

# Simultaneous Reduction and Surface Functionalization of Graphene Oxide by Mussel-Inspired Chemistry

Sung Min Kang, Sungjin Park, Daewon Kim, Sung Young Park, Rodney S. Ruoff, and Haeshin Lee\*

This study presents a method of simultaneous reduction and surface functionalization of graphene oxide by a one-step poly(norepinephrine) functionalization. The pH-induced aqueous functionalization of graphene oxide by poly(norepinephrine), a catecholamine polymer inspired by the robust adhesion of marine mussels, chemically reduced and functionalized graphene oxide. Moreover, the polymerized norepinephrine (pNor) layer provided multifunctionality on the reduced graphene oxide that includes surface-initiated polymerization and spontaneous metallic nanoparticle formation. This facile surface modification strategy can be a useful platform for graphene-based nano-composites.

The DOPA-Lys motif provided a new insight into the identification of catecholamines as they share key chemical functionality with the side chains of DOPA-Lys: catechol from DOPA and amine from lysine. Catecholamines such as dopamine and norepinephrine have been studied as 'minimalist mimics' of Mefp-5 (Figure 1c), and it was found that they have the ability to modify virtually any material surfaces.<sup>[7]</sup> For instance, oxidative polymerization of dopamine modified a wide variety of surfaces, and, moreover, the functionalized surfaces were chemically active to various thiol- or amine-containing molecules,

## 1. Introduction

Adhesion pads of marine mussels have been intensively analyzed and mimicked due to their robustness, versatility, and applicability of mimics such as adhesives for biomedical devices and surface modification reagents.<sup>[1–7]</sup> A high content of 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine (Lys) has been found in the mussel adhesive protein Mefp-5 (*Mytilus edulis* foot protein-5) located at the top of the adhesive pad, which is in direct contact with substrates.<sup>[8]</sup> The DOPA-Lys motif, which is ~40 mol% of the total amino acid content of Mefp-5, plays a crucial role in the adhesion of marine mussels, *Mytilus edulis* (Figure 1a,b).<sup>[7,8]</sup>

demonstrating a new platform of surface chemistry. Norepinephrine, a derivative of dopamine, also forms chemically adherent films on virtually all material surfaces, including poly(tetrafluoroethylene) (PTFE), under alkaline conditions via oxidative polymerization. The poly(norepinephrine) layer acts as a platform for surface-initiated, ring-opening polymerization.<sup>[9]</sup> Besides the polydopamine and poly(norepinephrine) coatings, the mussel-inspired surface chemistry has been widely implemented for various purposes, including material-independent layer-by-layer deposition,<sup>[10]</sup> surface functionalization of iron oxide nanoparticles<sup>[11]</sup> and gold nanoparticles,<sup>[12]</sup> material-independent surface immobilization of proteins,<sup>[13]</sup> enhancement of cell<sup>[14]</sup> and hydroxyapatite adhesions,<sup>[15]</sup> modification of medical devices,<sup>[16]</sup> and formation of polymer capsules.<sup>[17]</sup>

Despite the widespread use of mussel-inspired surface chemistry, surface functionalization of carbon nanomaterials such as graphene or graphene oxide remains unexplored. In particular, the chemical modification of graphene oxide has received a great deal of attention for a wide range of applications.<sup>[18–30]</sup> A representative example is cross-linking of graphene oxide by divalent anions and polyallylamine, resulting in enhanced mechanical strength 'paper-like' materials.<sup>[18,19]</sup> Chemical reduction of graphene oxide has produced various graphene-based materials that exhibit excellent electrical, thermal, and mechanical properties.<sup>[20,25–30]</sup>

Herein, we report a facile method for the surface modification of graphene oxide utilizing mussel-inspired catecholamine reagent, poly(norepinephrine) (pNor). pH-triggered oxidative polymerization of norepinephrine (i.e. pNor) resulted in chemically functionalized graphene oxide. Further investigations of the pNor-coated graphene oxide revealed simultaneous surface

