

Supporting Information

Synthesis of Graphene/Polyaniline Composite Nanosheets Mediated by Polymerized Ionic Liquid

Xiaosi Zhou, Tianbin Wu, Baoji Hu, Guanying Yang, and Buxing Han*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

*Fax: 86-10-62559373; Tel: 86-10-62562821; E-mail: Hanbx@iccas.ac.cn

1. Experimental

Materials Aniline monomer (Beijing Chemical Reagent Co.) was distilled under reduced pressure prior to use. Natural graphite flake (325 mesh), 1-vinylimidazole, and hydrazine monohydrate (>99%) were purchased from Alfa Aesar. Ammonium peroxydisulfate and other chemicals of analytical grade were purchased from Beijing Chemical Reagent Company. Double distilled water was used throughout the experiments.

Characterization Transmission electron microscopy (TEM) images were performed on a JEOL JEM-1011 electron microscope operating at 100 kV. Atomic force microscopy (AFM) images were taken with a NanoScope IIIa (Veeco, US) operating in the tapping mode. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 spectrophotometer. The photographs of the samples were taken with a digital camera (Canon IXUS 95 IS). X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The base pressure was about 3×10^{-9} mbar and the binding energies were referenced to C1s line at 284.8 eV from adventitious carbon. The UV-vis spectra were recorded on a UV-1601PC UV-visible spectrophotometer (Shimadzu). The molecular weight of poly(1-vinyl-3-butylimidazolium chloride) was measured with a gel permeation chromatography (GPC) system equipped with a Waters 2414 differential refractive index detector, a Waters 1515 HPLC pump and three Waters styragel columns (HT3, HT4 and HT5) using DMF as eluent at a flow rate of 1 mL/min at 50 °C. The calibration curve was obtained by applying polystyrene standards. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Dynamic light scattering (DLS) analysis was performed using a Malvern Zetasizer Nano instrument. The thickness of the films deposited on glass substrates were determined by a surface profilometer (Ambios XP-2). The room temperature electrical conductivities of the films were measured using a Loresta EP MCP-T360 (Mitsubishi).

Synthesis of graphite oxide The graphite oxide was synthesized from natural graphite flake by a modified Hummers method.^{S1, S2} In the experiment, concentrated H₂SO₄ (15 mL) was mixed with K₂S₂O₈

(3.0 g) and P₂O₅ (3.0 g) at 90 °C in a 150 mL beaker. The mixture was cooled to 80 °C. 3.6 g of natural graphite flake was slowly added to the above solution under stirring. The mixture was kept at 80 °C for 4.5 h. Afterwards, the mixture was diluted with 600 mL of water and left to stand for 12 h. Then the mixture was filtered and washed with excess water using a 0.2 micron Nylon Millipore filter until the pH of the filtrate was neutral. The solid product was dried in air for one day. Then, a half of this pretreated graphite flake was added to cold (3 °C) concentrated H₂SO₄ (70 mL). While keeping the reaction temperature less than 10 °C, KMnO₄ (9.0 g) was added slowly until completely dissolved. This mixture was stirred at 35 °C for 2 h. 150 mL of water was added to the mixture slowly and the reaction temperature was kept less than 50 °C using an ice bath. Then the mixture was stirred for 2 h followed by adding additional 420 mL double distilled water. Successively, 10 mL of 30% H₂O₂ was added to the mixture, resulting in a brilliant yellow color along with bubbling. The mixture was deposited overnight and then the clear supernatant was decanted. The remaining mixture was centrifugated and washed with 750 mL of 10% HCl solution and 1000 mL water. The resulting graphite oxide was then diluted into a 400 mL brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Finally, 0.5% w/w dispersion was obtained by dialysis for one week, and the dispersion was used to prepare all the following dispersions.

