Graphene@Poly(m-phenylenediamine) Hydrogel Fabricated by A Facile Post-Synthesis Assembly Strategy

Liyuan Zhang,[a] Ting Wang,[a] Haiying Wang[a,b] Yun Meng,[a] Wanting Yu,[a] and Liyuan Chai*[a,b]

[a] Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha 410017, China

[b] National Engineering Research Center for Pollution Control of Heavy Metals, Changsha 410017, China

Electronic Supplementary Information

ESI-1. Experimental Section.

All of the chemicals were of analytical grade and used as received.

Graphite oxide: The preparation of graphene oxide was according to Shi's research but without adding $NaNO_3$.[1]

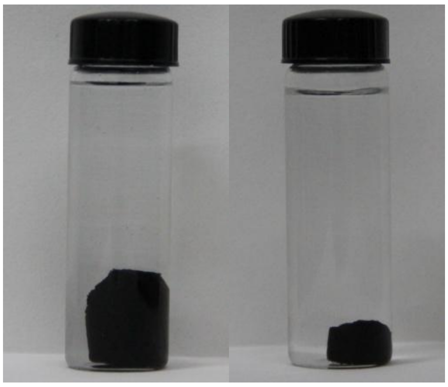
Poly(m-phenylenediamine) nanoparticles: 3 g m-phenylenediamine was dissolved in 100 mL distilled water, which was pre-warmed to 30 °C. 5 mL $CuCl_2$ solution was then poured into the monomer solution. The molar ratio of Cu^{2+}:monomer is 1:20. 20 mL sodium persulfate solution used as oxidant was given to oxidize the monomer dropwise with speed of 1.22 mL min^{-1} by a syringe pump. The molar ratio of oxidant:monomer is 1:1. The sample was rinsed with distilled water, ammonium water, distilled water and ethanol in sequence to remove the impurity. The black powders collected were dried in vacuum at 60 °C.

Hydrogel: A specific amount of poly(m-phenylenediamine) powders was dispersed in 10 mL distilled water with ultrasonication for 1 h with acidification by 2 mL of 1 M HCl solution. To the polymer dispersion, 10 mL graphene oxide solution with specific concentration was rapidly added. The mixture in the sealed bottle was put into the oil bath at 95 °C for a specific time (h). The hydrogel staying in the solution is flexible and can be readily collected by hand or spoon.

Characterization: Photo image was pictured by a camera (Canon EW 73B). For other characterizations, the hydrogel was first air-dried at 60 °C and then grinded into powders for the convenience of the operation. Field-emission SEM (Sirion 200) was taken to measure the morphology of the hydrogel by adhering a small amount of the grinded powders onto the conducting tape. The accelerating voltage is 20 kV. Raman (LABRAM-HR 800, 513 nm He-Ne laser excitation) and FTIR (Nicolet IS10, resolution 4 cm^{-1}) were applied to study the molecular structure of the hydrogel. Typically, for FITR, the KBr and sample were blended together and pressed into a disk. XRD (Rigaku D/max $2550VB^{+}$) was adopted to investigate the supermolecular structure of the hydrogel.

[1] Xu, Y.; Sheng, K.; Li, C.; Shi, G. *ACS Nano*, **2010**, *4*, 4324- 4330.

ESI-2. Graphene@Poly(m-phenylenediamine) Hydrogel with Different Size.



Increasing (Left, 80 mg) or decreasing (Right, 10 mg) the dosage of poly(m-phenylenediamine) nanoparticles directly affects the size of hybrid hydrogel.

ESI-3. Swelling property and conductivity of hybrid hydrogel.

Part 1:

Swelling property of the hybrid hydrogel was measured by the following method:[2]

$$S = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where S is swelling ratio, W_{wet} is the wet weight of hydrogel, W_{dry} is the dry weight of hydrogel.

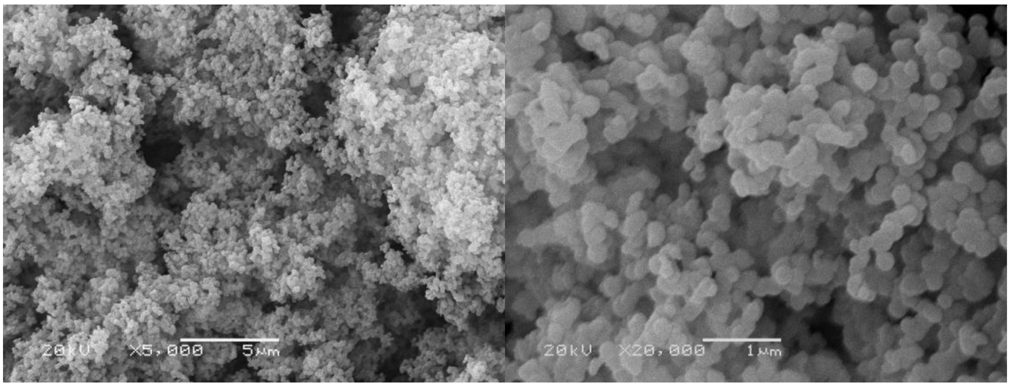
The dry weight was first detected by electronic balance. Then the dried hydrogel was immersed into the distilled water for 12 h and was taken out, on which the surface water was removed by filter paper, to obtain the wet weight. The swelling rate measured is 448.5 %.