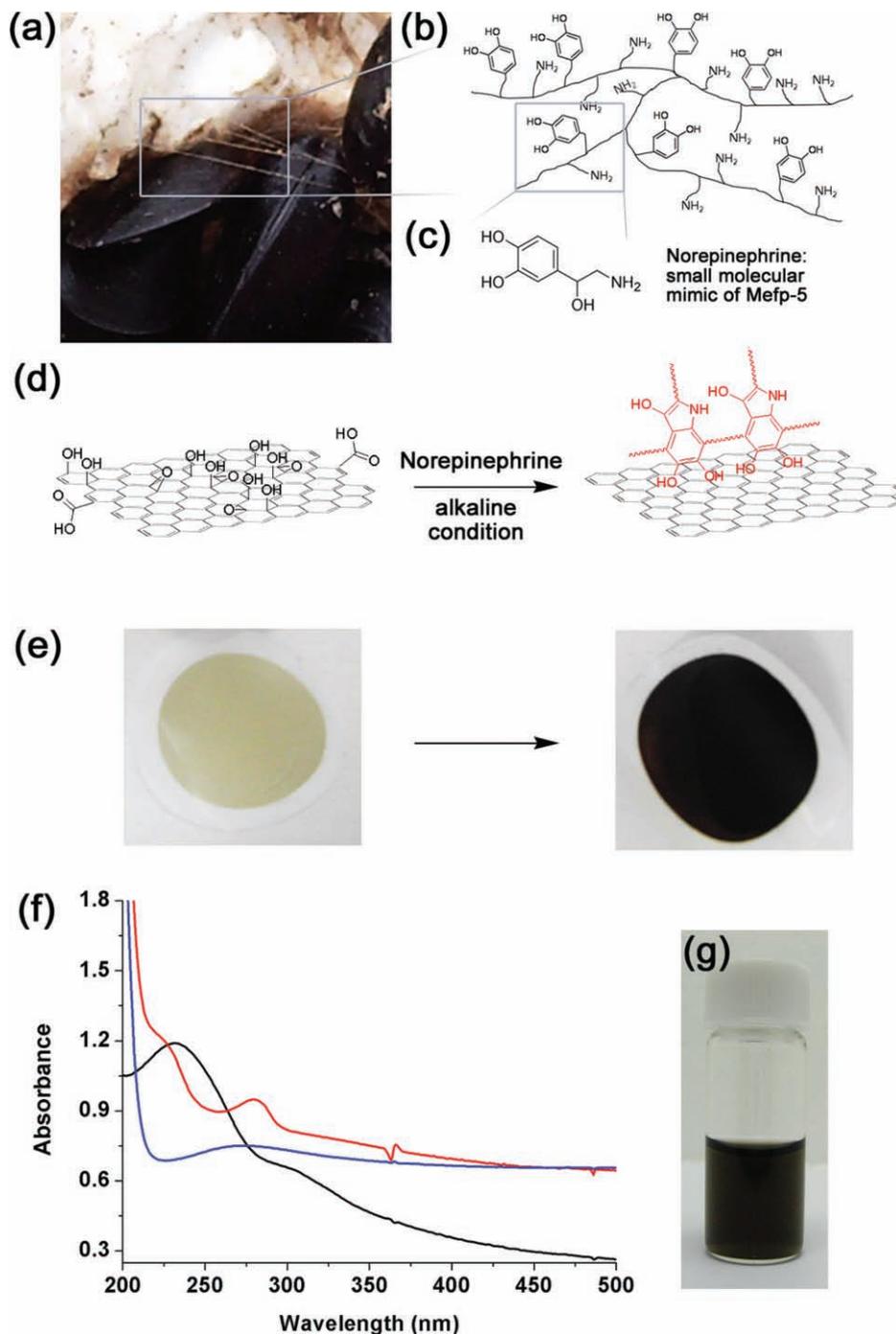
Dr. S. M. Kang, Mr. D. Kim, Prof. H. Lee  
Department of Chemistry and Graduate School of  
Nanoscience & Technology (WCU)  
KAIST Institute of NanoCentury, KAIST  
Daejeon 305–701, Korea  
E-mail: haeshin@kaist.ac.kr

Prof. S. Park  
Department of Chemistry  
Inha University  
Incheon 402–751, Korea

Prof. S. Y. Park  
Department of Chemical and Biological Engineering  
Chungju National University, Korea

Prof. R. S. Ruoff  
Department of Mechanical Engineering  
and the Texas Materials Institute  
the University of Texas at Austin  
One University Station C2200, 78712, USA

