Facile and Large-scale Synthesis of Functional Poly(m-phenylenediamine) Nanoparticles by Cu^{2+}-assisting Method with Superior Ability for Dye Adsorption

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Electronic Supplementary Information

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Fig. S1 The synthesis sketch map of the PmPD.

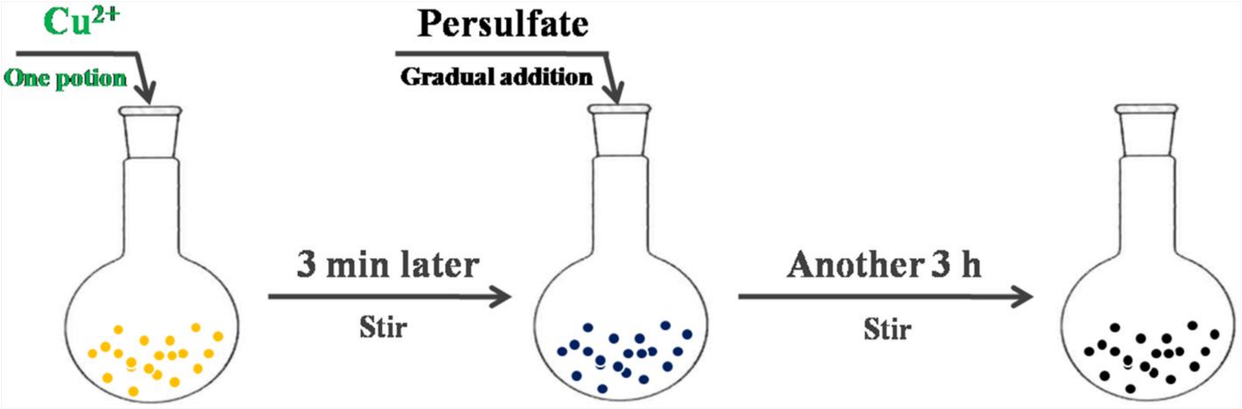


Fig. S2 Calibrated curve of Orange G.

The Orange G concentration was selected in the range of 5~15 mg·L^{-1} since the absorbance of Orange G in such concentration is within 0.2~0.8, which is the best choice for spectrophotometric method. The linear regression equation is: Y=0.04727×X-0.029. The correlation efficiency of the relationship is 0.99913.

