Electronic supplementary information (ESI)

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Facile Fabrication of Stable Monolayer and Few-layer Graphene Nanosheets as Superior Sorbents for Persistent Aromatic Pollutant Management in Water

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Supporting Information consists of 6 pages, including this one.

There are four Figures and two Tables.

Contents

Synthesis of Graphene Oxide (GO) and Graphene

GO was synthesized from natural graphite flakes (325 mesh, 99.8%, Alfa Aesar) according to a modified Hummers method. $K_2S_2O_8$ (8.33 g) and P_2O_5 (8.33 g) were dispersed in concentrated H_2SO_4 (30 mL), then graphite flake powder (10 g) was added gradually upon continuous stirring, and the mixture was kept at 80 ºC for 4.5 h under stirring. After that, the product was collected through filtration and washing with water until the pH became neutral; the product was then dried in the oven overnight at 60 ºC to obtain the preoxidized graphite. The preoxidized graphite powder (10 g) and $NaNO_3$ (5 g) were placed into cold (0 ºC) concentrated H_2SO_4 (230 mL) in an ice bath, and $KMnO_4$ (30 g) was slowly added under continuous stirring to keep the temperature below 4 ºC. Then, the mixture was stirred at 35 ºC for 2 h; deionized water (460 mL) was then gradually added, producing a large amount of heat. The mixture was further stirred for 15 min at 98 ºC to increase the oxidation level. The reaction was terminated by adding deionized water (460 mL) and 30% H_2O_2 (25 mL) to obtain graphite oxide. The resultant bright yellow mixture was rinsed with a 10% HCl solution (3.6 L) to remove the residual SO_4^- (verified using 0.01 mol/L $BaCl_2$) and metal ions, followed by centrifugation at 8000 rpm. Then, the solid phase was redispersed in deionized water and peeled by ultrasonication for 30 min at a power of 250 W. The centrifugation and ultrasonication were repeated 3 times, and the solution was then subjected to dialysis to remove the acid and other impurities. After being vacuum dried at 60 ºC, GO was obtained as a powder.

Graphene was prepared by the hydrazine reduction of the GO nanosheets. Briefly, a 1L GO aqueous dispersion (1 mg/mL) was ultrasonicated (250 W) until it became clear and contained no visible particulate matter. The dispersion was then centrifuged at 3000 rpm for 5 min to remove any unpeeled sheets. The supernatant was loaded in a 1-L round-bottom flask, followed by adjusting the solution pH to 10 using ammonium hydroxide (28%). Then, 10 mL of hydrazine hydrate (98%, Aladdin Co. Ltd.) was added, and the solution was heated in an water bath at 98 ºC under a water-cooled condenser for 24 h. The resultant black solid was isolated by filtration through a 0.22 μm membrane filter, washed by deionized water and methanol to remove the excess hydrazine, and finally freeze dried. The black powder was graphene.

Synthesis of Aminosilica Particles (NH_2-SiO_2)

Nanosilica particles (SiO_2, 50±5 nm) were purchased from Aladdin Industrial Corporation. NH_2-SiO_2 was synthesized from SiO_2 by binding –NH_2 to the surface through a simple one-step process. SiO_2 (10 g) was added gradually to ethyl alcohol (300 mL) under continuous stirring and ultrasonication. Then, APTES (1 mL) was added to the mixture. The reaction was processed for 12 h at 50 ºC, and the product was collected by filtration, washed with alcohol and water several times and dried under vacuum at 60 ºC.

Fabrication of Aminosilica-Support-Graphene (ASG)

The fabrication of ASG included two brief steps. First, 100 mL of 0.1 mg/mL GO solution was completely peeled off under ultrasonication. NH_2-SiO_2 (2 g) was dispersed in deionized water (100 mL) under stirring and ultrasonication to ensure good dispersion. Then, the GO solution was gradually added under stirring to the NH_2-SiO_2 mixture. Due to the electrostatic interactions between them, the GO layers immediately attached to the surface of the NH_2-SiO_2. The wrapped nanoscale particles were obtained by filtration and dried under vacuum. Second, ASGO (800 mg) was added to water (800 mL) with the addition of hydrazine hydrate (0.04 mL). The reaction was processed in a water bath at 98 ºC. The final ASG particles were collected by filtration and dried in a vacuum at 60 ºC.