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**Figure 1.** (a) Photograph of mussels attached to a solid substrate. (b) Simplified molecular representation of the adhesive protein, Mefp-5. The amine from lysine and the catechol from DOPA are highlighted. (c) The chemical structure of norepinephrine, a minimalized molecular mimic of Mefp-5. (d) Poly(norepinephrine) coating on the surface of graphene oxide. (e) Photograph of the filtered graphene oxide (left) and pNor/RG-O (right). (f) UV-vis spectra of the graphene oxide (black), pNor/RG-O (red line), and RG-O prepared using hydrazine (blue line). (g) Image of an aqueous pNor/ RG-O suspension.

functionalization and reduction of graphene oxide in a one-step procedure, resulting in pNor-coated, reduced graphene oxide (pNor/RG-O) (Figure 1d). The pNor/RG-O platelet shows promise as a versatile platform for various graphene-composites by surface-initiated polymerization (SIP) or through on-surface synthesis of metal nanoparticles.

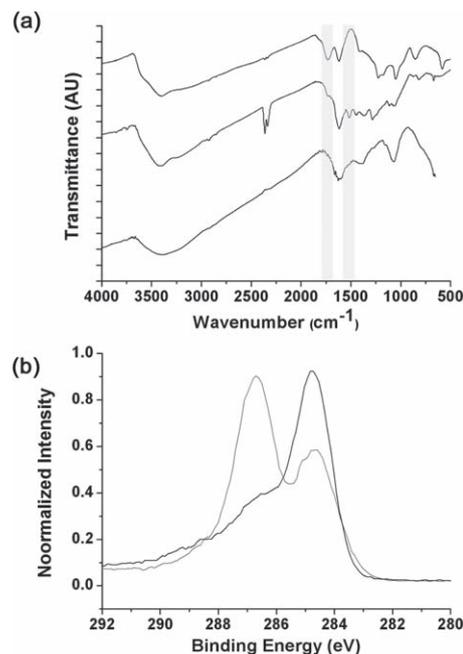
## 2. Results and Discussions

pNor/RG-O platelets were produced by mixing an aqueous suspension of graphene oxide platelets (50  $\mu\text{g}/\text{mL}$ ) with a solution of norepinephrine (2 mg of norepinephrine per mL of 10 mM Tris buffer, pH 8.5) (see Experimental Section). After 2 h shaking

(150 rpm, Wisemix, Daihan Scientific, Korea) at room temperature, the dark brown graphene oxide suspension turned into a black solution, the color typically observed for a dispersion of RG-O platelets. The pNor/RG-O platelets were collected with a cellulose membrane filter (0.45- $\mu\text{m}$  pore size, Agilent, Germany) and dried for 1 day under vacuum. The products exhibited a visible change in color (Figure 1e). The ultraviolet-visible (UV-vis) spectrum of the aqueous pNor/RG-O suspension demonstrated that the pNor layer remains stable; a new peak at 280 nm, a characteristic absorption by pNor due to the presence of catechols, was detected (Figure 1f).<sup>[31]</sup> A previous report stated that the RG-O prepared by hydrazine treatment of graphene oxide also absorbs UV light (<300 nm), but the broadness and difference in maximum absorption ( $\lambda_{\text{max}}$ ) of the peak from RG-O differed from the peak from pNor (Figure 1f). The possible presence of pNor on the RG-O platelet surfaces was further evaluated by the alkaline etching method (1 M NaOH).<sup>[9]</sup> After the removal of pNor, no peak at 280 nm was detected (Figure S1). pNor/RG-O platelet powder (0.1 mg/mL) was dispersed into various solvents by ultrasound sonication (5 s), and the solvents – water, methanol, acetone, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and toluene (stable for ~30 min) – were found to be compatible to the pNor/RG-O platelets. A representative image of an aqueous suspension of pNor/RG-O platelets is shown in Figure 1g.