Synthesis of poly(1-vinyl-3-butylimidazolium chloride) (PIL) The ionic liquid (IL) 1-Vinyl-3-butylimidazolium chloride ([Vbim][Cl]) was prepared using the method reported in the literature.^{S3, S4} In the experiment, 1-vinylimidazole (12.0g, 127 mmol) and 1-chlorobutane (37.0 g, 400 mmol) were added to a three-necked flask in an oil bath of 70 °C under nitrogen atmosphere. The mixture was stirred vigorously for 75 h. After cooling to room temperature, the top liquid was decanted and the bottom viscous liquid was diluted in ethanol, and then precipitated in ethyl acetate. The resulting solid was filtered and dried under vacuum at 50 °C overnight to obtain [Vbim][Cl] as a white solid. The polymerization of [Vbim][Cl] was conducted using the similar procedures to synthesize the polymer supported ILs.^{S3, S4} In the experiment, [Vbim][Cl] (3.0g), AIBN (0.061g) and chloroform (50 mL) were added into a three-necked flask in an oil bath of 70 °C under nitrogen protection. After stirring for 12 h, the reaction mixture was cooled to room temperature, and then precipitated in ethyl ether. The residual [Vbim][Cl] was removed by dialysis in water. Then the solution was concentrated with a rotary evaporator at 70 °C. Finally, the product PIL was obtained after being dried under vacuum. The molecular weight of the PIL was measured by GPC analysis (M_w = 219,566, PDI = 1.12). [Vbim][Cl]: ¹H NMR (400 MHz, D₂O) δ = 0.97 (t, J (H, H) = 7.2 Hz, 3H), 1.38 (m, 2H), 1.92 (m, 2H), 4.29 (t, J (H, H) = 7.2 Hz, 2H), 5.47 (dd, J (H, H) = 8.8, 2.8 Hz, 1H), 5.84 (dd, J (H, H) = 15.6, 2.8 Hz, 1H), 7.18 (dd, J (H, H) = 15.6, 8.8 Hz, 1H), 7.62 (s, 1H), 7.81 (s, 1H). ¹³C-NMR (100MHz, D₂O) δ = 12.70, 18.71, 31.14, 49.71, 109.35, 119.47, 122.92, 128.28, 134.11.

Synthesis of aqueous dispersion of graphene/polyaniline composite (GPC) nanosheets In a typical synthesis of aqueous dispersion of graphene/polyaniline composite (GPC) nanosheets, the graphene (G) was first prepared by reducing graphene oxide (GO).^{S5} In the experiment, 3.0 mL of graphite oxide aqueous solution (5.0 mg mL^{-1}) was diluted to 5.0 mL (3.0 mg mL^{-1}) with double distilled water, and then the exfoliation of GO was achieved by sonicating the mixture in a water bath (KQ-100, 40 kHz) for 1 h. The obtained brown dispersion was mixed with 45 mL of N,N-dimethylformamide (DMF) to produce a homogeneous suspension. The resulting homogeneous suspension was transferred into a 100 mL flask by pipet, followed by reduction with hydrazine monohydrate (30 μL) at 80 °C for 12 h. Then, 40 mL of the obtained homogeneous suspension of the graphene in DMF/H₂O (a total of 50 mL) was mixed with PIL (120 mg) followed by dialysis in water to remove DMF. (NH₄)₂S₂O₈ (81 mg) was added into a half of the resulting PIL stabilized graphene sheet (PIL-G) aqueous dispersion (41 mL). The black precipitate (PIL-S₂O₈-G) was isolated by centrifugation, followed by redispersing in water and centrifugating three times to remove residual salts. Subsequently, the as-purified PIL-S₂O₈-G was dispersed in 10 mL of water via vigorously shaking, and then 60 mg of aniline monomer dissolved in 1 M HCl (5 mL) was added into the suspension to initiate the polymerization of aniline under vigorously stirring. The polymerization of aniline was performed at room temperature for 2 h. The aqueous dispersion of GPC nanosheets was obtained after 3 mL of the mixture (a total of 15 mL) was washed with 1 M HCl ($5 \times 10 \text{ mL}$) and then subjected to disperse in water (10 mL). The resulting dispersion (0.42 mg mL^{-1}) was sonicated for 10 minutes and then centrifugated for 30 minutes (4000 rpm) to remove any conglomeration, and the supernatant containing the GPC nanosheets was transferred. Finally, the GPC nanosheets supernatant (0.35 mg mL^{-1}) was diluted further to achieve dispersions with concentrations ranging from 0.018 to 0.123 mg mL^{-1} , and the corresponding pHs of these dispersions were 3.4, 3.1, 2.9, 2.8, 2.7, 2.6, and 2.5, respectively.

