

Recent Nanoarchitectures in Metal Nanoparticle-Graphene Nanocomposite Modified Electrodes for Electroanalysis

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While increasing attention has been devoted to the use of carbon-based nanomaterials or metal nanoparticles (MNPs) as electrode modifiers for electroanalysis, there is a noticeable development in studies using MNP-graphene nanocomposites or nanohybrids in very recent years. In this review, first, very recent nanoarchitectures in MNP-graphene nanocomposites for modifying electrodes (mainly in 2013) are summarized together with the targets and achievements of electroanalysis. The variety of nanoarchitectures comes from the fact that graphene oxide and metal precursor ions can be reduced chemically or electrochemically, and concurrently or stepwisely. By browsing various preparation methods of the modified electrodes, some characteristic and interesting features of the preparations of MNP-graphene nanocomposites are described together with the possibilities and prospects as electrode modifiers for electroanalysis.

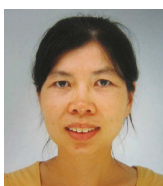
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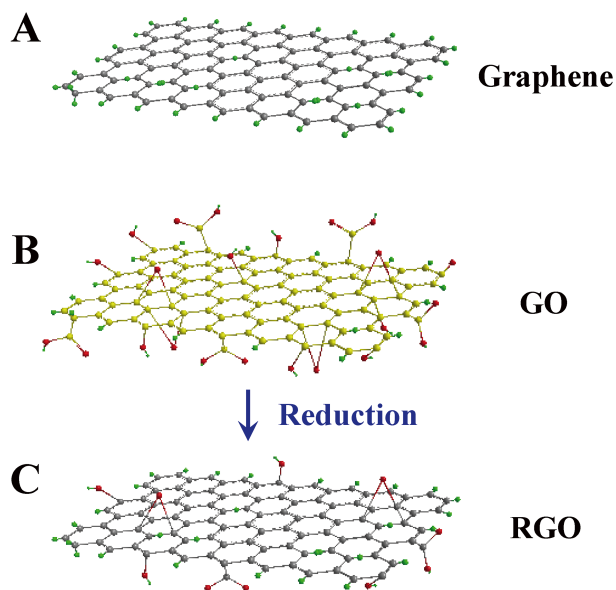


Fig. 1 Structures of (A) graphene, (B) graphene oxide (GO) and (C) reduced graphene oxide (RGO). Red balls indicate oxygen atoms.

1 Introduction

In a previous review, one of the authors (M. O.) focused on nanoarchitectures in metal nanoparticle-modified electrodes for electroanalysis, covering studies up to 2009.¹ While this area is still a focus of active interest, the combination of metal nanoparticles (MNPs) and graphene could be regarded as one of the new emerging hot topics in very recent years. Graphene (whose structure is shown in Fig. 1A) can be utilized as a functional modifier of base electrodes, so it has come to play a very important role in electroanalytical chemistry and analytical sciences as shown in some recent reviews.²⁻⁵ Guo and Dong summarized the development of graphene and its derivative-based sensing materials for analytical devices for electrochemical and optical sensing.² Chen *et al.* presented the advances of graphene and graphene-based nanomaterials for electroanalytical chemistry.³ Pérez-López and Merkoçi reviewed the trends of carbon nanotubes and graphene in analytical sciences, in particular in biosensing.⁴ Walcalrius *et al.* reported the trend of nanomaterials for bio-functionalized electrodes,⁵ in which graphene was focused as well as carbon nanotubes and MNPs.

While the combination of MNPs and graphene has been addressed in the above mentioned reviews, there has been an explosion of research in the use of MNP-graphene nanocomposites or nanohybrids. In this field, one typical application is for use as electrocatalysts in fuel cells as reported in some recent papers.⁶⁻¹⁰ However, applications of MNP-graphene nanocomposites as electrode modifiers are quite important also in the field of electroanalysis. Thus, in the present special review, we would like to summarize very recent trends in nanoarchitectures of MNP-graphene nanocomposites for constructing modified electrodes. By reviewing some achievements published mainly in 2013 for electroanalysis, we would like to discuss the possibilities and prospects concerning MNP-graphene nanocomposite modified electrodes.

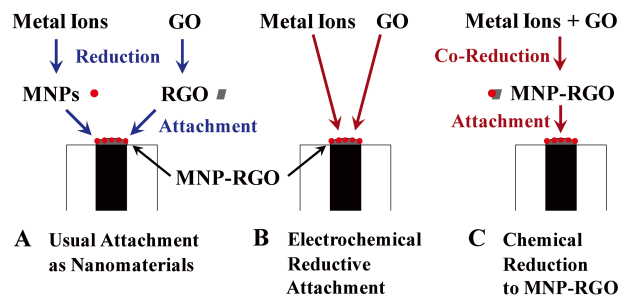


Fig. 2 Schematic representation of the modification of MNP-RGO on the electrode surface. (A) A method to prepare MNPs and RGO separately, and then to attach on the electrode surface. This approach is the most commonly adopted for modifying inert nanomaterials that do not interact with each other. (B) Because metal ions and GO can be reduced electrochemically, reductive attachment on the electrode surface is possible. (C) If chemical co-reduction of metal ions and GO can form MNP-RGO, it can be modified on the electrode surface after the preparation.

2 Basic Background

Active research studies on graphene were initiated recently by the first isolation of a single layer graphene sheet with mechanical exfoliation from highly oriented pyrolytic graphite in 2004,¹¹ and the interesting characteristics and advancements of graphene were summarized later by Geim and Novoselov in 2007.¹² However, in recent electrochemical works using graphene, the starting material has usually been graphene oxide (GO) that is prepared in a solution phase. Figure 1B shows the typical structure of GO. The preparation method is often referred to as the modified Hummer method.¹³⁻¹⁵ The liquid phase synthesis of GO is suitable for mass-production, and the GO can be chemically reduced to change the electrical characteristics from insulating to conducting.¹⁶ For example, as a result of the reduction of GO by hydrazine, it was shown that the conductivity of the reduced GO was comparable to that of pristine graphite, but that O atoms remained in an atomic C/O ratio analysis.¹⁷

In general, it may be difficult to regard reduced GO (RGO) as genuine graphene. Figure 1C shows a possible state of RGO after the reduction of GO; the graphene structure (Fig. 1A) should be formed after the complete removal of O atoms. In some literature, RGO or rGO has been used as the abbreviation of “reduced graphene oxide”. On the other hand, in some simplified cases, “reduced graphene oxide” has been simply written as “graphene” without a presentation of the results of detailed analysis. Thus, in this review, hereafter we use the abbreviation of “RGO” for “reduced graphene oxide” even if it is differently abbreviated in the original papers, though “graphene” was used in the title of this review to represent the derivatives.

