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# Exploring the Interaction between Graphene Derivatives and Metal Ions as a Key Step towards Graphene–Inorganic Nanohybrids

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**Abstract:** The assembly of graphene derivatives and inorganic nanostructures opens up an exciting new field in the functionalization of nanomaterials. However, a better understanding of the interaction between graphene derivatives and inorganic precursors remains a challenge. This work provides an efficient strategy for exploring this interaction by first modifying graphene oxide

with aniline, glycine, and glycylic acid, respectively, and thus engineering the chemical microenvironments on graphene sheets for anchoring metal ions. After that, the affinities of graphene

**Keywords:** electrochemistry • functionalization • graphene • metal ions • nanohybrids

derivatives to various metal ions can be investigated with the help of a conventional electrochemical method. The method highlights the importance of graphene chemistry in hybrid preparation and provides design principles for chemical modifiers used in the construction of multifunctional carbon–inorganic nanostructures.

## Introduction

Recently, the hybridization of graphene derivatives (e.g., graphene oxide, graphene functionalized with nitrogen-containing groups) and various inorganic nanostructures opens up a new approach toward multifunctional nanomaterials. Huge efforts have been made to construct functional graphene–inorganic hybrids for applications such as electronic devices, optical sensing, solar energy harvesting, electrochemical energy storage, and catalysis.<sup>[1–4]</sup> For instance, Dai and co-workers constructed a hybrid material consisting of Co<sub>3</sub>O<sub>4</sub> nanocrystals grown in situ on reduced graphene oxide and demonstrated their great potential as high-performance bifunctional catalyst for the oxygen reduction reaction and oxygen evolution reaction involved in renewable-energy technologies, including fuel cell and water splitting devices.<sup>[5]</sup> While diverse synthetic protocols have been developed for hybridizing graphene and its derivatives with a series of different inorganic substances including metals (Au, Ag, Pt, Pd, Cu, Ru), metal oxides (TiO<sub>2</sub>, MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, ZnO, Cu<sub>2</sub>O, NiO, Fe<sub>3</sub>O<sub>4</sub>, SnO<sub>2</sub>, RuO<sub>2</sub>), and metal sulfides

(CdS, CdSe, CuS, PdS, MoS<sub>2</sub>), the chemistry associated with the hybrid assembly processes, an important aspect for organic–inorganic hybridization,<sup>[6]</sup> has attracted little attention. More specifically, the widely used in situ hybridization techniques often require adsorption of inorganic nanostructure precursors (e.g., metal ions) on graphene derivatives before the transformation of the precursors into metals, metal oxides, or metal sulfides. However, a better understanding of the interaction of these graphene derivatives with metal ions remains scarce, which results in variable hybrid architectures and properties from case to case, and leads to difficulties on reliable mass production of the hybrids. One of the main reasons for this drawback is the presence of mixed functional moieties on graphene sheets and the consequent complex interactions, which has not only limited the controlled and uniform decoration of graphene derivatives with inorganic species, but also hampered the rational design and construction of more sophisticated or biomimetic hybrid architectures.

Herein, we provide a novel strategy for efficiently exploring the interactions between the functionalized graphene oxides and metal ions by revisiting a conventional electrochemical technique: differential pulse anodic stripping voltammetry (DPASV). As schematically shown in Figure 1, by first modifying graphene oxide with aniline, glycine, and glycylic acid, respectively, the chemical microenvironments of graphene sheets for coordinating metal ions can be engineered in a controlled fashion. The thus produced interaction changes between introduced functionalities and metal ions is then tracked by DPASV with high efficiency, which provides reliable information for more deeply understanding the interactions. This strategy holds promise for the rational design and controllable construction of new graphene–inorganic hybrid materials.

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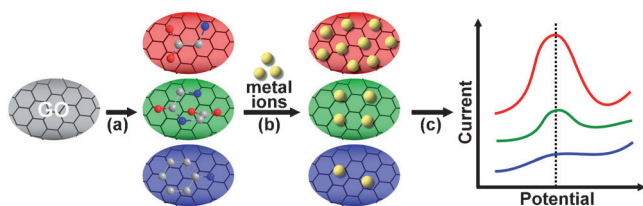


Figure 1. The strategy for addressing the correlations between chemical microenvironments of graphene derivatives and their affinities to metal ions through a) chemical modification of graphene oxide (GO) with different chemical modifiers (aniline, glycine, and glycyglycine), b) adsorption of metal ions on graphene derivatives, and c) electrochemical determination of metal ions attached onto graphene sheets.