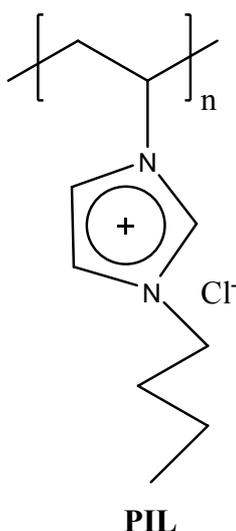
Synthesis of aqueous dispersion of polyaniline (PANI) In a typical synthesis of aqueous dispersion of PANI,^{S6} ammonium peroxydisulfate (36.7 mg) dissolved in water (10 mL) and aniline monomer (60.0 mg) dissolved in 1 M HCl (5 mL), respectively. The newly prepared solutions were mixed rapidly in a 25 mL flask, and then stirred vigorously at room temperature for 2 h. The aqueous dispersion of PANI was obtained after 7.5 mL of the mixture (a total of 15 mL) being washed with 1 M HCl ($5 \times 10 \text{ mL}$) by centrifugation and then subjected to dispersion in water (10 mL). The dispersion (0.98 mg mL^{-1}) was sonicated for 10 minutes and then centrifugated for 30 minutes (4000 rpm) to remove any aggregation, and the supernatant containing the PANI was transferred. Finally, the PANI supernatant (0.37 mg mL^{-1}) was diluted further to obtain an aqueous dispersion of 0.037 mg mL^{-1} , and the pH of the resulting dispersion was 3.1.

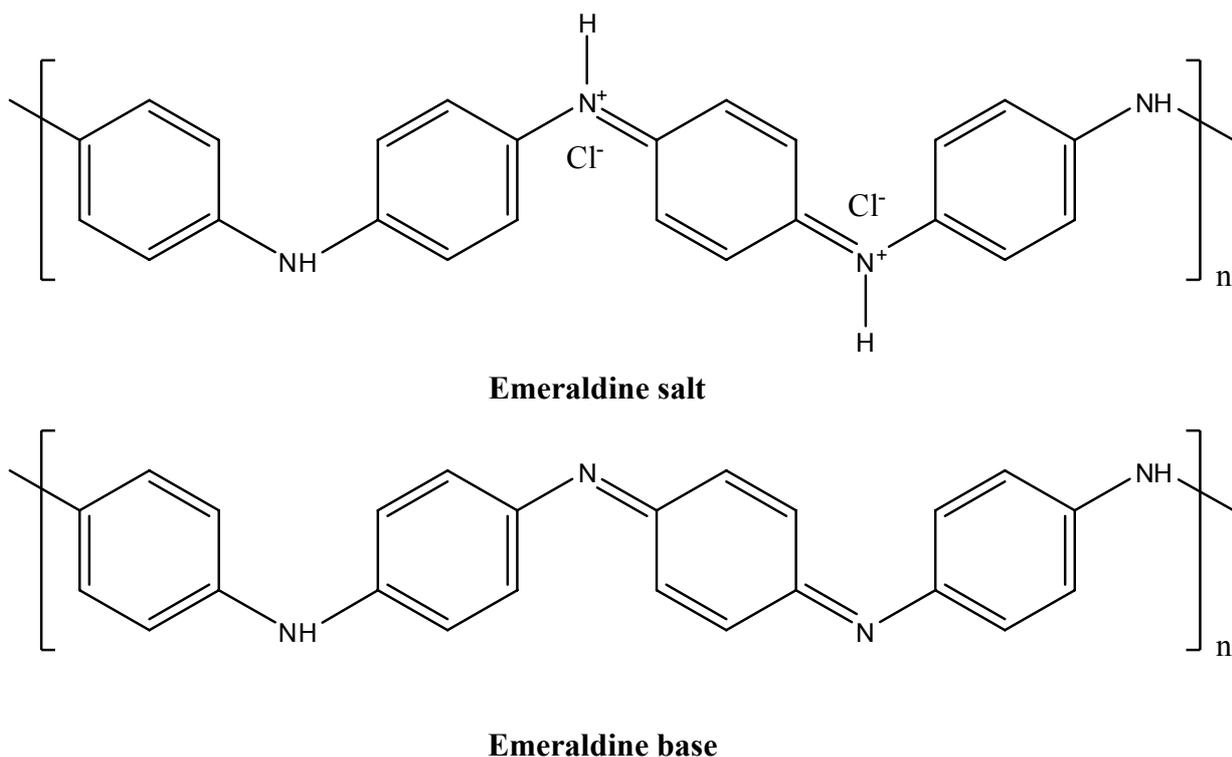
Synthesis of a mixture of aggregated graphene and PANI nanofibers (P-G mixture) The procedures were similar to that to prepare the GPC nanosheets described in the experimental section. The