For modifying base electrodes, typically a glassy carbon electrode (GCE), one approach would be a simple modification using MNPs and RGO prepared *via* the reduction in advance as shown in Fig. 2A. This would be expected from usual modifications of general nanomaterials. However, there is a wide variety in the modification of MNP-graphene nanocomposites (hereafter we abbreviate it as MNP-RGO), because the reduction can be performed using either chemical or electrochemical methods for the precursors of MNPs (*i.e.*, appropriate metal complex ions) and GO, and because the reduction can be carried out concurrently or stepwisely.

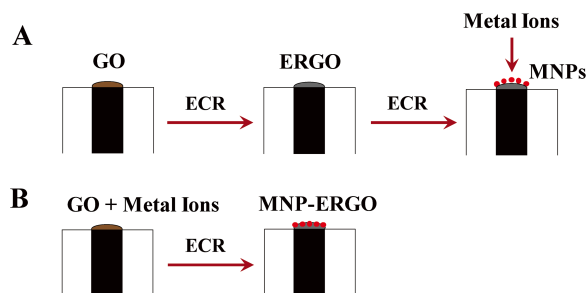


Fig. 3 Schematic representation of electrochemical preparations. (A) Electrochemical reduction of GO followed by the electrodeposition of MNPs. (B) Co-electrodeposition of MNPs and ERGO. ECR denotes "electrochemical reduction".

Figures 2B and 2C show the schematic representations of a typical electrochemical reductive attachment and a typical chemical reduction to form MNP-RGO followed by the attachment, respectively. However, in addition to these typical ones, various nanoarchitectures are possible for preparing MNP-RGO modified electrodes. In the following sections, we summarize the actual state-of-the-art nanoarchitectures in this field together with the electroanalytical targets.

3 Electrochemical Preparations

3-1 Electrochemical reduction of GO followed by electrochemical depositions of MNPs

The first example is a stepwise electrochemical preparation, *i.e.*, the first step is the reduction of GO to form electrochemically reduced GO (ERGO) and the next is the reduction of metal ions to form MNPs on ERGO (Fig. 3A). Ting *et al.* reported the preparation of gold NPs (AuNPs) decorated ERGO for detecting nitric oxide (NO).¹⁸ As the actual procedures, GO nanosheets with negative charges were attached on the surface of a GCE *via* an electrophoretic deposition. Then, the attached GO was electrochemically reduced to form ERGO by cyclic voltammetric scanning. Finally, AuNPs were *in situ* synthesized onto ERGO film by electrochemically reducing HAuCl₄. Because the ERGO network provided high conducting pathways and a large surface area for catalyst support and because AuNPs act as efficient electrocatalysts for NO oxidation, the prepared electrode showed good performance for the detection of NO observing amperometric responses. It was also demonstrated that the electrode could be used to detect the dynamic release of NO from live human umbilical vein endothelial cells (HUVECs).

Concerning the same combination of AuNPs and ERGO, Tang *et al.* developed a new electrochemical sensor for 4-nitrophenol.¹⁹ In their experiment, the electrochemical deposition of RGO on a GCE was performed by direct cyclic voltammetric electrolysis under magnetic stirring and N₂ bubbling. Then, AuNPs were electrodeposited on ERGO/GCE at a constant potential electrolysis of HAuCl₄. It has been reported that the synergetic effect of AuNPs and ERGO as co-modifiers greatly facilitate electron-transfer processes, and thus lead to remarkable sensitivity for 4-nitrophenol detection in two detection modes, differential pulse voltammetry and square wave voltammetry. In the paper, the analytical performances for 4-nitrophenol were compared with 12 different modified electrodes in a table. Also, the application for river water samples was described.

As an example of different MNPs by the same scheme of Fig. 3A, Zhang *et al.* fabricated PdNP-ERGO nanocomposite modified GCE for the detection of nitrite (NO₂⁻).²⁰ In their experiment, firstly, GO modified GCE was prepared by drop casting GO suspensions onto the surface of GCE. Then, GO was reduced by a cyclic voltammetric reduction. PdNPs were electrochemically deposited on the ERGO/GCE by applying a constant potential to reduce PdCl₄²⁻. The prepared electrode exhibited enhanced electrocatalytic behavior to the oxidation of nitrite.

Similarly, the electrodeposition of PdNPs was performed by Hossain and Park.²¹ In their work, chemically modified GO (CGO) was prepared, and then CGO was attached on a gold electrode (AuE) by a cast method. The CGO on the Au electrode was electrochemically reduced by cyclic scans while noting the conductivity change of CGO,²² and then PdNPs were electrodeposited on the ERGO/AuE. The formed electrode was used for the non-enzymatic detection of H₂O₂ and glucose by recording amperometric responses. In their paper, the researchers compared the analytical performance for H₂O₂ with the previous results obtained using four different modified electrodes.

For preparing ERGO, Shang *et al.* mixed 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide dissolved in DMF with a GO aqueous suspension to form an ionic liquid-GO (IL-GO).²³ It was transferred onto a GCE and electrochemically reduced to form an IL functionalized ERGO. Then, the electrochemical reduction was performed in a solution containing PdCl₂ and HAuCl₄ to form Pd-Au alloy NPs. The formed electrode was used for the detection of oxalic acid. In the paper, the analytical performances for oxalic acid were compared with the previous results obtained using four different modified electrodes.

