM, Choi JW. *Biosens Bioelectron* 2012;38:184–8.
- [19] Kudin KN, Ozbas B, Schniepp HC, Prud'homme RK, Aksay IA, Car R. *Nano Lett* 2008;8:36–41.
- [20] Xu Y, Bai H, Lu G, Li C, Shi G. *J Am Chem Soc* 2008;130:5856–7.
- [21] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS. *Carbon* 2007;45:1558–65.
- [22] Luo J, Jang HD, Huang J. *ACS Nano* 2012;2:1464–71.