

Solution Processible Metal Nanoparticle Embedded Reduced Graphene Oxide for Stretchable and Conductive Electrode

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Abstract

The emergence of stretchable devices that combine with conductive properties offers new exciting opportunities for wearable applications. Here, a novel, convenient and inexpensive solution process was demonstrated to prepare *in situ* silver (Ag) or platinum (Pt) nanoparticles (NPs)-embedded rGO hybrid materials using formic acid duality in the presence of AgNO₃ or H₂PtCl₆ at low temperature. The AgNP-embedded rGO hybrid electrode on an elastomeric substrate exhibited superior stretchable properties including a maximum conductivity of 3012 S cm⁻¹ (at 0 % strain) and 322.8 S cm⁻¹ (at 35 % strain). Its fabrication process using a printing method is scalable.

1. Introduction

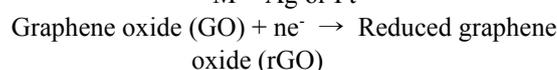
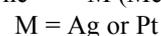
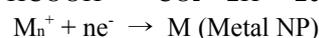
Graphene oxide (GO) derived from graphite with acid treatments, a single layer of sp² and sp³-bonded carbon atoms arrayed into a paradigmatic 2D carbonaceous nanomaterial, has attracted wide interest due to its extraordinary solubility and easily achievable chemical functionalities with other inorganic materials under various solution process. Recently, metal fabricated-rGO/hybrid materials or nano-composites have attracted intense research interest due to their optical, electronic, thermal, mechanical, and catalytic properties.¹ An overall goal is to fabricate composites or hybrid materials which can integrate GO or rGO with polymers, metal nanoparticles (NPs) or even nanotubes and fullerenes. Herein, we report a novel method to prepare new hybrid rGO-AgNP conducting materials by carefully designed reduction duality of formic acid at low temperature (Fig. 1(a)). To get the homogenous rGO-metal NP film without any kinds of aggregation, a dispersibility issue in any solvent system is very important. Since a conductive rGO and silver NP are not dispersible in water at all, to find an *in-situ* direct reduction of dispersible GO to rGO and simultaneously direct reduction to dispersible Ag ion into Ag metal NP in aqueous phase is a key issue. Fortunately, we found that the formic acid could reduce silver positive ion into silver metal NP and also simultaneously reduce GO into rGO in aqueous phase. As expected, these composite materials can be applied for highly stretchable conductive electrodes using a simple printing technique.

2. Results

In situ synthesis of metal embedded graphene materials by reduction duality of formic acid

We carefully designed an *in situ* synthesis of rGO-metal NPs by using reduction duality of the formic acid in presence of AgNO₃ or other metal salts. Here, AgNO₃ acts as an initiator of the reduction process as well as the source of AgNPs. Once the reduction process starts, the reduction duality of the formic acid can convert graphene oxide (GO) to rGO and also simultaneously deposit the positively charged metal ion to metal NP on the rGO nano-sheets. In a typical reaction, 40 mg GO was dispersed in DI water, and then 1-2 mL of formic acid and a catalytic amount (5 mg) of AgNO₃ were added. The reaction mixture was then heated to 80 °C to yield rGO-AgNP hybrid materials (Fig. 1(a)).

We also carried out these reactions taking formic acid and AgNO₃ separately under similar conditions for the control experiments. GO was not reduced, and no AgNPs were generated in either case. When catalytic amounts of AgNO₃ were added to the formic acid, the reaction performed well. As we mentioned earlier, AgNO₃ initiated the reduction of GO by formic acid, and once the reduction process began, formic acid reduced both the GO and AgNO₃ simultaneously to produce AgNP-embedded rGO hybrid materials *in situ*. The formic acid plays a dual role to reduce GO into rGO and simultaneously convert Ag ions to AgNP via a reduction process.² We have postulated mechanism for the reduction duality of a formic acid, indicating the conversion of metal ions to metal nanoparticles and also simultaneous reduction of GO into rGO.



Fabrication and characterization of rGO-AgNP based stretchable hybrid films

To prepare stretchable and conductive rGO-AgNP hybrid films, as-prepared rGO-AgNP powder was grounded and sonicated in a polyvinylidene fluoride (PVDF) solution. Firstly, the rGO-AgNP hybrid film with an average thickness of 30 μm on PET or glass substrate was prepared by doctor blade technique, and then for an embedding, elastomeric polymer solution such as nitrile butadiene rubber (NBR) was poured onto the rGO-AgNP film (Fig. 1(b)).