As the base electrode, a carbon fiber electrode (CFE) was examined for layer-by-layer assembly of RGO and AuNPs by Du *et al.*²⁴ In the study, referring to a previous preparation of RGO wrapped carbon cloth electrode,²⁵ 0.5 mg/mL GO dispersed aqueous solution was prepared, and it was drop-cast onto a CFE. After drying in air, a constant potential electrochemical reduction was performed at first, and then AuNPs were electrochemically deposited from AuCl₄⁻. In addition to AuNPs/ERGO/CFE, the researchers prepared RGO/AuNPs/ERGO/CFE by repeating one reduction process of GO. The RGO/AuNPs/ERGO/CFE was reported to have good performance for simultaneous determination of uric acid (UA) and dopamine (DA) in comparison with the ERGO/CFE and the AuNPs/ERGO/CFE.²⁴

3-2 Co-electrodeposition of ERGO and MNPs

While several examples of stepwise preparation (Fig. 3A) are summarized in section 3-1, co-electrodeposition from GO and metal ions can be performed to form MNP-ERGO nanocomposites as shown in Fig. 3B.

Liu *et al.* reported the formation of an AuNPs-ERGO composite film by cyclic voltammetric electrodeposition on a GCE.²⁶ In their experiment, the GO purchased from a provider was exfoliated in 0.1 M carbonate buffer solution by ultrasonication, and then, the cyclic voltammetric electrodeposition was performed for the dispersion containing GO and HAuCl₄. An electrochemical quartz crystal microbalance was used to trace the film formation processes and detect the interactions of arsenic species with the AuNP-ERGO film. The formed film was used in anodic stripping voltammetry analysis of As(III). In their paper, the researchers compared the analytical performance of As(III) with

the previous results obtained using 11 different modified electrodes.

Lu *et al.* also used the co-electrodeposition method.²⁷ However, as a difference from Ref. 26, they added chitosan, which has excellent film-forming ability and good water permeability, into 0.1 M acetate buffer suspension containing HAuCl_4 and GO, followed by the cyclic voltammetric electrodeposition. The formed film was used in differential pulse anodic stripping voltammetry analysis of Pb(II) . In the paper, the analytical performances for Pb(II) were compared with the previous results obtained using seven different modified electrodes.

For preparing PdNPs, Palanisamy *et al.* pretreated PdCl_2 and GO before electrolysis.²⁸ Actually, the mixture of GO and PdCl_2 was sonicated to attach Pd^{2+} on to GO sheets, and then centrifuged to remove free Pd^{2+} . The resulting Pd^{2+}/GO solution was drop casted onto a GCE and reduced at a constant potential to form PdNPs-RGO. The analytical performances for DA were explored in this work, and were compared with the previous results obtained using five different modified electrodes.

3.3 Other electrochemical-based approaches

Electrochemical methods have been used for reducing GO and metal precursor ions as summarized above. However, in some cases, non-electrochemical processes can be combined with electrochemical processes for unique nanostructuring.

Qin *et al.* developed *in situ* synthesis of highly loaded ultrafine PdNP-decorated GO for glucose biosensor applications.²⁹ In the study, referring to a previous work on the reaction of a water-soluble Pd precursor and GO,³⁰ a water-insoluble precursor, Pd(OAc)_2 , was used. By dissolving it in 1,2-dichloroethane and by volatilizing, the contact between Pd(OAc)_2 and GO dispersion was enhanced, and consequently, highly loaded and ultrafine PdNPs supported on GO (PdNP-GO) was synthesized. While the PdNP-GO was obtained *via* this non-electrochemical manner, it was reduced to PdNP-ERGO after dropping a dispersion of PdNP-GO on a GCE and air drying. In this manner, a PdNP-ERGO based glucose sensor was constructed with the modification of glucose oxidase and applied for amperometric detection. In their paper, the researchers compared the analytical performance of glucose with earlier results obtained using four different MNPs and carbon nanomaterials-modified electrodes.

Instead of the electrochemical reduction of GO, Wang *et al.* adopted a chemical reduction of GO in their work to enhance the stability of modified electrodes.³¹ GO was reduced by hydrazine and mixed with chitosan (CS) to form the RGO-CS composite. After dropping a homogeneous solution of RGO-CS on a GCE and air drying, the PdNPs were electrochemically formed on the surface of the modified GCE with cyclic potential scans. The thus fabricated electrode was used for simultaneous determination of ascorbic acid (AA), DA and UA with cyclic voltammetry and differential pulse voltammetry. As the merits of the proposed electrode, stability, sensitivity, facility and economy were mentioned.

4 Chemical Preparations

4.1 Chemical co-reduction of GO and metal ions

As mentioned in the last example in section 3.3,³¹ GO can be reduced using chemical reagents, *e.g.*, hydrazine.¹⁷ Also, MNPs can be prepared *via* chemical reductions from appropriate metal precursor ions. Thus, chemical methods can be utilized to reduce GO and metal ions concurrently (Fig. 4A).

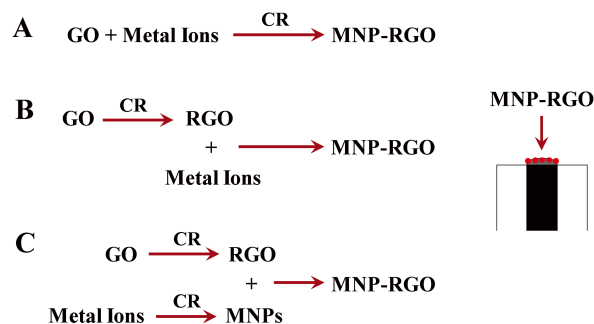


Fig. 4 Schematic representation of chemical preparations. (A) Chemical co-reduction of GO and metal ions. (B) Chemical reduction of GO followed by the *in situ* formation of MNPs. (C) Chemical reduction of GO followed by the attachment of prepared MNPs. CR denotes “chemical reduction”. In all the cases, MNP-RGO was modified on the electrode surface after the preparation of MNP-RGO.

As the first example of this chemical co-reduction of GO and metal ions, Ma *et al.* reported a chemical co-reduction procedure using NaBH_4 , in which the reduction of GO and deposition of AuNPs on graphene nanosheets were achieved in a single-step process.³² Compared with previous single step approaches,³³ it was mentioned that nearly monodisperse AuNPs uniformly dispersed on the surface of graphene nanosheets without aggregation using the proposed method. The dispersion of AuNPs-RGO was dropped onto the surface of the GCE, followed by drying in an infrared lamp. The fabricated electrode was applied to the simultaneous determination of hydroquinone (HQ) and catechol (CC). In their paper, the researchers compared the analytical performance of HQ and CC with the previous results obtained using six different modified electrodes.