Structural Characterization

Elemental (C, H, N) analyses were conducted using an EA112 CHN elemental analyzer (Thermo Finnigan). The Brunauer-Emmett-Teller (BET) nitrogen specific surface areas were estimated by nitrogen adsorption-desorption at -196 ºC with a NOVA-2000E surface area analyzer. Four data points, with relative pressures of 0.05 to 0.3, were used to determine the monolayer adsorption capacity. Raman spectra were obtained using a LabRamHRUV Raman spectrometer (Jobin-Yvon, FR); the laser excitation was provided by an Ar^+ laser at a wavelength of 514 nm. The surface functional groups were examined using Fourier transform infrared spectroscopy (FTIR). The FTIR spectra were recorded in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1} using a Bruker Vector 22 FTIR spectrometer. The surface morphologies were characterized using an S-4800 field-emission scanning electron microscope (FE-SEM) (Hitachi, Tokyo) and a JEM-2010 transmission electron microscope (TEM) (JEOL, Japan). The surface charge properties of the biochars were evaluated using zeta potential measurements, which were conducted at a different equilibrium pH values using a Nano-ZS90 Zetasizer (Malvern Instruments Ltd.). The samples were pre-equilibrated for 24 h in different pH solutions. The zeta potential was measured three times at each pH, and the average was calculated. The isoelectric point (pH_{IEP}), defined as the pH value at which the electrokinetic potential equals zero, of the biochars was determined by plotting the zeta potentials vs. pH.

Batch Adsorption Experiment

Phenanthrene (98%+, J&K Chemical) was selected as a model aromatic organic pollutant. Adsorption kinetics and batch adsorption experiments were performed in PTFE screw-cap vials sealed with tin foil at 25±1 ºC. Concerning the adsorption kinetics of ASG, the water-to-solid ratio was 1.5 mg per 8 mL, and the initial phenanthrene concentration was 5.6 µmol/L. The reaction time ranged from 10 min to 1440 min. The adsorption capacities of SiO_2, NH_2-SiO_2 and the original graphene obtained at various times (36 h and 72 h) were the same, suggesting that equilibration was achieved before 36 h.

Batch adsorption experiments with SiO_2, NH_2-SiO_2, pristine graphene and ASG were conducted in background solution at a water-to-solid ratio of 200 mg per 8 mL, 200 mg per 8 mL, 1 mg per 240 mL, and 1 mg per 8 mL, respectively. The background solution contained 0.01 mL/L $CaCl_2$ and 200 mg/L NaN_3 to control the ionic strength and eliminate the effect of microorganisms. The phenanthrene in acetonitrile was dissolved in the background solution (pH=7) to prepare the working solution; the volume of acetonitrile in the background solution was maintained at less than 0.1% to avoid cosolvent effects. The initial concentrations of the phenanthrene solution were controlled to obtain equilibrium concentration ranges over 3 orders of magnitude including 0.0056, 0.017, 0.034, 0.056, 0.17, 0.34, 0.56, 1.7, 3.4, 5.6 μmol/L. Each point, either the blank or calibration control, was evaluated in duplicate. The vials were placed on a shaker and agitated in the dark at 120 rpm for 36 h to reach apparent equilibrium. The solution was separated from the solid. Then, 500 μL of the supernatants was mixed with 500 μL of acetonitrile to determine the PAH concentration on an Agilent 1200 HPLC (Agilent Eclipse XDB-C 18 column, 4.6 mm × 250 mm × 5 μm) equipped with a G1321A fluorescence detector. The mobile phases were acetonitrile:water (90:10, v:v) and a flow rate of 1 mL·min^{-1} was used. The determination of phenanthrene was performed using an excitation wavelength of 244 nm and an emission wavelength of 360 nm. The results revealed no noticeable mass loss, and the amount of PAH adsorbed by the materials was calculated from the difference between the initial and equilibrium concentrations.

Table S-1. Elemental analysis results of SiO_2, NH_2-SiO_2 and ASG.

Sample	Relative atomic percentage (%)		
	Nitrogen	Carbon	Hydrogen
SiO_2	0	0.0650	0.6916
NH_2-SiO_2	0.4185	1.1110	0.7886
ASG	0.3189	1.6986	0.7011

Table S-2. BET-N_2 surface area of SiO_2, pristine graphene and ASG.

Sample	Surface area (m^2/g)
SiO_2	120.041
NH_2-SiO_2	108.5
pristine graphene	715.8
ASG	118.7

Table S-3. Regression parameters of adsorption isotherms of phenanthrene onto SiO_2, NH_2-SiO_2, ASG and pristine graphene.