[2] A. Çay, M. Miraftab, *J. Appl. Polym. Sci.*, 2013, **129**, 3140-3149.

Part 2:

Conductivity of hybrid hydrogel was measured by a four-probe method. Prior to the four-probe measurement, the dried hydrogel was grinded and pressed at 30 atm into a disk. The conductivity is 1.12×10^{-3} S/cm. This value is far less than the graphene conductivity, which is possibly ascribed to the incorporation of semiconducting poly(m-phenylenediamine).

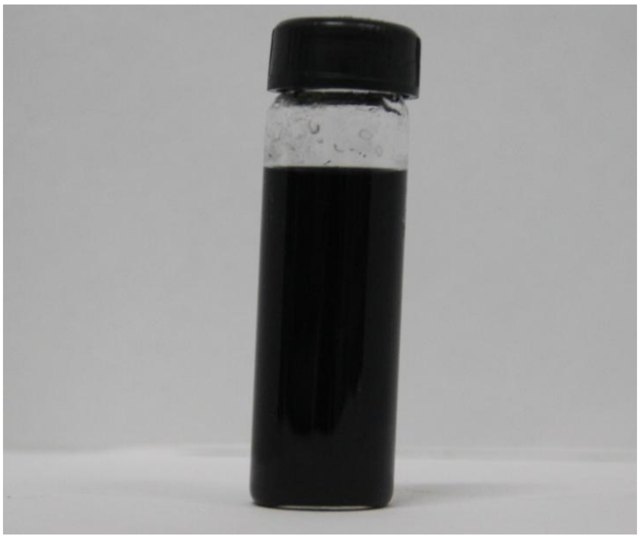
ESI-4. SEM Images of Poly(m-phenylenediamine)



This is a typical SEM image of poly(m-phenylenediamine) nanoparticles by JSM-6360 microscope, which has been reported in our previous research.[3]

[3] Zhang, L.; Wang, H.; Yu, W.; Su, Z.; Chai, L.; Li, J.; Shi, Y. *J. Mater. Chem.*, **2012**, *22*, 18244-18251.

ESI-5. Interaction between Graphene Oxide and Poly(m-phenylenediamine) With No Protonation.



This is the sample prepared without the flocculation step. There is no any shrinkage after heating at 95 °C for 5 h.

ESI-6. Fabrication of Adsorption Column.

Procedure

1) 15 mg graphene oxide was dispersed in 10 mL distilled water. 15 mg poly(m-phenylenediamine) nanoparticles were dispersed in mixture of 10 mL distilled water and 2 mL HCl solution (1 M).
2) Then the graphene oxide and poly(m-phenylenediamine) nanoparticles were rapidly mixed together to generate the floccus.
3) The floccus was carefully added into a chromatographic column with G-2 sand-core plate inserted within the column bottom.
4) The column was heated at 95 ^{o}C in a sealed sample bottle accommodating 200 mL distilled water for 15 h.
5) After that, the solution in the column was removed through permeation.

ESI-7. Adsorption Detail.

Part 1:

10 mg orange G was dissolved in 1 L volume-metric flask. Note that the toxicity of acidic orange G is much higher than neutral orange G, so the solution pH was adjusted to 1 by HCl. The detection method can be found in literature [3] below.

Generally, the column loaded with the as-prepared monolith was fixed on an iron-support stand. The acidic orange G solution was constantly feed into the column while the solution outlet speed was controlled at 50 L m^{-2} h^{-1}. The effluent at specific time was collected and analyzed.

[3] Zhang, L.; Wang, H.; Yu, W.; Su, Z.; Chai, L.; Li, J.; Shi, Y. *J. Mater. Chem.*, **2012**, *22*, 18244-18251.

Part 2:

For adsorption-desorption cycle experiment, 65 mL of 30 mg L^{-1} Orange G solution was first added into the column accommodating 25 mg hybrid hydrogel. Then, 0.5 mL of 1 M NaOH and 5 mL ethanol was added to regenerate the adsorbents. The calculation of desorption rate is based on literature [4].

