

High-yield synthesis of poly(m-phenylenediamine) hollow nanostructures by diethanolamine-assisted method and their enhanced ability for Ag⁺ adsorption

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Fig. S1 X-ray diffractograms of PmPD.

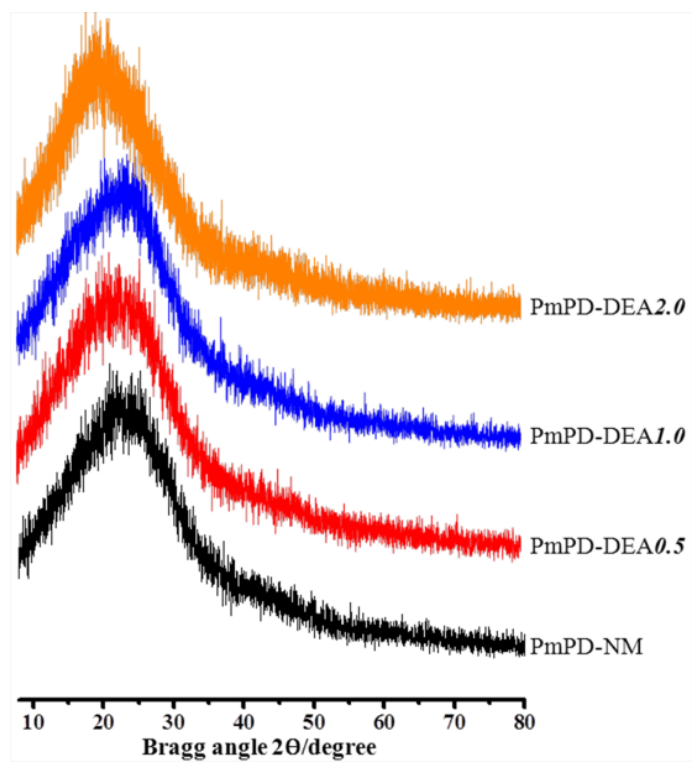


Fig. S2 TG of PmPD prepared with or without the aid of DEA.

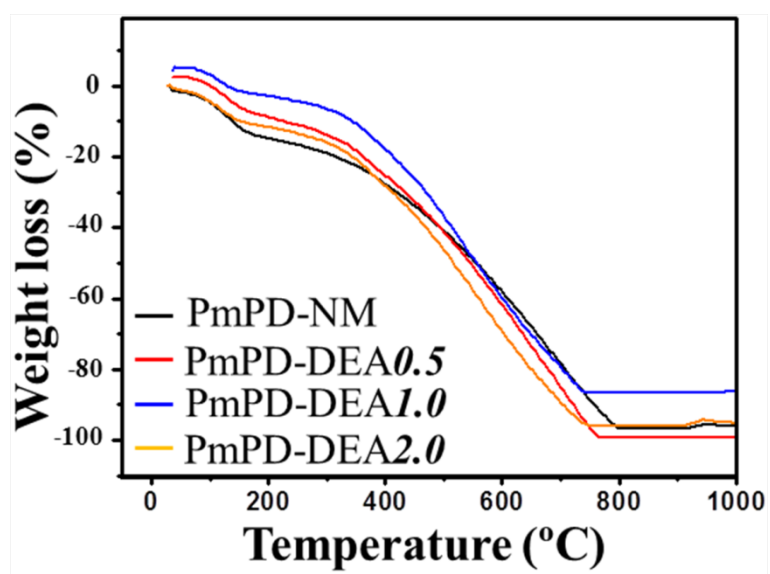


Fig. S3 TEM image of PmPD synthesized with the aid of DPA (~1.0 M)