Further characterization by Fourier transform infrared (FT-IR) spectroscopy was performed to evaluate simultaneous surface functionalization and reduction of graphene oxide by pNor coatings. The IR peak at 1514  $\text{cm}^{-1}$  (ring stretching from a benzene ring) confirmed presence of the coated pNor layer on graphene oxide. (Figure 2a) Our previous study showed that the pNor-coated gold surface exhibited the same characteristic peak at 1514  $\text{cm}^{-1}$ ,<sup>[9]</sup> and Li et al. demonstrated that the peak at 1514  $\text{cm}^{-1}$  was not detectable from the reduced graphene oxide.<sup>[25]</sup> The peak decreased at 1732  $\text{cm}^{-1}$  was a strong indication of graphene oxide reduction; After treatment of pNor/RG-O with 1 M NaOH to remove the coated pNor layer<sup>[9]</sup>, the FT-IR spectrum showed no peaks both at 1514 and 1732  $\text{cm}^{-1}$ , strongly indicating that the graphene oxide was reduced by one-step pNor functionalization (Figure 2a). The sloping background in the FT-IR spectra is due to scattering of radiation.<sup>[32]</sup> The reduction of graphene oxide was characterized by X-ray photoelectron spectroscopy (XPS). A significant decrease of XPS signals at 286–290 eV, which corresponds to C–O and C=O groups indicated that the pNor-functionalized graphene oxide was chemically reduced. (Figure 2b). Investigation by thermogravimetric analysis (TGA) also suggests a chemical reduction of graphene oxide (Figure S2). The weight loss of a sample composed of stacked and overlapped graphene oxide platelets at 200 °C was about 40 wt%, which is due to the evaporation of interlamellar water and the decomposition of labile oxygen. In contrast, the weight loss of the dried pNor/RG-O was about 25 wt% at 200 °C (dashed line, Figure S2). This result is likely due to the reduction of graphene oxide by the pNor coating.

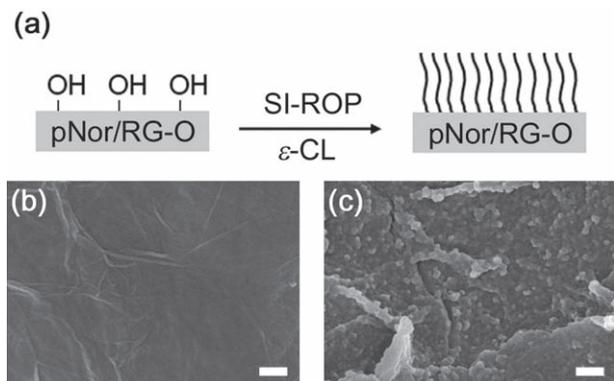
We hypothesized that the release of electrons during oxidative polymerization of norepinephrine reduces graphene oxide. To test the hypothesis, an aqueous suspension of graphene oxide and an acidic norepinephrine solution (pH 4.3) were mixed. In acidic conditions, oxidative polymerization of norepinephrine



**Figure 2.** FT-IR and XPS characterization of the pNor modified RG-O. (a) FT-IR spectra of unmodified graphene oxide (top), pNor/RG-O (middle), and RG-O after removing the pNor layer by 1 M NaOH treatment (bottom). (b) XPS spectra of graphene oxide (grey) and pNor removed RG-O (black).

did not occur, and therefore, it is expected that the reduction of graphene oxide and the pNor coating can be hindered. After 2 h, the mixture was filtered, purified, vacuum-dried, and characterized by UV-Vis and FT-IR spectroscopy. The UV-Vis spectrum showed no catechol peak at 280 nm, and the FT-IR spectrum had the carbonyl peak at 1730  $\text{cm}^{-1}$ . The data suggested that neither the surface modification by norepinephrine nor the reduction of the graphene oxide occurred (Figure S3). Thus, the reduction of graphene oxide is likely due to the released electrons when norepinephrine is oxidized, suggesting direct coupling of oxidation and reduction in pNor/RG-O.

Surface polymerization of biodegradable/biocompatible polymers is of interest because of various biomedical applications.<sup>[33–36]</sup> Passivation of biomedical devices using biodegradable polyester is a good example of surface-initiated ring-opening polymerization (SI-ROP). Moreover, graphene/polymer composites are a promising candidate for materials with good mechanical and conducting properties. Thus, facile incorporation of polymer(s) into graphene-based materials is of interest. To prepare such polymer/graphene composites, the hydroxyl group connected to the alkyl chain of norepinephrine was used as a surface initiator for SI-ROP. Polymerization was carried out using  $\epsilon$ -caprolactone ( $\epsilon$ -CL) as a monomer in the presence of a tin alkoxide catalyst. For polymerization from the surface of the pNor/RG-O platelets, vacuum-dried pNor/RG-O platelets were dispersed in anhydrous toluene and treated with the tin alkoxide catalyst for 1 h at 55 °C. SI-ROP was carried out for 24 h at 55 °C after the addition of the monomer,  $\epsilon$ -CL. After the polymerization, the poly( $\epsilon$ -caprolactone) (PCL)-grown pNor/RG-O platelets were separated by centrifugation at