As for the preparation of AuNP-RGO *via* a co-reduction method, the use of sodium citrate was previously reported to be applicable together with heat treatment at 80°C .³⁴ Cui and Zhang utilized this method for preparing AuNP-RGO, and modified a GCE using the DMF/aqueous (9:1) solution containing the AuNP-RGO.³⁵ The performance of the modified electrode was studied for the detection of epinephrine by comparing AuNPs/GCE and RGO/GCE. While sodium citrate was used to prepare AuNP-RGO from AuCl_4^- and GO, the researchers used hydrazine in the reduction of GO to RGO.

While nanocomposite materials such as AuNP-RGO can be normally prepared in solutions or as solids, one-pot green synthesis of self-assembled AuNP-RGO hybrid membranes was reported by Zhang *et al.*³⁶ They used glucose for reducing GO and AuCl_4^- by heating at 95°C , and prepared the hybrid membrane film with polyethylene terephthalate (PET). The hybrid membrane was transferred onto the surface of a GCE, and the sensing ability for H_2O_2 was studied.

For preparing a nanocomposite of silver NPs (AgNPs) and RGO, Kaur *et al.* reported a synthetic method to heat the mixture of GO and silver nitrate aqueous solution at 80°C in the presence of NaOH .³⁷ The formed AgNP-RGO was dispersed in an aqueous solution containing Nafion, placed on the GCE, and dried in air. The fabricated electrode exhibited excellent electrocatalytic activity toward the oxidation of AA, DA, UA and tryptophan, allowing for the simultaneous determination of their quaternary mixture. The analysis was applied for the determination of AA and DA in vitamin C tablets.

Wang *et al.* reported one pot green synthesis of AgNP-RGO with a hydrothermal method (190°C , 5 h) using gallic acid as a reducing agent.³⁸ In this method, AgNPs with an average size of

12 nm were successfully decorated on RGO sheets, and applied as a non-enzymatic H_2O_2 sensor by modifying a GCE with AgNP-RGO using Nafion.

Meanwhile, Li *et al.* reported a green synthesis of AgNP-GO nanocomposite using glucose as a reducing and stabilizing reagent.³⁹ Compared with the previous AgNP-GRO,^{37,38} Ag^+ was similarly reduced but GO was not reduced, which followed the manner of the previous fabrication of AgNP films on GO.⁴⁰ The thus prepared AgNP-GO nanocomposite was dissolved in DMF, cast on the surface of the GCE, and dried with an infrared lamp. Whereas the target was only tryptophan in this work, the determination performances were compared with the previous results obtained using 21 different modified electrodes.

Bimetallic NPs can be prepared by the chemical co-reduction method. Wu *et al.* reported the preparation of Cu-Ag bimetallic NPs on RGO and applied to an amperometric H_2O_2 sensor.⁴¹ In the preparation, ethylenediamine was at first modified on GO to anchor Cu^{2+} and Ag^+ , and then the co-reduction was performed using hydrazine. Yan *et al.* reported simultaneous electrochemical detection of AA, DA and UA using RGO modified with Pd-Pt bimetallic NPs.⁴² In their preparation, poly(diallyldimethylammonium chloride) (DPPA) was used according to a previous report for anchoring PtCl_6^{2-} and PdCl_4^{2-} .⁴³ For preparing similar Pd-Pt bimetallic NPs, another anchoring with Sn^{2+} was also reported.⁴⁴

Chen *et al.* reported a synthetic method of Pt-Pd bimetallic nanocubes on RGO using *N,N*-dimethylformamide (DMF) as a bifunctional solvent for the reductions of both GO and metal ions and for confining the growth of Pt-Pd nanocubes on the surface.¹⁰ By using the Pt-Pd bimetallic nanocube-RGO, nonenzymatic sensing of glucose at neutral pH was explored, and the performances were compared with the previous results obtained using seven different modified electrodes.⁴⁵

4.2 Chemical reduction of graphene oxide followed by the *in situ* formation of MNPs

While GO can be concurrently treated with the reductive formation of MNPs from metal ions, another approach would be the reduction of GO to form RGO (as the first step) followed by the *in situ* formation of MNPs from metal ions (as the second step) to form MNP-RGO (Fig. 4B). Although the chemical reduction of GO is the usual technique as mentioned in section 4.1, other methods, *e.g.*, solvent-assisted thermal reduction, are also possible for preparing RGO.⁴⁶

Chen *et al.* reported a preparation of ultrafine PdNPs on RGO for sensing hydrogen peroxide.⁴⁷ While the preparation of clean well-dispersive ultrafine PdNPs on GO by the redox reaction between PdCl_4^{2-} and GO was reported previously,³⁰ in Ref. 47 the thermal reduction of GO was performed (in an oil bath at 100°C for 24 h) before reacting with PdCl_4^{2-} . As a result, ultrafine, well-dispersed and clean PdNPs were modified on RGO nanosheets with higher conductivity. The PdNP-RGO nanocomposite was fixed on the surface of GCE with 0.5% Nafion ethanol solution, and applied for electrochemical detection of H_2O_2 utilizing the higher performance for the electrocatalytic reduction. In the study, the sensing performances for H_2O_2 were compared with the previous results obtained using eight different modified electrodes.