Freundlich			
Adsorbent	K_f	N	R^2
SiO_2	0.0060±0.00034	1.0598±0.0994	0.944
NH_2-SiO_2	0.0048±0.00062	0.8708±0.1634	0.866
pristine graphene	149.26±20.24	0.9450±0.0721	0.967
ASG	1.7371±0.05054	0.3239±0.0186	0.976

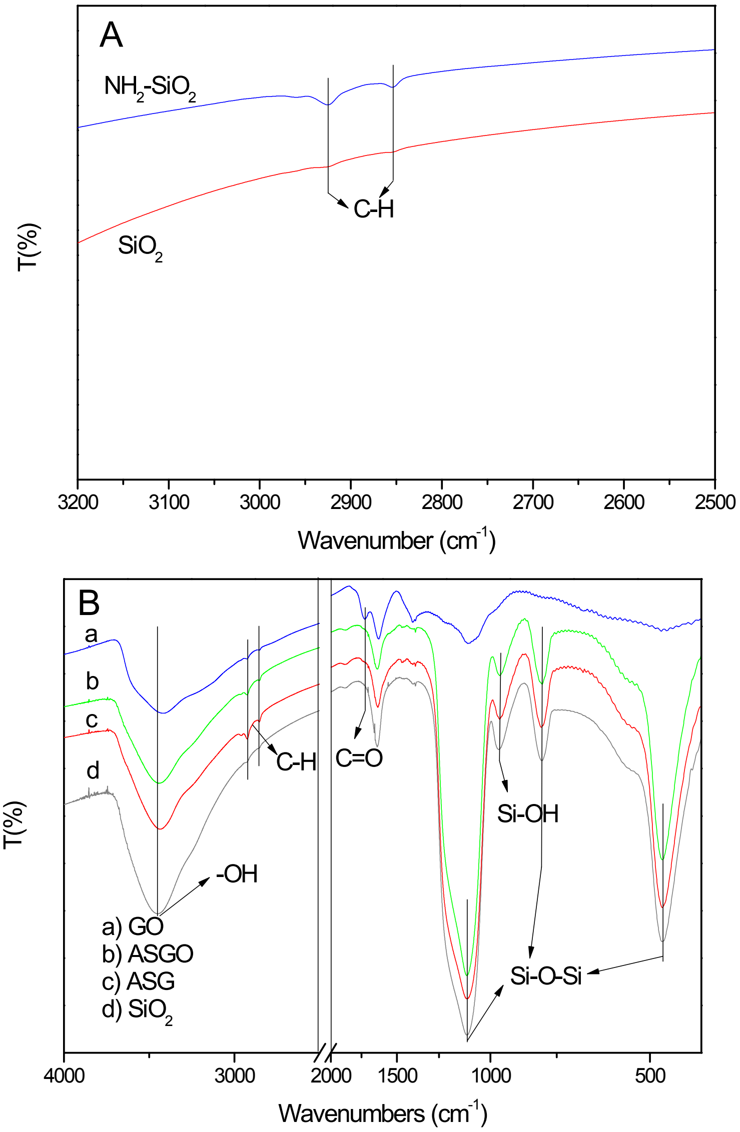

Figure S-1. Selected FT-IR spectra curves of SiO$_2$ and NH$_2$-SiO$_2$ nanoparticles (A), and whole FT-IR spectra of SiO$_2$, GO, ASGO, ASG nanoparticles (B).