**Figure 3.** (a) Schematic description of SI-ROP on the pNor/RG-O. SEM images of (b) pNor/RG-O and (c) poly( $\epsilon$ -caprolactone)-functionalized pNor/RG-O. The scale bar is 200 nm.

1500 rpm for 5 min (Centrifuge 5810R, Eppendorf, Germany) and washed with toluene several times. IR peaks appeared at 2850–2960 (C–H stretching), 1734 (C=O stretching), and 1160–1260  $\text{cm}^{-1}$  (C–O–C stretching) (Figure S4). Also, SEM images

showed significant changes in surface morphology and roughness, demonstrating the presence of PCL (Figure 3).<sup>[37]</sup>

The pNor layer has another important functionality: it allows on-surface formation of metallic nanoparticles. The redox activity of catechol groups in pNor spontaneously form silver nanoparticles on surfaces.<sup>[7,10]</sup> Simple immersion of the pNor/RG-O platelets into a silver nitrate solution at room temperature overnight resulted in silver nanoparticle/RG-O (AgNP/RG-O) composites. The surface morphology and the elemental composition of such AgNP/RG-O composites were characterized by atomic force microscopy (AFM), SEM, and energy dispersive spectroscopy (EDS). AFM images and height profile data clearly visualized the formation of AgNP by the change in the surface morphology (Figure 4b,c). SEM images showed significant coverage of AgNP, and EDS analysis confirmed that the nanoparticles were made of silver (Figure 4d,e). The average diameter of AgNPs was  $147.16 \pm 31.30$  nm. The AgNP/RG-O composites is potentially useful as a novel antimicrobial agent<sup>[10]</sup> and for surface enhanced Raman scattering.<sup>[38,39]</sup>

### 3. Conclusions

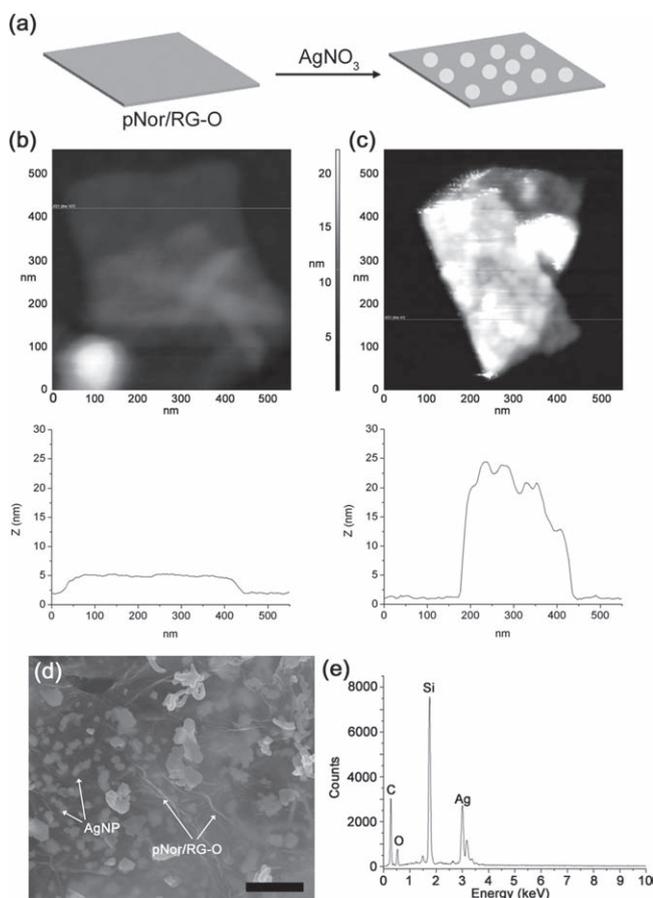
In summary, a new mussel-inspired surface chemistry to functionalize graphene oxide was developed. The surface chemistry is based on the oxidative polymerization of norepinephrine, which resulted in simultaneous surface functionalization and reduction of graphene oxide. The poly(norepinephrine)-coated RG-O became a multi-purpose platform for graphene nano-composite materials via the ability of ring-opening polymerization of caprolactone and formation of silver nanoparticles on RG-O surfaces. The mussel-inspired surface modification is non-toxic as it uses water as a solvent. Our study is the first demonstration of several advantages utilizing mussel-inspired surface chemistry to graphene oxide. Further exploration of the surface chemistry can provide a general method to fabricate graphene-based nano-composites in the future.