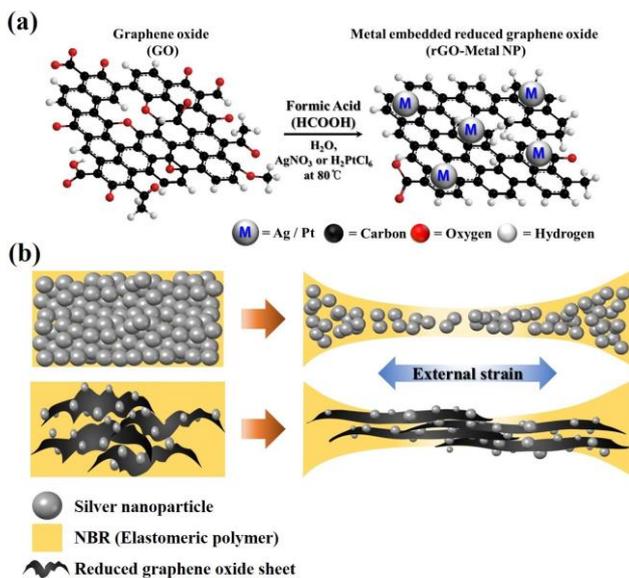


Fig. 1 Schematic illustration of in situ synthesis of metal nanoparticle embedded reduced graphene oxide (rGO-AgNP) and possible stretchable mechanism of rGO-AgNP hybrid films in a polymer matrix. (a), Synthesis of metal-embedded rGO from GO by reduction duality of formic acid. (b), a schematic representation of the stretchable and conductive rGO-AgNP hybrid films.

Finally, the rGO-AgNP hybrid film was easily peeled off from the substrate after drying and curing with hot-roll pressing at 150 °C. Fig. 2(a) shows the conductivity of the rGO-AgNP hybrid films at 0 % strain as a function of a mass fraction of AgNPs. The masses of the other components (rGO 100 mg, 10 wt% of PVDF solution in NMP 100 μ L) were fixed.

The conductivity of the rGO-AgNP hybrid film was started to increase when the mass fraction of AgNPs was reached at a 9.0 wt%. The mass fraction of AgNP above 20.01 wt% resulted in a brittle film with a phase separation. Surprisingly, a bare AgNP film was not stretchable at all and had a relatively low conductivity. Theoretical prediction for the conductivity of the hybrid film was calculated using a power-law relationship and 3D percolation theory. Simply, the power-law relationship³ is describe by

$$\sigma = \sigma_0(V_f - V_c)^s \quad (1)$$

where σ is the electrical conductivity of the composite, σ_0 is the conductivity of the conductive filler, V_f is the volumetric fraction of the filler, V_c is the volumetric fraction at the percolation threshold, and s is the fitting exponent. AgNPs were modeled as uniformly distributed nanoparticles with a random orientation, and the percolation threshold was calculated using the average interparticle distance model. The calculated percolation threshold (5.86 vol% after the drying process, which is equivalent to 9.57 wt% in the initial mixture) and the power-law relationship indicated good agreement with our experimental results.

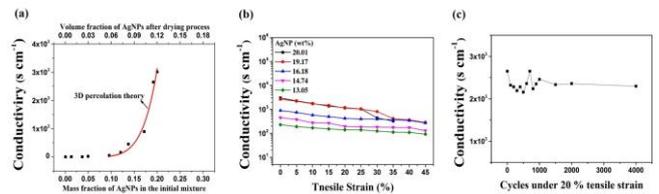


Fig. 2 Electrical characteristics of rGO-AgNP hybrid films. (a), Conductivity of the hybrid rGO-AgNP film, composed of rGO decorated with varying amount of silver nanoparticles, investigated at 0 % strain. The red line is a prediction based on a power-law relationship and three dimensional percolation theory. (b), Conductivity of the hybrid rGO-AgNP films under tensile strain for five different fraction of silver nanoparticles. (c), cycling test of rGO-AgNP hybrid film (19.17 wt%) under 20% tensile strain.

Fig. 2(b) shows that the conductivity of the rGO-AgNP hybrid film (40 \times 5 \times 0.03 mm) was measured under varying tensile strains using four-point probe system. The as-prepared hybrid film embedded in elastomeric polymer showed a maximum conductivity around 3012 S cm⁻¹ at 0% strain and the conductivity of the rGO-AgNP hybrid film was reduced with an increasing strain, and a conductivity of 322.8 S cm⁻¹ was measured at 35% strain. The mass fraction of AgNPs rarely affected a stretchability, and all hybrid films were ruptured at 50 % strain. Cycling test was carried out up to 4,000 cycles, which are shown in Fig 2(c). Conductivity was initially fluctuated and then stabilized after 1,500 cycles.

3. Conclusions

In conclusion, a novel, convenient, and inexpensive solution process were demonstrated for fabrication of metal NP-embedded rGO hybrid materials using reduction duality of formic acid. The highly conductive and stretchable electrode with a high conductivity 3012 S cm⁻¹ at 0 % and 322.8 S cm⁻¹ at 35 % strain was successfully prepared using printable metal embedded rGO ink on a substrate that provided highly stretchable through elastomeric polymer embedding process. These wet-processible, stable rGO-metal hybrid materials can be applied to a graphene based conductive ink for the stretchable electrode including large-area electronic circuit, epidermal electronics and wearable energy storage devices as charge collectors, and in other modern nano-electronics.

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