only difference was that PIL was not used. Briefly, graphene (G) was first prepared by reducing graphene oxide (GO) according to the method reported by Park et al.^{S5} Then, 20 mL of the obtained homogeneous suspension of graphene in DMF/H₂O was dialyzed in water to removed the DMF, resulting in aggregated graphene sheets. The aggregated graphene sheets were sonicated to suspend in 10 mL of water and ammonium peroxydisulfate (36.7 mg) was dissolved in the suspension. Aniline monomer (60.0 mg) was dissolved in 1 M HCl (5 mL) and mixed rapidly with the suspension. Then the mixture was stirred vigorously at room temperature for 2 h. Finally, a mixture of aggregated graphene sheets and PANI nanofibers was obtained.

Preparation of GPC and PANI films The GPC and PANI films were prepared according to the procedures reported by Eda et al.^{S7} To prepare the GPC nanosheet film, a GPC nanosheets aqueous dispersion (0.35 mg mL⁻¹) was filtrated under vacuum using nitrocellulose membrane with 0.2 μm pores. The membrane with captured GPC nanosheets was then cut into size of choice, wetted with water, and pressed against the glass substrate surface with the GPC nanosheet side in contact with the glass. The GPC nanosheet film was allowed to dry and adhere to the glass employing an assisting glass and two small clips at 50 °C under vacuum overnight. The assisting glass and clips were removed and the nitrocellulose membrane was dissolved using acetone (successively washing with pipet) to leave a GPC nanosheet film on the glass. Then, the film was dried at 50 °C under vacuum overnight. The PANI film was prepared using the same procedures. The thicknesses of the GPC nanosheet and PANI films measured by a surface profilometer were 3.4 μm and 2.5 μm, respectively.

Structures of PIL, emeraldine salt and emeraldine base The structures of PIL, emeraldine salt and emeraldine base are shown in Scheme S1.





Scheme S1. Structures of PIL, hydrochloride doping PANI (emeraldine salt) and ammonia dedoping PANI (emeraldine base).

2. Supplementary Figures and Table

Images of the graphene oxide (GO), PIL stabilized graphene sheets (PIL-G), and graphene/polyaniline (GPC) nanosheets The tapping mode AFM images of the GO, PIL-G, and GPC nanosheets on freshly cleaved mica are given in Figure S1, and the height profiles along the lines are also presented.

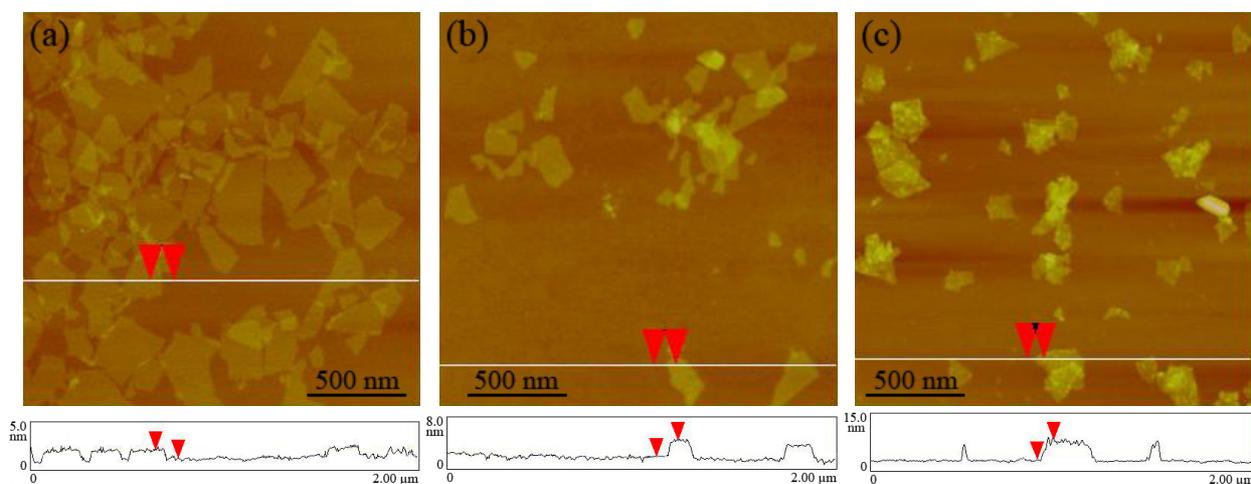


Figure S1. (a) Tapping mode AFM images of (a) GO, (b) PIL-G, and GPC nanosheets.