### 4. Experimental Section

**Materials:** Graphite (SP-1, Bay Carbon, MI), DL-norepinephrine hydrochloride (97%, Sigma), trizma base (99%, Sigma), trizma HCl (99%, Sigma), tin(II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ , 95%, Aldrich),  $\epsilon$ -caprolactone ( $\epsilon$ -CL, TCI), silver nitrate ( $\text{AgNO}_3$ , 99%, Sigma), and anhydrous toluene (Aldrich) were used as received.

**Poly(norepinephrine) (pNor) Coating on the Surface of Graphene Oxide:** Graphite oxide (GO) was synthesized by the modified Hummers method.<sup>[40]</sup> Aqueous suspensions of platelets of graphene oxide (10 mL of a 1 mg/mL solution) were prepared by 30-min sonication of GO (Ultrasonic cleaner, UC-05, Lab companion, Korea). Poly(norepinephrine) coating was performed by mixing these graphene oxide suspensions (50  $\mu\text{g}/\text{mL}$ ) with a buffer solution (2 mg of norepinephrine per mL of 10 mM Tris buffer, pH 8.5) at room temperature. After 2 h of shaking, the sample was collected by a cellulose membrane filter (0.45- $\mu\text{m}$  pore size, Agilent, Germany), washed with deionized water several times, and dried under vacuum.

**Polymerization of  $\epsilon$ -caprolactone on the Surface of pNor/RG-O:** For polymerization, pNor/RG-O (0.6 mg) was placed in a reaction vessel and dried under vacuum at 55  $^\circ\text{C}$  for 24 h. After drying, the pNor/RG-O was treated with  $\text{Sn}(\text{Oct})_2$  (10  $\mu\text{L}$ ) in 10 mL of anhydrous toluene for 1 h at 55  $^\circ\text{C}$ . The monomer,  $\epsilon$ -CL (1.0 mL), was then slowly added by



**Figure 4.** (a) Schematic description of AgNP deposition on the surface of pNor/RG-O. AFM images and surface profiles of a pNor/RG-O platelet (b) before and (c) after AgNP deposition. The scale bar applies to both images. (d) SEM image and (e) EDS spectrum of on-surface synthesized AgNP on pNor/RG-O surfaces. Si peak is originated from silicon wafer. The scale bar is 1  $\mu\text{m}$ .

syringe, and the mixture was heated at 55 °C for 24 h. The PCL-coated pNor/RG-O was separated and washed with toluene.

**Deposition of AgNPs on the Surface of pNor/RG-O:** pNor/RG-O (1.0 mg) was placed in a reaction vessel, and 10 mL of AgNO<sub>3</sub> solution (50 mM) was added. The reaction was carried out overnight at room temperature. After the reaction, the resulting AgNP-deposited pNor/RG-O was separated from the suspension by centrifugation and washed with water several times.

**Characterization:** Field-emission scanning electron microscopy (FE-SEM) micrographs and EDS spectra were obtained with a Hitachi S-4800 (Japan) and a Nova230 (FEI company, USA). For the SEM analysis, samples were prepared by dropping and drying on silicon wafers. The FT-IR spectra were recorded using a Vector 33 (Bruker, Germany). Forty scans were averaged to yield spectra with a resolution of 4 cm<sup>-1</sup>. The UV-vis spectra of the samples were recorded with a UV-vis absorption spectrometer (Agilent 8453, USA). The thermal characteristics of graphene oxide and pNor/RG-O were measured by thermogravimetric analysis (TA instruments, TGA 2050, USA) at a heating rate of 10 °C/min under a nitrogen atmosphere. AFM imaging was performed in tapping mode on a NTEGRA (NT-MDT, Russia) with a tapping mode silicon probe.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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