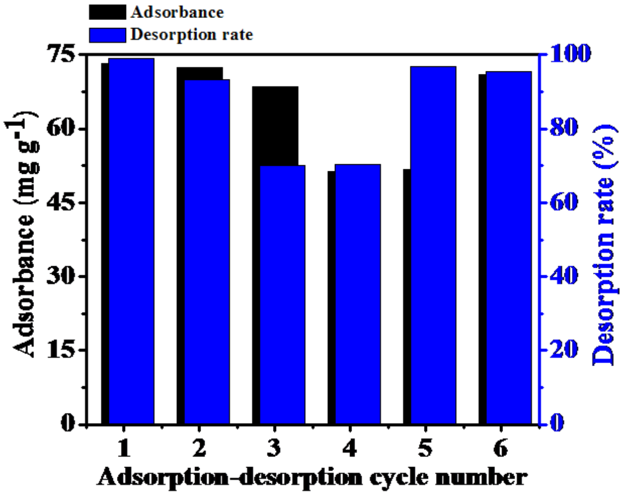


Figure ESI-7-1. Results of adsorption-desorption cycles

As shown in Figure ESI-7-1, the adsorbance in the first adsorption is 73.3 mg g^{-1} while the desorption rate is 98.9 %. But with the increase of cycle number from 2 to 4, the adsorbance and desorption rate gradually decrease to a nearly equilibrium value of ~51 mg g^{-1} and ~70 %. For desorption in the fifth cycle, 5 mL of 1 M NaOH and 10 mL ethanol were used and the desorption rate increases again to 96.7 %. The subsequent adsorbance in the sixth adsorption correspondingly increases to 70.9 mg g^{-1}. The desorption rate in the sixth cycle can still reach 95.5 % with 5 mL of 1 M NaOH and 10 mL ethanol as desorption agents.

[4] Huang, M.-R.; Lu, H.-J.; Li, X.-G. *J. Colloid Interf. Sci.*, 2007, 313, 72-79.

Part 3:

For adsorption isotherm, 8 mg of hybrid hydrogel was added into 8 mL of Orange G solution with different initial concentration. The solution was shaken for 24 h at constant 30 °C. After that, the solution was collected by filtration and was tested by UV-vis spectrometer. The result was given in Figure ESI-7-2 and Table ESI-7-1 below:

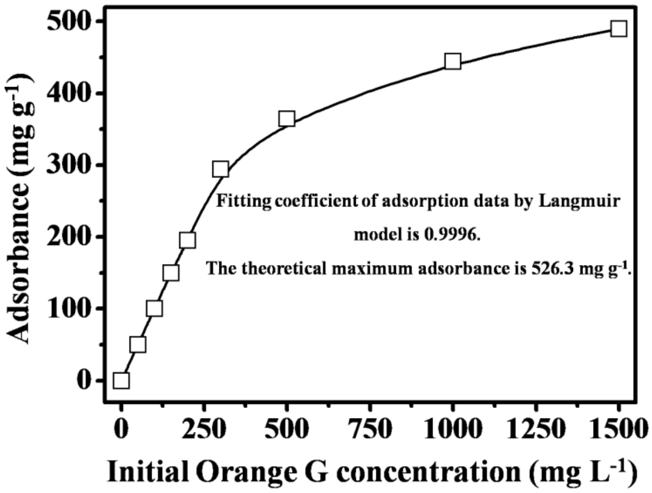


Figure ESI-7-2. Orange G adsorption isotherm.

Table ESI-7-1. Comparison of the Orange G adsorbance with that of other common materials.

Materials	Adsorbance (mg g^{-1})	Reference
Magnetic silica	65.89	[5]
Activated carbon	9.129	[6]
Bagasse fly ash	18.796	[7]
Polyaniline	220	[8]
Poly(m-phenylenediamine)	378.8	[3]
Hybrid hydrogel	526.3	This work

[5] Atia, A. A.; Donia, A. M.; Al-Amrani, W. A. *Chem. Eng. J.*, 2009, 150, 55-62.

[6] Arulkumar, M.; Sathishkumar, P.; Palvannan, T. *J. Hazard. Mater.*, 2011, 186, 827-834.

[7] Mall, I. D.; Srivastava, V. C.; Agarwal, N. K. *Dyes Pigm.*, 2006, 69, 210-223.

[8] Mahanta, D.; Madras, G.; Radhakrishnan, S.; Patil, S. *J. Phys. Chem. B*, 2008, 112, 10153-10157.