## Results and Discussion

Three kinds of typical chemical microenvironments are established by chemical modification of graphene oxide with three selected nitrogen-containing modifiers (aniline, glycine, and glycyglycine). The resulting graphene derivatives are denoted as NG1, NG2, and NG3, respectively. All these chemically modified graphene oxides were characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), elemental analysis, and X-ray photoelectron spectroscopy (XPS). Powder XRD was used to disclose structural changes (Figure 2a). Indeed, the diffraction peaks are located at lower  $2\theta$  values in NGs than in GO, thus indicating an increased layer distance of graphene sheets. This increase results from the attachment of the nitrogen-containing molecules on the surface of GO sheets and confirms that the chemical functionalization has occurred. The types of chemical bonding of GO and NGs were investigated by FTIR (Figure 2b). After the modification, the absorption peaks of

GO at 1720 and 1610  $\text{cm}^{-1}$ , which are attributed to the carboxy stretching vibration and the deformation of the O–H band of the strongly intercalated water absorbed by GO, respectively, have nearly disappeared in NGs.<sup>[7]</sup> Moreover, new peaks are seen at 1560  $\text{cm}^{-1}$  due to the C–N–H bending and at 1650  $\text{cm}^{-1}$  due to the amide carbonyl stretching.<sup>[8]</sup> These findings suggest that the reaction between carboxyl groups of GO and amino groups of the modifiers results in covalent binding. As exhibited in Figure S1 in the Supporting Information, the EDS spectra clearly show the presence of nitrogen. Furthermore, the atomic ratios of nitrogen to the total number of atoms presented in graphene derivatives were characterized using elemental analysis to be approximately 2.5, 2.7, and 3.5% for NG1, NG2, and NG3, respectively, in agreement with the EDS and wide-survey XPS results (Table 1, Figures S1 and S2 in the Supporting Informa-

Table 1. The element analysis results of C and N contents in NGs.

	C (at %)	N (at %)
NG1	47.2	2.5
NG2	40.1	2.7
NG3	39.5	3.5

tion). The nitrogen contents in NG1 and NG2 are comparable, suggesting that similar amounts of chemical functionalities are introduced from aniline and glycine, respectively, onto the graphene sheets of NG1 and NG2. It is notable that the nitrogen content in NG3 is less than two times that in NG1 or NG2, thus indicating that the number of attached functional molecules (glycyglycine) in the case of NG3 is lower than those in the samples NG1 and NG2 since there are two nitrogen atoms in each glycyglycine molecule.

To unveil the possible reason for the above observations, high-resolution XPS scans of N 1s were taken. As shown in

Figure 2c–e, two peaks are observed at approximately 400 and 402 eV, assignable to two forms of nitrogen, namely, amide N and protonated N, respectively.<sup>[9,10]</sup> The distinguishable shifts in the binding energies can be attributed to subtle change in their respective bonding situation. While the formation of amide N originates from the dehydration of amine groups ( $-\text{NH}_2$ ) of chemical modifiers and carboxy groups ( $-\text{COOH}$ ) of graphene oxide, the appearance of protonated N in these derivatives may be attributed to the formation of ionic compounds through electrostatic interactions between two oppositely charged ions derived from

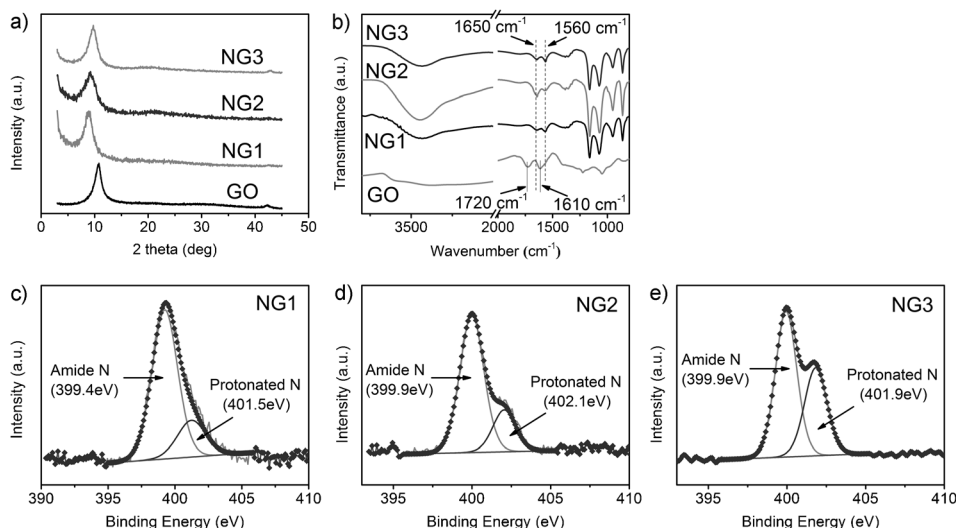


Figure 2. a) XRD pattern and b) FTIR spectra of GO and NGs. c–e) N 1s XPS spectra of NG1 (c), NG2 (d), and NG3 (e). All three characterizations demonstrate that the modifiers have been successfully attached to the GO sheets through covalent and ionic bonding.