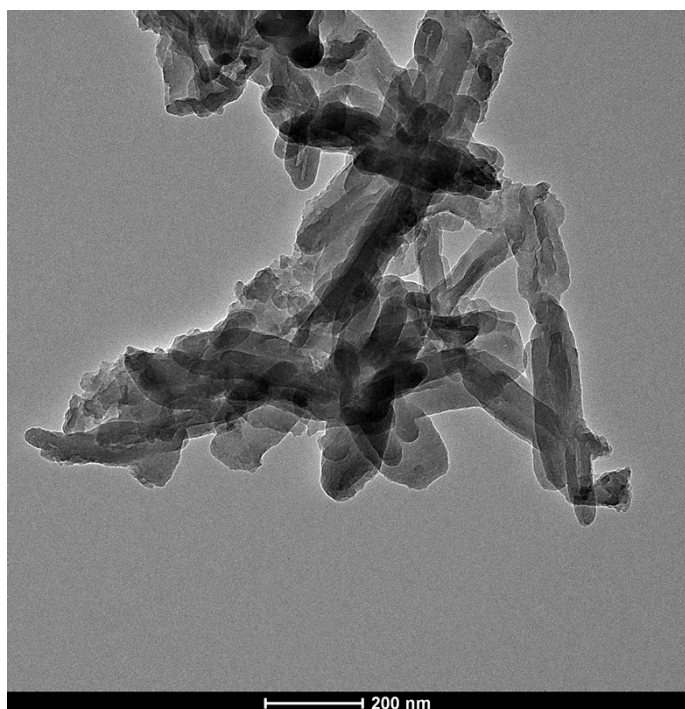


Table S1 Comparison of the Ag⁺ adsorbance of other common adsorbents.

Adsorbent	Dosage (g·L ⁻¹)	pH	Initial conc. (mM)	Adsorbance (mg·g ⁻¹)	Ref.
Modified vermiculite	20	4	0.1	69	1
Activated carbon	1	-	3.0	152	2
polyaniline	2	3.3	50	631	3
Poly(o-phenylenediamine)	2	5.4	100	533	4
Poly(1,8-naphthylenediamine)	2	5.3	82	885	5
Poly(aniline-co-5-sulfo-2-anisidine)	2	5.5	185	2034	6
PmPD-NaOH ₂	1.25	5.1	200	1693	7
PmPD-DEA 1.0	1.25	5.1	199.5	2359.3	This study

1. A. Sari and M. Tuzen, *Microporous Mesoporous Mater.*, 2013, **170**, 155.
2. X. Song, P. Gunawan, R. Jiang, S. S. J. Leong, K. Wang and R. Xu, *J. Hazard. Mater.*, 2011, **194**, 162.
3. Z. W. He, Q. F. Lu and J. Y. Zhang, *ACS Appl. Mat. Interfaces*, 2012, **4**, 369.
4. X. G. Li, X. L. Ma, J. Sun and M. R. Huang, *Langmuir*, 2009, **25**, 1675.
5. X. G. Li, M. R. Huang and S. X. Li, *Acta Mater.*, 2004, **52**, 5363.
6. X. G. Li, H. Feng and M. R. Huang, *Chem. Eur. J.*, 2010, **16**, 10113
7. L. Y. Zhang, L. Y. Chai, J. Liu, H. Y. Wang, W. T. Yu and P. L. Sang, *Langmuir*, 2011, **27**, 13729.

Fig. S4 TEM image of PmPD-DEA1.0 after adsorbing AgNO_3 solution.