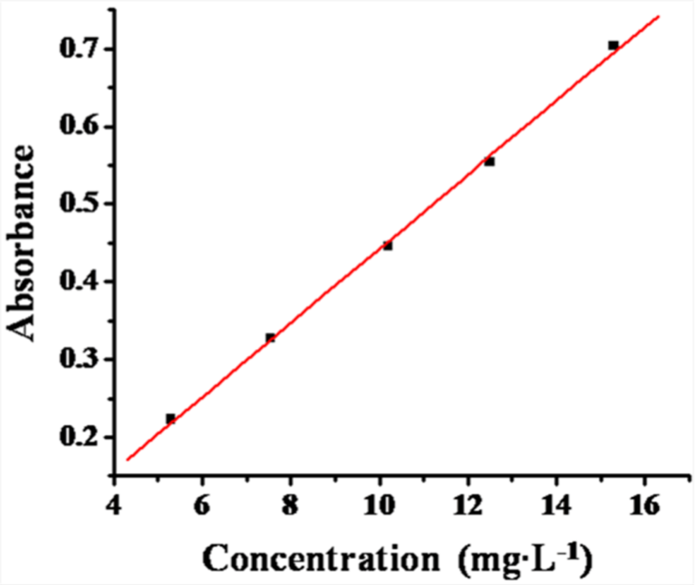
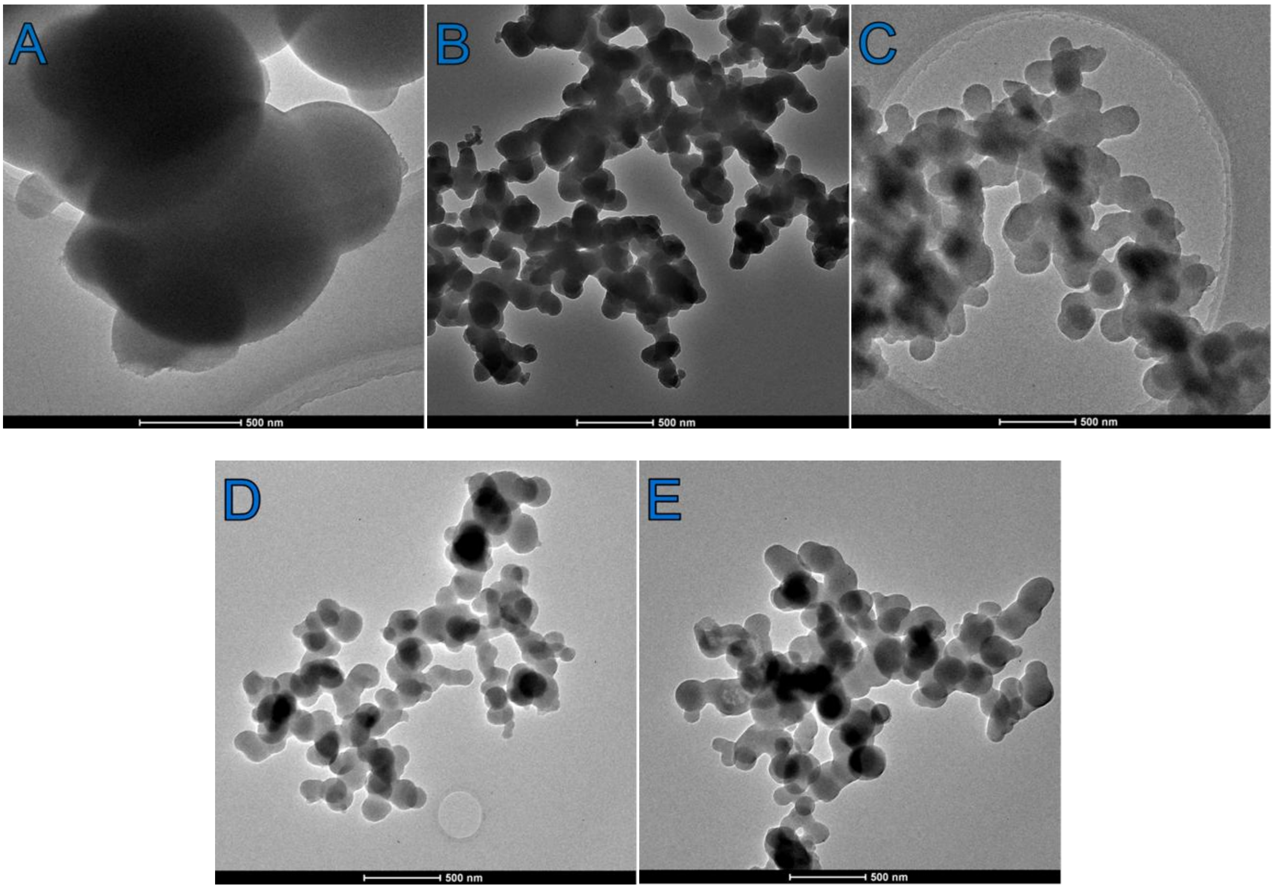


Fig. S3 Representative TEM images of the PmPD.

A: PmPD-N0; *B*: PmPD-C1; *C*: PmPD-C2; *D*: PmPD-C3; *E*: PmPD-C4.



From TEM images in Fig. S3, the size of PmPD-C1 (B), -C2 (C), -C3 (D) and -C4 (E) is similar, but much smaller than that of the PmPD-N0 (A). This is identical with the SEM results in the main text.

Fig. S4 Procedures and results of polymerization by “rapid mixing”.

Synthesis procedure: 3 g of mPD was dissolved in 100 mL of distilled water and pre-warmed in water bath at 30 ℃. Then persulfate solution (~1.47 mol L^{-1}) was given rapidly and solution was vigorous stirred for 10 s. Then the reaction was proceeded for another 3 h.

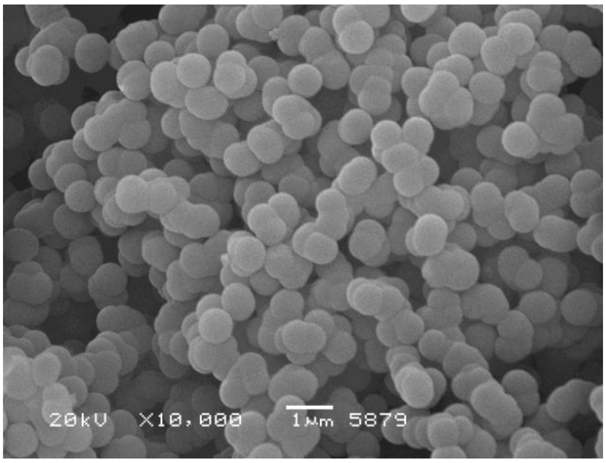


Fig. S5 FTIR spectra of suspended intermediate formed before the polymerization.