Furthermore, the researchers verified the same approach was applicable to prepare PtNP-RGO nanocomposite,⁴⁸ while it was previously found that Pt nanoflowers could be formed on GO using a co-reduction method with ethanol at room temperature.⁴⁹ The fabricated PtNP-RGO modified GCE was examined as a non-enzymatic oxalic acid sensor.⁴⁸

In order to prepare RGO from GO, Zhang *et al.* adopted a

treatment of GO with DA.⁵⁰ Because polydopamine (PDA) was prepared by self-polymerization of DA, PDA/RGO was reported to be formed in the treatment of GO and DA previously.⁵¹ After preparing the PDA/RGO, well-dispersed PtNPs were modified on PDA/RGO by reducing PtCl_6^{2-} with NaBH_4 . The isolated powder of PtNP-PDA/RGO was dispersed in water, cast onto the surface of GCE, and dried in air. The electrocatalytic activities of the thus prepared electrode were examined for the detection of H_2O_2 and O_2 .⁵⁰

4.3 Chemical reduction of graphene oxide followed by the attachment of MNPs

By performing special treatments during the reduction of GO, it is possible to attach MNPs prepared in advance separately (Fig. 4C). As one of the examples, similar to the case of PDA/RGO⁵⁰ discussed in section 4.2, Zhu *et al.* prepared PVP functionalized graphene from GO by using hydrazine for reduction in the presence of PVP.⁵² Then, hollow AuNPs were prepared in accordance with the procedure described in a previous report,⁵³ and mixed with the PVP/RGO to attach the hollow AuNPs. The prepared nanocomposite was dispersed in DMF, dropped on the surface of GCE and dried in an infrared lamp. The modified electrode was applied for the selective detection of DA in the presence of AA and UA.⁵²

Instead of the simple reduction of GO, it is known that water soluble RGO, or graphene, can be synthesized by introducing a small number of *p*-phenyl- SO_3H .⁵⁴ This sulfonated graphene (SG) was prepared by Si and Samulski to overcome the aggregations and precipitations of graphene that was yielded by removing the oxygen functionality of GO.⁵⁴ Using this SG, Li *et al.* reported a sensitive and selective nitrite sensor based on the AuNPs-SG modified GCE.⁵⁵ For the fabrication of the modified electrode, SG was modified first by casting and air dried, and then AuNPs prepared in advance were attached by achieving a saturated adsorption by electrostatic attraction. In the work, some analytical performance characteristics for nitrite were compared with the previous results using seven different modified electrodes. The same modified electrode was also applied for the simultaneous determination of HQ and CC.⁵⁶ In the related paper, anti-adsorption properties of AuNP-GS toward aromatic species were noted.

In section 4.1, one example for the preparation of AuNP-RGO hybrid PET membranes was described as Ref. 36. Similar to the PET membranes, some efforts have been devoted to form freestanding paper-like materials composed of RGO by Duan and coworkers.⁵⁷ In their work, the GO paper was fabricated using a mold-casting method. Namely, an aqueous dispersion of GO was placed in a casting mold, and an integrated layer of GO paper with smooth surfaces could be peeled out after water was completely evaporated. A RGO paper was prepared by the chemical reduction of a GO paper with HI, based on procedures described in a previous work.⁵⁸ Following their earlier 2D-assembly of AuNPs on GO paper by a dip casting method,⁵⁹ 2D-assembly of Au@Pt NPs were similarly formed on RGO paper, and the fabricated Au@Pt NPs attached RGO paper electrode was applied as a flexible biosensor to monitor live cell secretion of nitric oxide.⁶⁰

4.4 Other approaches

As chemical approaches, the co-reduction of GO and metal ions (Fig. 4A), the *in situ* formation of MNPs after the formation of RGO (Fig. 4B), and the attachment of MNPs on RGO (Fig. 4C) are the three major processes as summarized above. However, Zhuo *et al.* reported a different approach *via* self-catalysis reduction at room temperature; *i.e.*, MNPs with

Table 1 Summary of the recent electroanalytical works cited in this review

Ref.	Base Electrode ^a	Metal of MNPs	Preparation Method ^b	Analyte ^c	Detection Method ^d	Comparison ^e	Interference ^f	Application ^g	Submitted month, year ^h
18	GCE	Au	3.1	NO	A	8 (txt)	Oxalate, glucose UA, AA, Na ⁺ , Cl ⁻	NO from HUVECs	Mar. 2013
19	GCE	Au	3.1	4-Nitrophenol	DPV	12 (tbl)	9 phenol derivatives	River water (R)	May 2013
20	GCE	Pd	3.1	NO ₂ ⁻	A	—	Cl ⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , K ⁺ , Ca ₂ ⁺ , SO ₄ ²⁻	Drinking and river water (R)	Feb. 2013
21	AuE	Pd	3.1	H ₂ O ₂	A	4 (tbl)	AA, UA, AP	—	Mar. 2013
				Glucose	A	2 (txt)	AA, UA, AP	—	
23	GCE	Au-Pd	3.1	Oxalic acid	LSV	4 (txt)	—	Spinach	Oct. 2012
24	CFE	Au	3.1	DA + UA	DPV	3 (txt)	Na ⁺ , K ⁺ , NH ₄ ⁺ , Cl ⁻ , NO ₃ ⁻ , AA, Cu ²⁺	—	(May 2013)
26	GCE	Au	3.2	As ³⁺	ASV	11 (tbl)	—	Tap, spring and river water (R)	Feb. 2013
27	GCE	Au	3.2	Pb ²⁺	DPASV	7 (tbl)	Cu ²⁺ , Cd ²⁺ and 7 cations	River water (R)	Nov. 2012
28	GCE	Pd	3.2	DA	LSV	5 (tbl)	AA, UA, glucose	—	Feb. 2013
29	GCE	Pd	3.3	Glucose	A	5 (tbl)	AA, UA	Human blood serum	Aug. 2012
31	GCE	Pd	3.3	AA + DA + UA	DPV	—	—	—	Dec. 2012
32	GCE	Au	4.1	HQ + CC	DPV	6 (tbl)	AA, UA, phenol, 9 ions, resorcinol	Tap water (R)	Sep. 2012
35	GCE	Au	4.1	EP	CV	—	AA	EP solution (R)	Nov. 2011
36	none	Au	4.1	H ₂ O ₂	A	—	AA, UA, DA, glucose	—	Sep. 2013
37	GCE	Ag	4.1	AA + DA + UA + tryptophan	LSV	—	Na ⁺ , K ⁺ , Mg ²⁺ , Zn ²⁺ , glucose	Vitamin C tablet and human urine (R)	Jan. 2013
38	GCE	Ag	4.1	H ₂ O ₂	A	—	AA, UA, DA, glucose	—	Apr. 2013
39	GCE	Ag	4.1	Tryptophan	DPV	21 (tbl)	AA, UA, DA, glucose,	Human blood serum (R)	Jul. 2012
41	GCE	Ag-Cu	4.1	H ₂ O ₂	A	2 (txt)	—	—	Aug. 2013
42	GCE	Pd-Pt	4.1	AA + DA + UA	A, DPV	6 (tbl)	Glucose, citric acid, Na ⁺ , K ⁺ , Cl ⁻	Human blood serum and urine (R)	Mar. 2013
45	GCE	Pd-Pt	4.1	Glucose	A	7 (tbl)	AA, UA, Cl ⁻ , <i>p</i> -acetamidophenol	—	Sep. 2013
47	GCE	Pd	4.2	H ₂ O ₂	A	8 (tbl)	AA, DA, glucose	—	Dec. 2012
48	GCE	Pt	4.2	Oxalic acid	DPV	6 (tbl)	—	Spinach (R)	Feb. 2013
50	GCE	Pt	4.2	H ₂ O ₂	A	2 (txt)	7 ions, AA, UA, glucose, L-glycine, AA, UA	—	May 2013
52	GCE	hollow-Au	4.3	DA	A, DPV	5 (txt)	—	DA solution (R)	Feb. 2013
55	GCE	Au	4.3	NO ₂ ⁻	A	7 (tbl)	12 ions, HQ, CC, aminophenol	River water	Jan. 2013
56	GCE	Au	4.3	HQ + CC	DPV	5 (txt)	Phenol, glucose, resorcinol, AA	Tap water (R)	Jan. 2013
60	none	Au@Pt	4.3	NO	A, DPV	5 (tbl)	AA, DA, UA, NO ₂ ⁻ and 17 ions	NO from HUVECs	Feb. 2013
62	GCE	Pt	4.4	H ₂ O ₂	A	8 (tbl)	AA, AP, glucose, citric acid, urea	—	Jan. 2012