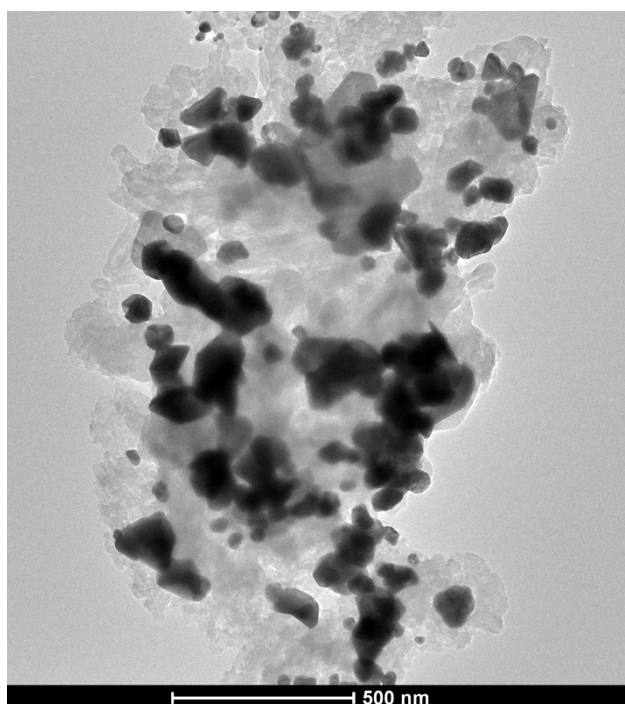
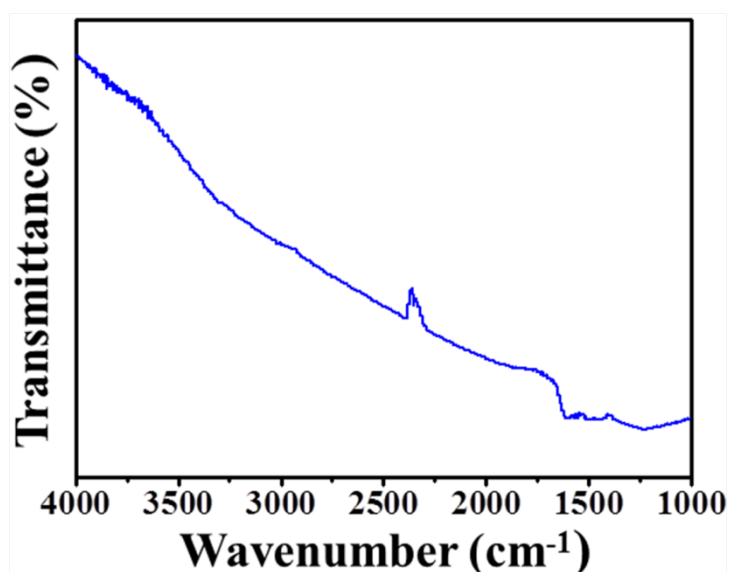
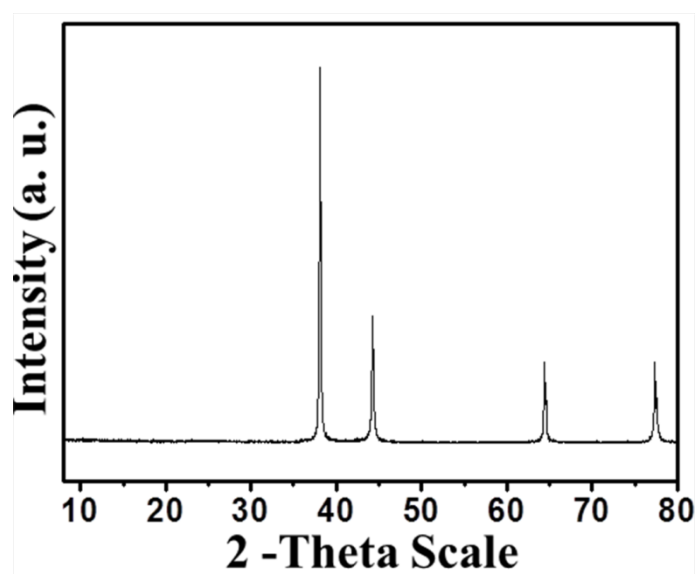


Fig. S5 FTIR of PmPD-DEA1.0 after adsorbing AgNO₃ solution.



The FTIR spectrum of PmPD-DEA1.0 after Ag⁺ adsorption further confirms the redox sorption mechanism. The broad peaks between 3500-3000 cm⁻¹ due to -NH- stretching vibration in the polymer tremendously declines after Ag⁺ adsorption, which may suggest that they are oxidized to -N= groups. Notably, the peak at 1500 cm⁻¹ representing benzenoid amine structure has disappeared on Ag⁺ adsorption indicating that the benzenoid ring has been oxidized to quinoid ring.

Fig. S6 XRD of the PmPD-DEA1.0 after Ag^+ adsorption.



XRD patterns were indexed using Jade 5.0.

38.02, 44.21, 64.39, 77.29° are corresponding to the (111), (200), (220) and (311) reflections of the face-centered cubic (fcc) structure of metallic silver, respectively.

Scheme S1. Reaction of benzenoid amine and quinoid imine with Ag^+ .