amine groups of chemical modifiers and carboxy/hydroxy groups of GO.<sup>[11]</sup> That is, there are two main functionalization mechanisms for the modification of graphene oxide with amine-group-containing modifiers: covalent bonding and ionic bonding. Furthermore, compared with NG1 and NG2, the relative peak intensity of protonated N is significantly higher in NG3, showing that the chemical modifier for NG3 prefers to form ionic bonds with carboxy and hydroxy groups of graphene oxide. This result may be also responsible for the lower amount of functional moieties in NG3 in comparison to NG1 and NG2. Besides that, the preferred formation of ionic bonds in NG3 endows graphene sheets with a specific chemical microenvironment (e.g., positively charged outer domains) clearly different from those in NG1 and NG2.

While different “additives” have induced different chemical microenvironments, the TEM images (insets of Figure S1 in the Supporting Information) reveal transparent and flexible graphene sheets similar to those of pristine graphene oxide. Based on the above analyses, Figure 3a schematically illustrates the structures of graphene oxide before and after chemical modifications. This is important for studying their interaction with lead ions ( $\text{Pb}^{2+}$ ). DPASV implemented on a CHI660D electrochemical station with a conventional three-electrode cell was used where GO, NG1, NG2, or NG3 served as an active material of the working electrode. Figure 3b exhibits the DPASV curves obtained with these electrodes, which reflect affinities of the active materials to-

wards  $10^{-10} \text{ mol L}^{-1} \text{ Pb}^{2+}$ . The anodic peaks observed at around  $-0.65 \text{ V}$  are associated with the redox behavior of adsorbed lead ions, whereby the peak intensities represent the amount of lead adsorbed onto the graphene derivatives.<sup>[12]</sup> As summarized in Figure 3c, all three samples (NG1, NG2, and NG3) clearly exhibit improved affinities to lead ions. Thus the chemical modification of graphene oxide with nitrogen-containing functions has tailored graphene sheets for anchoring metal ions such as  $\text{Pb}^{2+}$ . More specifically, the peak intensity of NG2 is more than seven times that of graphene oxide, and highest among these active materials, suggesting that the most favorable chemical microenvironment has been formed in NG2. Considering the structural difference between NG2 and graphene oxide (Figure 3a), the significant enhancement of the peak intensity indicates that the introduced nitrogen plays an important role in coordination with lead ions thanks to its lone-pair electrons.<sup>[12–15]</sup>

Interestingly, the peak intensity of NG1 is only slightly enhanced relative to that of graphene oxide, although NG1 has nearly the same amount of nitrogen as NG2 (2.5% vs. 2.7%) and a similar bonding mode between graphene sheets and the reagents (Figure 2c vs. Figure 2d). Several aspects come into play. On the one hand, the  $\pi$  coordination afforded by benzene rings may improve the interaction of the aromatic amine with metal ions.<sup>[16,17]</sup> On the other hand, the presence of benzene rings in addition to the nitrogen-containing anchoring sites could bring about a steric hindrance.

In comparison with NG2, the significantly weaker peak intensity for NG1 discloses that the latter effect dominates in NG1. In addition, the peak intensity of NG3 is apparently lower than that of NG2, whereas the nitrogen content in NG3 is higher than that in NG2 (3.5% vs. 2.7%). The positively charged outer domains of NG3 (due to the preferable formation of ionic bonding, see above) might repel positively charged lead ions and thus reduce the affinity of graphene sheets despite the higher degree of nitrogen functionalization. Semi-empirical calculations were carried out with a hybrid density functional theory (DFT) method to further unveil the effect of chemical microenvironments on the affinities of graphene derivatives to lead ions. To simplify the calculation, only the covalent bonding between graphene oxide and chemical