a. GCE; glassy carbon electrode, AuE; gold electrode, CFE; carbon fiber electrode. b. Classification in this review. c. Combination with “+” denotes “simultaneous determination.” DA; dopamine, UA; uric acid, AA; ascorbic acid, HQ; hydroquinone, CC; catechol, EP; epinephrine. d. A; amperometry, DPV; differential pulse voltammetry, LSV; linear sweep voltammetry, ASV; anodic stripping voltammetry, DPASV; differential pulse anodic stripping voltammetry. e. Number of other reported modified electrodes with which the electroanalytical performance features were compared in the text (txt) or as a table (tbl) including those in supporting information. f. Representative ions and molecules for which the interferences were examined. AP; acetaminophen. g. (R) means recovery percentages were examined for applying real samples. HUVECs; human umbilical vein endothelial cells. h. Month and year of publication online in parentheses.

desirable size and morphology were decorated at first on GO, and then used as catalyst to accelerate the hydrolysis reaction of NaBH₄ to reduce the GO.⁶¹ As the advantageous points of this approach, they summarized (i) possible control of the morphology and size of MNPs, (ii) a uniform distribution of MNPs with high density, (iii) no use of toxic reductants, (iv) reaction at room temperature and (v) applicability in a wide range of pH values.

As a method without using chemical or electrochemical reductions, Zhang *et al.* reported a microwave-assisted synthesis of PtNP-RGO for applying to a H₂O₂ sensor.⁶² Also, photochemical synthesis of AgNPs, PdNPs, AuNPs or PtNPs was reported on ZnO nanorod-modified RGO, and the electrocatalytic properties for H₂O₂ reduction were examined.⁶³

5 Characteristic Features in the Preparations of MNP-RGO

5-1 Remarkable variety of preparation methods

In the present review, we surveyed recent literature with the key words of “graphene” and “nanoparticles”, and selected works on electroanalysis. As a result, we found a remarkable variety of preparation methods. This would be due to the fact that there are various reductive routes from GO and metal ions. In Table 1, we summarize the characteristics and performance features of the recent electroanalytical works cited in this review.

While some examples of electrochemical and chemical preparations of MNPs on electrode surfaces were demonstrated in the previous review,¹ it is recognized that the combination of GO has significantly increased possible preparations. This would be a noticeable difference from the electrode modification of other carbon materials, such as fullerenes^{64,65} and carbon nanotubes.⁶⁶⁻⁶⁸ However, the variety of techniques available also suggests that there is no established method for electrode surface modification at present. It seems that each research group adopts their own methodology.

5-2 GO as the starting material

While GO has enhanced the variety of the preparations by involving the redox reactions, it is also worthwhile mentioning that the preparation of GO in solutions is now well-established¹³⁻¹⁵ and commonly carried out. Poor solubility of carbon materials would make treatment troublesome, but GO is soluble in water and other organic solvents. Hence, the chemical reactions of GO to form the nanocomposites can be easily carried out. Also, the solution phase preparation is suitable for mass production. Although the reduced form (RGO) might have lower solubility, some treatments are known to make RGO soluble;^{46,69,70} furthermore, if MNP-RGO is formed, it tends to become soluble. Therefore, the treatments in solution phase are inferred to lead to various advances of the MNP-RGO preparations.

As a practical point, the color of the solution is informative for determining the progress of the reduction of GO. Figure 5A shows a photo of an aqueous solution of GO and RGO prepared by reduction with hydrazine,⁶⁹ in DMF,⁷⁰ and by heat treatment.⁴⁶ The color change from brown to blackish is an indicator of the progress of the reduction. The degree of the reduction should change according to the reduction methods as recognized by the changes in absorption spectra as shown in Fig. 5B. In this case, the reduction with hydrazine (curve c) was effective in comparison with that by heat treatment (curve b), suggesting significant recovery of the electronic conjugation of graphene after the hydrazine reduction. While the difference appeared as the shift of the absorption maximum, the conversion of GO to RGO was recognized by the increase in the absorption in the visible region. The effects of the reduction degree are described in the next section.

5-3 Various degree of the reduction of GO

Since the conductivity of graphene is much better than that of GO,¹⁷ a recovery of the conductivity of RGO should be a measure of the progress of the reduction. The higher conductivity of RGO should be beneficial in electrochemical measurements. However, in some reports, even when GO was combined with MNPs without reduction, it seems that the lower conductivity of GO was not a cause of troubles in electrochemical measurements.^{30,39} Therefore, a complete or significant reduction of GO is not essential for preparing the MNP-RGO.