FT-IR spectra of the PANI, graphene, and GPC nanosheets The PANI, graphene obtained by reducing graphene oxide, and GPC nanosheets were investigated by Fourier-transform infrared (FT-IR) analysis (Figure S2). The characteristic bands of PANI nanofibers appeared at 1571, 1487, 1307, 1246, and 1148 cm^{-1} , corresponding to quinone ring deformation, benzene ring deformation, C-N stretching, C-N⁺ stretching, and -NH⁺ stretching, respectively.^{S8} For the sample of graphene, the peaks at 1563, 1201, and 1133 cm^{-1} could be assigned to aromatic C=C stretching, C-O stretching, and C-O-C stretching, respectively.^{S5} The bands for C-O stretching and C-O-C stretching could be observed because the graphene oxide could not be reduced completely in the reducing process.^{S9} Comparing the spectra of GPC nanosheets and graphene in Figure S2, the appearance of new absorption bands could be attributed to the introduction of PANI. Therefore, we can conclude that the GPC nanosheets contained both PANI and graphene sheets.

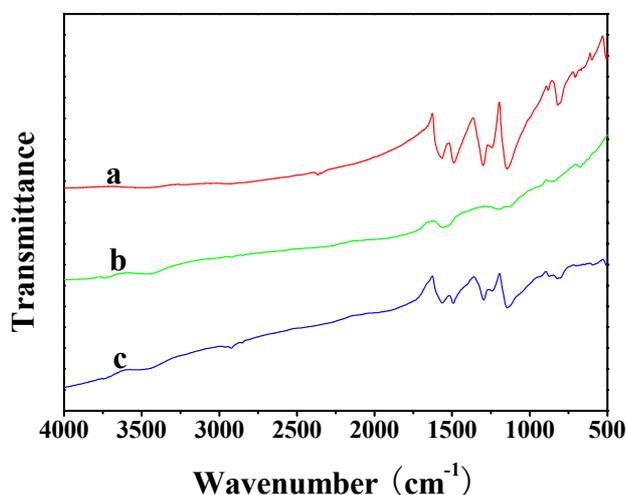


Figure S2. FT-IR spectra of (a) PANI, (b) graphene, and (c) GPC nanosheets.

X-ray photoelectron spectroscopy (XPS) spectra X-ray photoelectron spectroscopy (XPS) was used to analyze the samples of GO, graphene, and GPC nanosheets, which were fabricated by filtration under vacuum and then drying under vacuum at 70 °C. As shown in Figure S3, the main peak centered at 284.8 eV corresponded to extensively delocalized sp²-hybridized carbon atoms, and the separated peaks with binding energies of 285.9, 286.7, 287.8, and 289.0 eV were attributed to carbon atoms in C-N or C=N, C-O, C=O, and O-C=O species, respectively.^{S10} The oxygen functionalities in the graphite oxide were highly reduced after the reduction process, which could be observed by comparing the C1s XPS spectra of graphite oxide (Figure S3a) and graphene (Figure S3b), suggesting that significant de-oxygenation took place in the process of reduction. The N 1s spectrum of the graphene exhibited one peak corresponding to the nitrogen atom in C=N (Figure S3d), while the N 1s spectrum of the GPC nanosheets displayed two new peaks and one weak peak (Figure S3e) corresponding the nitrogen atoms in C=N⁺-C (401.7 eV), C-N-C (399.3 eV) and C=N (400.3 eV), respectively.^{S8} The two new peaks suggested the presence of hydrochloride doping PANI (Emeraldine salt) in the GPC nanosheets, which can be further

confirmed by the increase of peak intensity at 285.9 eV (Figure S3c). Since the relative intensity of C=N peak decreased (Figure S3d, S3e) and the XPS analysis was used to detect only 5 to 10 nm depth under the surfaces of samples, we can conclude that the PANI had grown on the surface of graphene sheets.