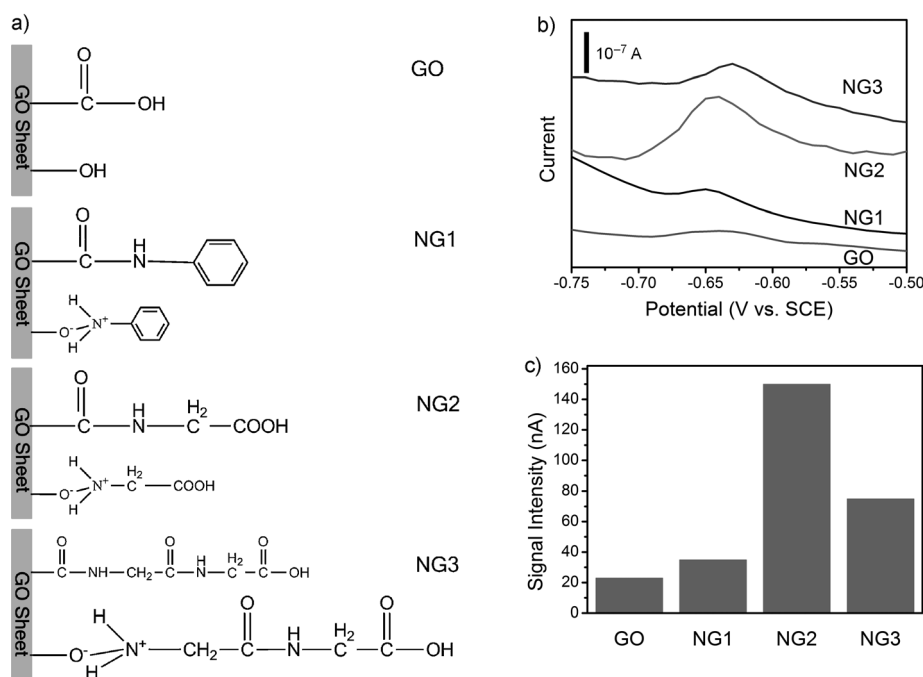


Figure 3. a) Schematic depiction of the structures of graphene oxide before and after chemical modifications. The size of attached groups is scaled to highlight different ratios of covalent and ionic bonding in the structures of graphene derivatives. b) Differential pulse anodic stripping voltammetric curves of  $10^{-10} \text{ mol L}^{-1} \text{ Pb}^{2+}$  by using glassy carbon electrodes coated with GO, NG1, NG2, and NG3. Preconcentration time: 2 min; deposition potential:  $-1 \text{ V}$ ; deposition time: 120 s. c) Comparison of the anodic peak intensities of graphene derivatives.

modifiers is considered, and graphene is represented by a benzene ring (Figure S3 in the Supporting Information). Compared with those for NG1 (−1.07 eV) and NG3 (−1.14 eV), the lower adsorption energy for NG2 (−1.19 eV) demonstrates its strong affinity to lead ions, in good agreement with the above observations.

To validate the above correlations between engineered chemical microenvironments of graphene sheets and their affinities towards metal ions, the interaction of graphene derivatives with  $10^{-9}$  mol L $^{-1}$  cadmium ions (Cd $^{2+}$ ) and  $10^{-8}$  mol L $^{-1}$  copper ions (Cu $^{2+}$ ) were investigated as well under the same conditions as Pb $^{2+}$  (Figure 4). The anodic

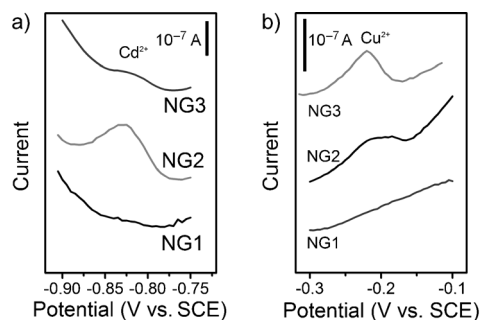


Figure 4. DPASV curves of a)  $10^{-9}$  mol L $^{-1}$  Cd $^{2+}$  and b)  $10^{-8}$  mol L $^{-1}$  Cu $^{2+}$  using glassy carbon electrodes modified with NG1, NG2, and NG3, respectively.

peaks of cadmium ions and copper ions are observed at around −0.82 and −0.22 V, respectively. There is no peak assignable to Cd $^{2+}$  or Cu $^{2+}$  when using NG1 as the anchoring substance, implying again that the steric hindrance effect plays a critical role in binding metal ions. In contrast, NG2 exhibits a high affinity to both ions, consistent with the above results for lead ions. NG3 displays a medium affinity to Cd $^{2+}$  and Cu $^{2+}$ , similar to the case of Pb $^{2+}$ .

## Conclusions

In summary, a novel strategy has been successfully developed for exploring the interaction of functional graphene oxides with metal ions. By modifying graphene oxide with different types of nitrogen-containing functionalities such as aniline, glycine, and glycyl glycine, the chemical microenvironments on graphene sheets for anchoring metal ions are engineered in a controlled fashion. These chemical microenvironments, including nitrogen-induced coordination, steric

hindrance, and electrostatic repulsion, hold dramatically different effects on anchoring metal ions, which can be tracked and identified efficiently by differential pulse anodic stripping voltammetry. The methodology highlights the importance of the graphene chemistry in hybrids preparation<sup>[18]</sup> and provides general principle for the rational selection of chemical modifiers in guiding the design and construction of other multifunctional carbon–inorganic nanostructures.

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