It is inferred that the degree of the reduction of GO would

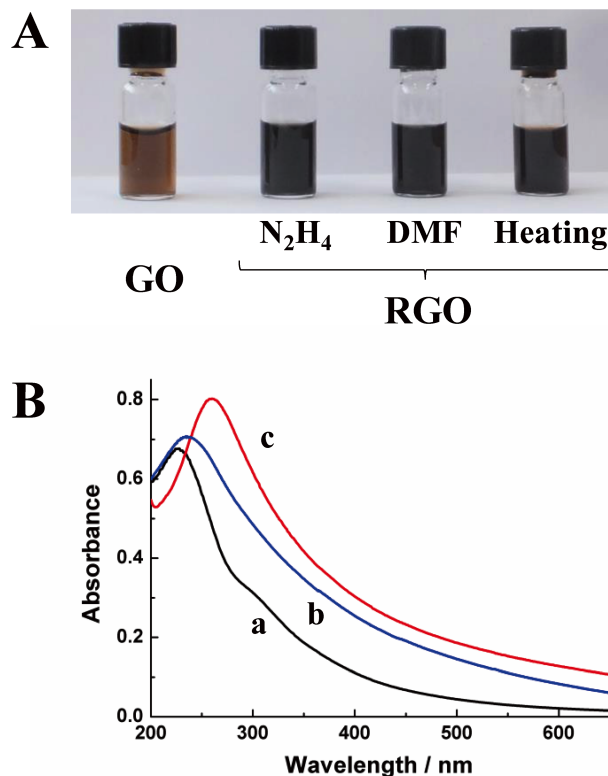


Fig. 5 (A) Photos of the solutions of GO and RGO. The solutions of RGO were prepared by hydrazine reduction,⁶⁹ in DMF⁷⁰ and by heat treatment.⁴⁶ (B) UV-visible absorption spectra of the solutions of (a) GO and (b, c) RGO. The solutions of RGO were prepared by (b) heat treatment⁴⁶ and (c) hydrazine reduction.⁶⁹

depend on the preparation method, and that some remaining oxygen atoms would not significantly affect the performance of electroanalysis. The degree of the reduction from GO to RGO is not reported explicitly in many cases. However, qualitative progress of the reduction would be recognized from the color change as mentioned in section 5-2.

5-4 Functions of GO in chemical reactions involving metal ions

In the chemical reactions of GO or RGO toward metal ions, the multi-functionality of GO should be noted. While the original purpose of GO moieties might be to serve as a support or counterpart for MNPs, GO can work as an anchor of metal ions or MNPs and a kind of capping or stabilizing reagent of MNPs. Therefore, in some cases, “clean” synthesis of MNP-GO^{30,49} or MNP-RGO^{8-10,45,47,48,71} is possible without using special capping reagents. The cleanness, *i.e.*, without using protective organic molecules, should be beneficial for electrochemical and catalytic applications. Furthermore, the synthesis would be suitable for strategically designing bimetallic NP-RGO.^{9,10,45,71} As for some actual formed structures and bimetallic characteristics, Figs. 6 and 7 show the representative TEM and HRTEM images of Pt nanoflower-RGO and Pt-Pd NP-RGO¹⁰ and the HAADF-STEM characterizations of Pt-Pd nanocube-RGO⁹ and Pt-Pd NP-RGO¹⁰ with element mappings, respectively.

In the chemical preparations, MNP-RGO can be prepared in solution or isolated as solids, and then modified on the electrode surface in the final step (see Fig. 4). The convenient usability of

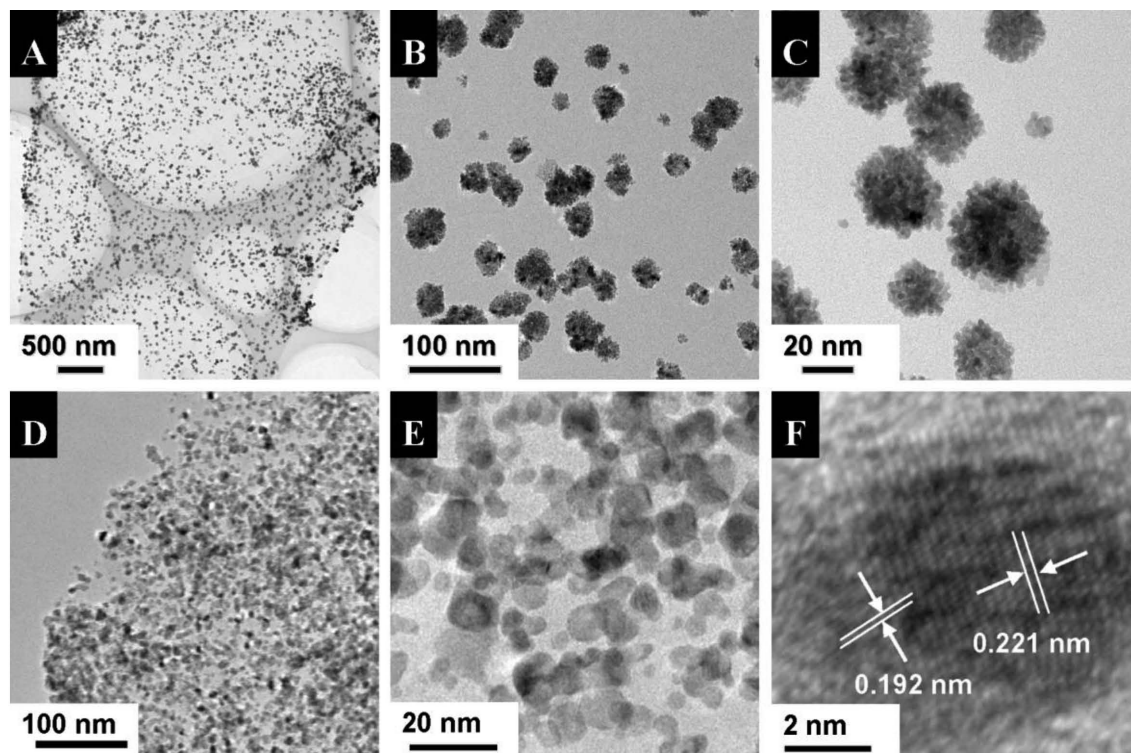


Fig. 6 Representative (A–E) TEM and (F) HRTEM images of (A–C) Pt nanoflower-RGO and (D–F) Pt-Pd NP-RGO. Reproduced from Ref. 10, copyright 2014, with permission from the Royal Society of Chemistry.