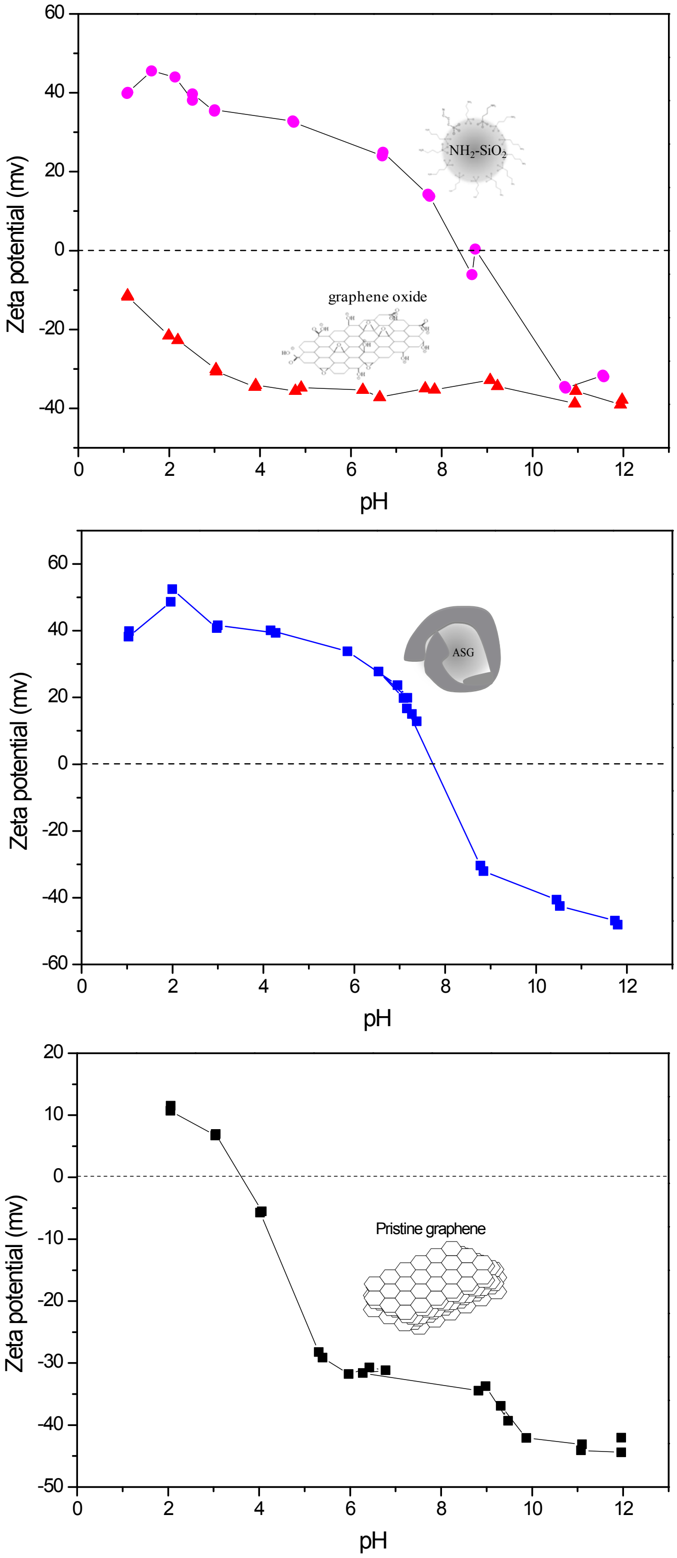

Figure S-2. Zeta potential curves of NH_2-SiO_2, GO and ASG at different pH values.

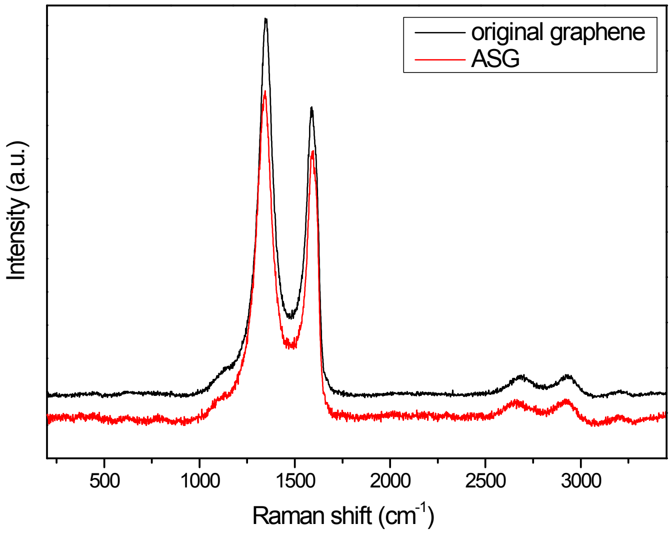

Figure S-3. The Raman spectra of original graphene and ASG.

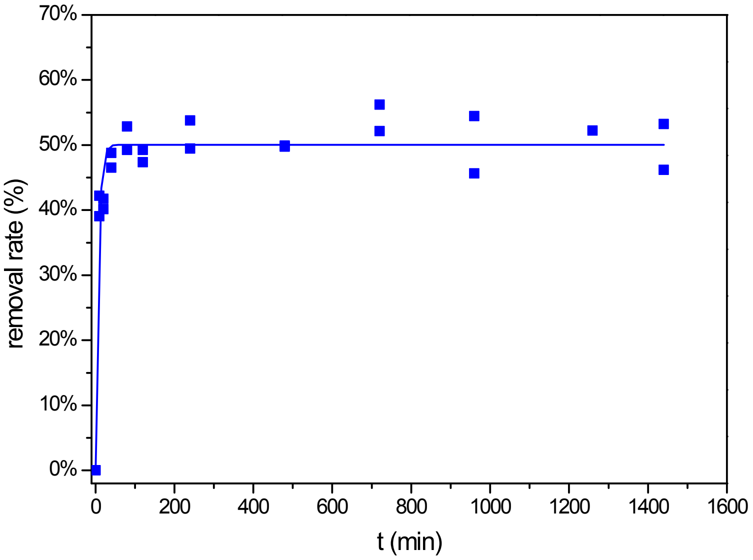

Figure S-4. The adsorption kinetic of phenanthrene onto ASG.