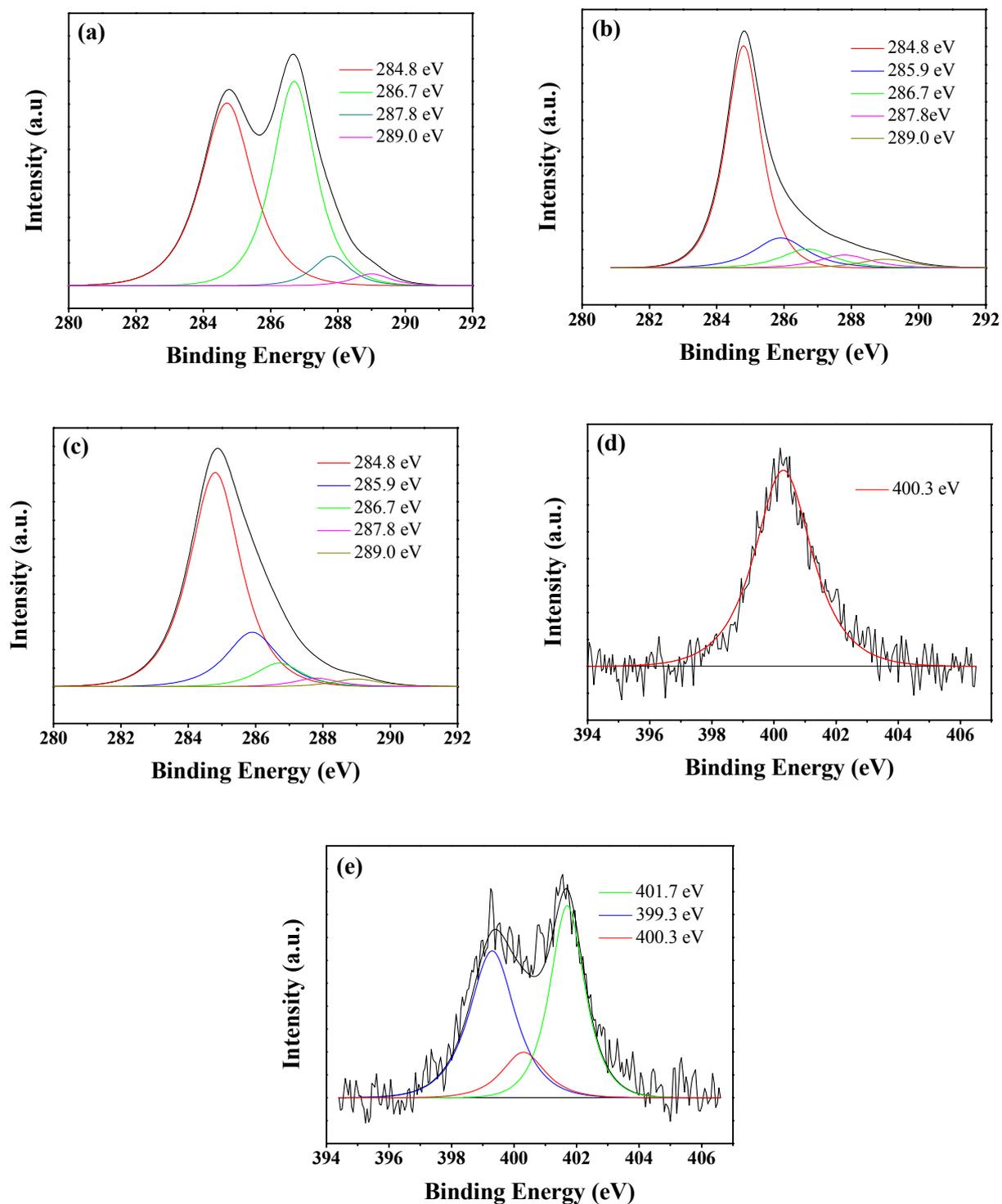


Figure S3. The XPS C 1s spectra of (a) graphite oxide, (b) graphene, and (c) GPC nanosheets. The XPS N 1s spectra of (d) graphene, and (e) GPC nanosheets.