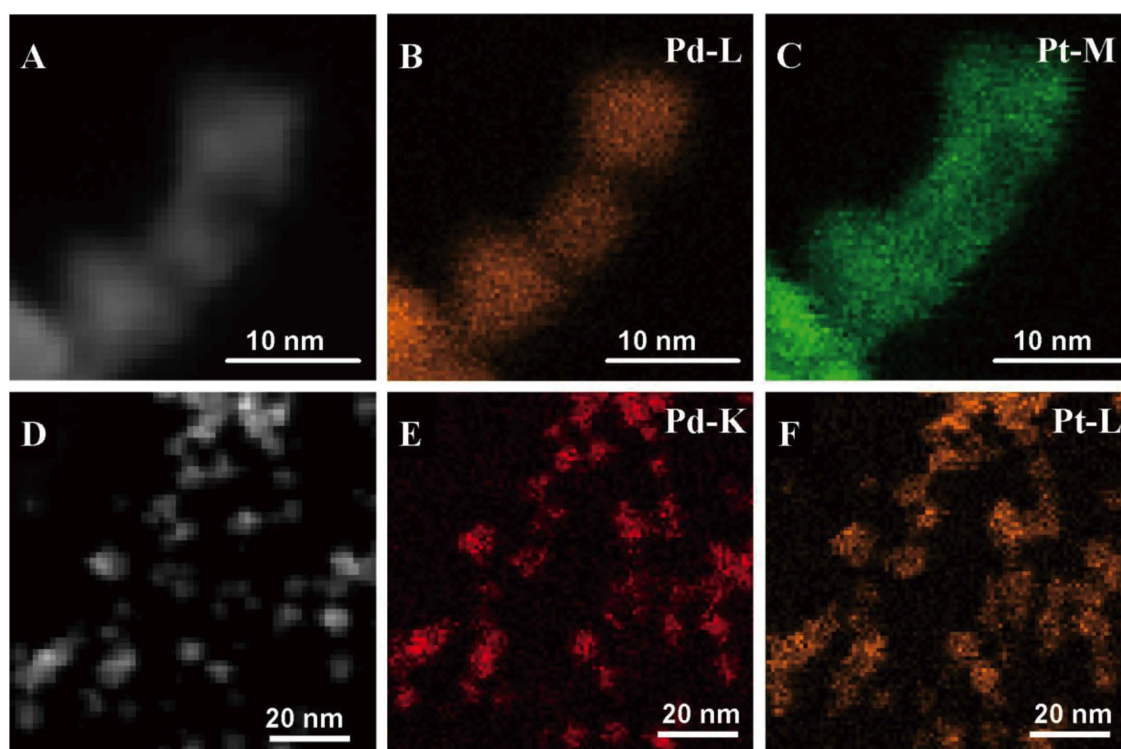


Fig. 7 HAADF-STEM characterizations of (A–C) Pt-Pd nanocube-RGO and (D–F) Pt-Pd NP-RGO. Elemental mapping of (B, E) Pd and (C, F) Pt. Reproduced from Refs. 9 and 10, copyright 2014, with permission from Elsevier and the Royal Society of Chemistry (color version of this figure can be viewed online).

chemically prepared MNP-RGO as an electrode modifier, for various electrodes just before the electrochemical measurements, is a significant practical merit for preparing modified electrodes for electroanalysis.

5.5 Variety of graphene derivatives

Various chemically modified graphenes have been identified in a previous review.¹⁶ In addition, some functionalized graphenes, such as PDA/RGO,^{50,51} PVP functionalized RGO,⁵² and sulfonated graphene^{54,55} can be utilized in preparing the MNP-RGO as mentioned in the previous section. Thus, the variety in functionalizing GO or RGO may lead to some advanced preparations of MNP-RGO. In our very recent work, some differences between citrate-functionalized graphene and PVP-functionalized graphene with AuNPs were explored.⁷²

In addition, doped graphenes may increase the variety. Browiec *et al.* reported the synthesis of N-doped graphene nanosheets decorated with AuNPs for electrochemical determination of chloramphenicol,⁷³ though we did not devote much attention to works on doped graphenes in this review.

6 Concluding Remarks

In this review, recent nanoarchitectures of MNP-RGO were collected and summarized. Among the notable properties of graphene are its large surface area, excellent electrical conductivity, high thermal conductivity, strong mechanical strength and good biocompatibility.²⁻⁵ As for the combination with MNPs, the diversity of preparation methods from GO in solutions might be regarded as a practical driving force for promoting the development of MNP-RGO modified electrodes. While in earlier works, preparation of graphene-modified electrodes was performed *via* the chemical vapor deposition of multilayer graphene nanoflake films,⁷⁴ nowadays, wet chemical methods can contribute significantly to the development of MNP-RGO modified electrodes.

The diversity of preparation techniques might imply some complexity. However, it may also indicate greater possibilities for the fabrication of tailor-made electrodes or electrochemical sensors. A variety of analytical targets are summarized in Table 1. Also, comparisons with other modified electrodes have been performed in many cases, and the importance of the MNP-RGO as electrode modifiers have been verified.

While studies in the area of electrochemical preparations are active, we sense that there is considerable potential and possibilities in the field of chemical preparation methods. The pursuit of clean synthesis of MNP-RGO^{45,47,48} should be effective for electroanalysis as well as for application as catalysts in homogeneous solutions.⁷¹

Despite the volume of research activity on MNP-RGO as summarized in Table 1, the publication of graphene-electrochemistry studies in Analytical Sciences is very limited.⁷⁵ Thus, we are happy if the present review helps to introduce the interesting properties of graphene derivatives, in particular its use in combination with MNPs in electroanalysis.

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