

# Silver-coated graphene electrode produced by electrolytic deposition for electrochemical behaviors



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## ABSTRACT

This study evaluates the excellent electrochemical performance of silver (Ag)-coated graphene electrode using an electrolytic deposition technique. Ag particles are introduced to the graphene surface as a function of the applied current. A half cell of the Ag-coated graphene electrode is fabricated to examine the electrochemical performance, such as the charge–discharge behaviors, cyclic voltammetry, and specific capacitance. As a result, the electrochemical performance of the Ag-coated graphene electrode is two times higher than that of the crude graphene electrode.

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## 1. Introduction

The use of graphite as an electrochemically active material for widely electrochemical applications, such as capacitors and fuel cells, has reached its limit due to the limited theoretical capacity, low specific surface area, and rigid chemical resistance. Many studies have reported the modification of graphite materials to overcome these limitations [1–3].

Recently its discovery in 2004 [4], graphene derived from graphite has been a major focus with enormous scientific and technological interest [5–7] due to the special properties including high mechanical strength [8,9], thermal conductivity [10], large specific surface area [11], and faster electron migration rate [12]. In particular, unlike carbon nanotubes, graphene can be obtained from graphite, and the excellent properties and potential for the utilization of graphite has made it a target of many studies [13,14].

Graphene has been widely considered as a building block for electrochemically active materials and as a substrate for loading of metal particles. Some studies have reported that the electric properties are enhanced by adding graphene as an additive to existing active substance, or forming a complex with other chemical

compounds [15,16]. Graphene was applied to a range of experiments to adjust the electric, chemical and optical, and magnetic properties after doping graphene with various chemicals [17–20].

The metal particles-loaded graphene has attracted application in fields of energy storage and conversion devices [21–23]. Some of those studies examined the metal particles-loaded graphene composites depending on the loading method, metal amount, and so on. Meanwhile, when a cheaper metal, such as manganese (Mn), copper (Cu), cobalt (Co) or nickel (Ni), is added, the voltage was revealed to poor stability, low conductivity and large volume change during the charge/discharge processes, recording either a too high or too low voltage [24–26].

The metal particles-loaded graphene composites were examined in the form of graphene suspension using metal precursors, a typical metal oxide, was used in most cases [27–30]. Such studies focused on enhancing the high speed charge and discharge, including the polymerization of graphene with metal oxides [31–33]. However, it is difficult to commercialize those methods due to the technical limitations caused by the additional hydro-thermal process or oxidation process with metal precursors.

To solve such problems, this study focused on coating graphene with metal particles by an electrolytic deposition technique. It has been regarded as the processing technique for the production of metal or ceramic coatings on a variety of substrates for numerous applications [34,35]. In particular, it has important advantages that metal ions or complexes are stable in the bulk of solutions at low

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pH, are hydrolyzed by electrogenerated base at the electrode surface to form colloidal particles. These particles coagulate to form cathodic metallic deposits [36].

In this study, a graphene electrode showed that the uniform Ag particles on the graphene surface uniformly with the aid of an electric current. The Ag-coated graphene electrode exhibited superior electrochemical properties to the crude graphene.

## 2. Experimental details

### 2.1. Materials and sample preparation

Graphene oxide (GO) was produced using the modified Hummer's way [37]. A 9:1 mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) was added to a mixture of graphite flakes and potassium permanganate ( $\text{KMnO}_4$ ). Details of the process are available in our precious paper [38]. Further, the GO was dispersed by ultrasound processing in distilled water for 2 h. Next, hydroquinone was added to the GO solution at a mass ratio of 1:1. After chemical reduction, the GO solution was then heated to  $150^\circ\text{C}$  for 24 h with agitation. The reduced GO solution was dried in a vacuum oven at  $80^\circ\text{C}$  after washing with distilled water, which labeled as 'Graphene' hereafter in this study.

The graphene (as an active material) and polyvinylpyrrolidone (PVP, as a binder) of ratio 9:1 (w/w) were put in *N*-methyl-2-pyrrolidone (NMP) as a solvent with agitation, which were used to produce the slurry. The graphene slurry was then coated on surface of the stainless steel sheet (SUS), which was used as a current collector in this study after drying fully at  $100^\circ\text{C}$  for 12 h.

### 2.2. Manufacturing of Ag-coated graphene electrode

Ag particles were introduced on the graphene electrode using an electrolytic deposition technique. The concentration of Ag solution was fixed to 0.1 M  $\text{AgNO}_3$ . The anode electrode and cathode electrode were connected to the SUS and the graphene electrode, respectively. The applied electric currents were varied to 0, 0.01, 0.05, 0.10, 0.50, and 1.00  $\text{mA cm}^{-2}$  for 30 min. The results were called 'Ag-0/Gr' to 'Ag-1.00/Gr' according to the current intensity ('Gr' means the graphene prepared by chemical reduction in this study).