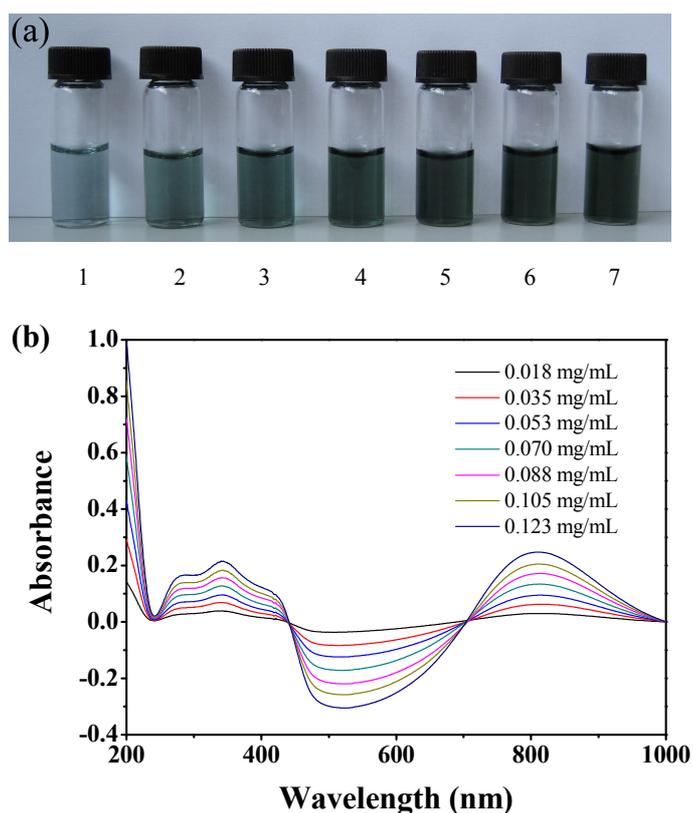
The weight percents of Cl and S in the samples The weight percents of Cl and S in PIL-G-S₂O₈, GPC nanosheets, and GPC-NH₃·H₂O were determined by mercurimetry and barium salt titration, respectively. The results are presented in Table S1.

Table S1. Weight percents of Cl and S in different samples; PIL-G-S₂O₈: the precipitate obtained from mixing PIL-G (PIL stabilized graphene sheets) aqueous dispersion with ammonium peroxydisulfate; GPC-NH₃·H₂O: the solid was obtained from washing GPC nanosheets with an excess amount of ammonia aqueous solution; Negligible: the content of Cl or S was lower than the detection limit of the methods used.

Samples	Cl (wt%)	S (wt%)
PIL-G-S ₂ O ₈	Negligible	12.30
GPC	12.94	Negligible
GPC-NH ₃ ·H ₂ O	Negligible	Negligible

Photographs and UV-vis absorption spectra of the samples of GPC nanosheets dispersed in water

The Photographs and UV-vis absorption spectra of the samples of GPC nanosheets dispersed in water with different concentrations are given in Figure S4.



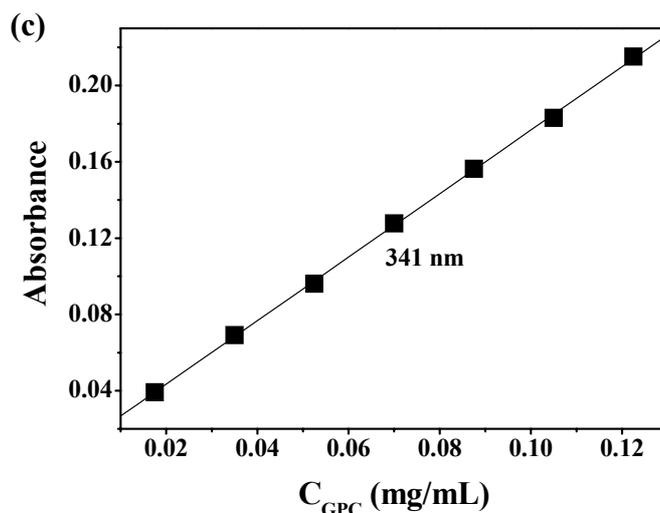


Figure S4. (a) Vials 1, 2, 3, 4, 5, 6, and 7 show GPC nanosheets dispersed in water with a concentrations of 0.018, 0.035, 0.053, 0.070, 0.088, 0.105, and 0.123 mg mL⁻¹, respectively, and the corresponding pHs are 3.4, 3.1, 2.9, 2.8, 2.7, 2.6, and 2.5, respectively; (b) UV-vis absorption spectra of GPC nanosheets dispersed in water with different concentrations, and the reference solution used in the measurement was water with corresponding pH; (c) dependence of the absorbance at 341nm as a function of the concentration of GPC nanosheets in the dispersion.

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