### 2.3. Characterization

The Ag-coated Gr electrodes (Ag/Gr) were examined by X-ray diffraction (XRD, Bruker Model D2 Phaser, Bruker Co.) using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The feature and morphology Ag/Gr were observed by scanning electron microscopy (SEM, Model S-4300, HITACHI Co.). X-ray photoelectron (XP) spectra were obtained using an achromatic  $\text{MgK}\alpha$  X-ray source operated at 150 W (Model ESCA LAB MK II, VG Scientific Co.) to confirm the Ag loading amount on Ag/Gr surfaces. To examine the electrochemical properties, cyclic voltammetry and galvanostatic method (Model Autolab PGSTAT 30, IviumStat instrument Co.) were carried out to measure the charge and discharge properties. The Ag-coated Gr electrode prepared in this study was used as the working electrode.  $\text{Ag/AgCl}$  was used as the reference electrode and a Pt electrode was used as the counter electrode. All the electrochemical properties were measured at room temperature using a 6 M KOH solution as the electrolyte.

## 3. Results and discussion

### 3.1. Surface and structural properties of Ag-coated graphene

XRD was performed to analyze the fine structure and crystal structure of the Ag/Gr samples. As shown in Fig. 1, the layers of

initial substance graphite were combined by van der Waals forces, exhibiting sharply at  $2\theta = 26, 57, \text{ and } 86^\circ$ . The GO possessed typical layered structure with larger interlayer spacing of 0.8 nm. The XRD peak of graphene of which the distance between the layers was 3.35  $\text{\AA}$  ( $d = 3.35 \text{ \AA}$ ), showed different properties from that of graphite. It was revealed that the graphene had typical characteristics of graphite, expressing as  $2\theta = 26^\circ$  (C 002). Compared to graphite, the (C 002) peak of graphene showed considerably broad characteristics at  $2\theta = 26^\circ$ , meanwhile, the (002) peak of GO at  $2\theta = 14^\circ$  disappeared. According to the result, the graphene prepared by the chemical oxidation and reduction had the characteristics of a thin film composed of one or more layers [39,40].

Fig. 2 shows the XRD patterns of the Ag-0/Gr and Ag-0.10/Gr samples to confirm the structural characteristics of graphene before and after Ag coating. As previously mentioned with graphene, Ag-0/Gr and Ag-0.10/Gr samples exhibited the broad characteristics of graphene composed of several layers. The Ag particles coated on the graphene surface was confirmed by the obvious peaks corresponding to the (111) and (200) diffraction of fcc Ag at  $2\theta = 38$  and  $44^\circ$ , respectively [41].

Fig. 3 shows SEM images of the Ag/Gr samples with applying the current intensities. In the case of Ag-0/Gr (a), no particles were observed on the graphene electrode. On the other hand, in the case of Ag-0.01/Gr (b), where the current intensity of 0.01 mA was provided, a wispy coating of Ag particles having average size of 35 nm on the surface was observed on the graphene electrode. Depending on the applied current intensity, the Ag particle size on graphene electrode varied from several hundred nanometers to several micrometers. When the applied currents were more than  $0.05 \text{ mA cm}^{-2}$ , the Ag particle had covered on the whole graphene surfaces and the sizes also increased with increasing the applied current intensities. The average sizes of Ag particles were 47, 88, 102, and 153 nm for Ag-0.05Gr, Ag-0.10/Gr, Ag-0.50/Gr and Ag-1.00/Gr, respectively. Meanwhile, no other significant change in morphology other than the particle size in accordance with the current was observed. Although the current intensity might be related to the growth behaviors of Ag particles, it did not have a large effect on the morphology.

The Ag loading amount on the Ag/Gr surfaces were confirmed by XPS measurements, as listed in Table 1. The Ag loading amount of Ag/Gr samples were increased with increasing the applied current intensities and the oxygen contents decreased after the electrolytic deposition of Ag. It could be investigated that the Ag particles were primarily anchored in the oxygen-functional groups

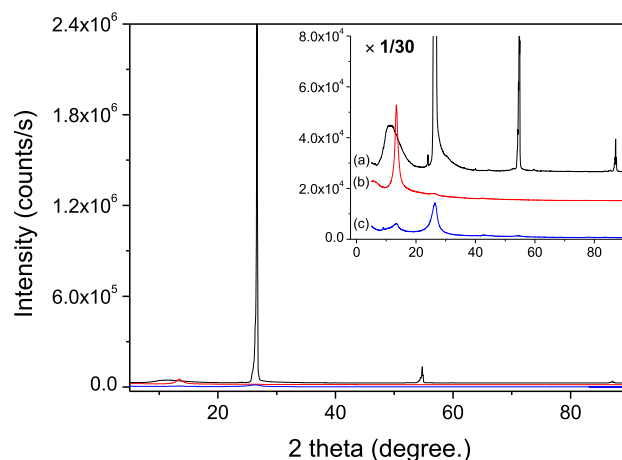


Fig. 1. Wide XRD patterns of graphite (a), graphene oxide (b), and graphene (Gr) (c).

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