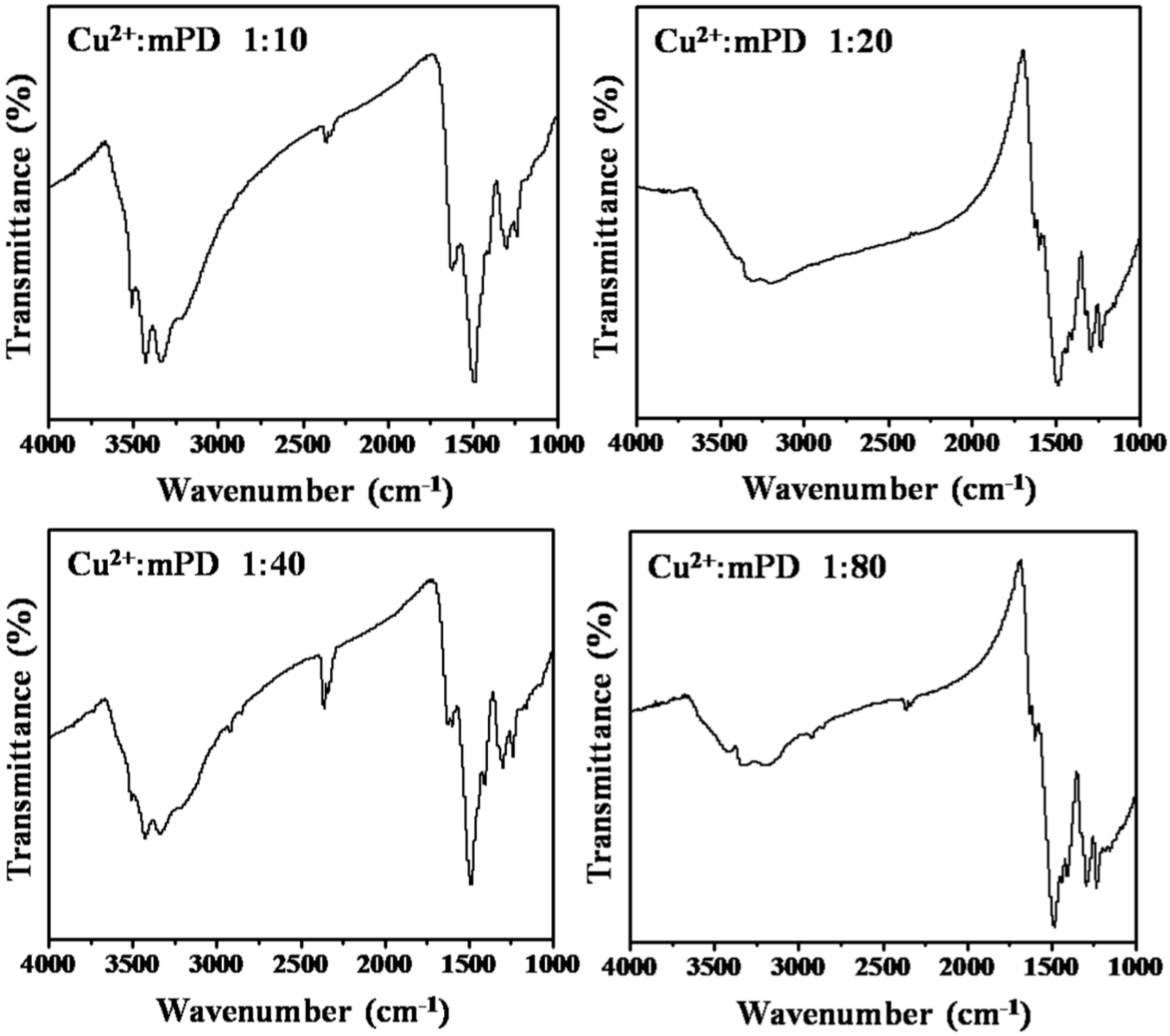


Fig. S6 EDS spectra of suspended intermediate formed before the polymerization.

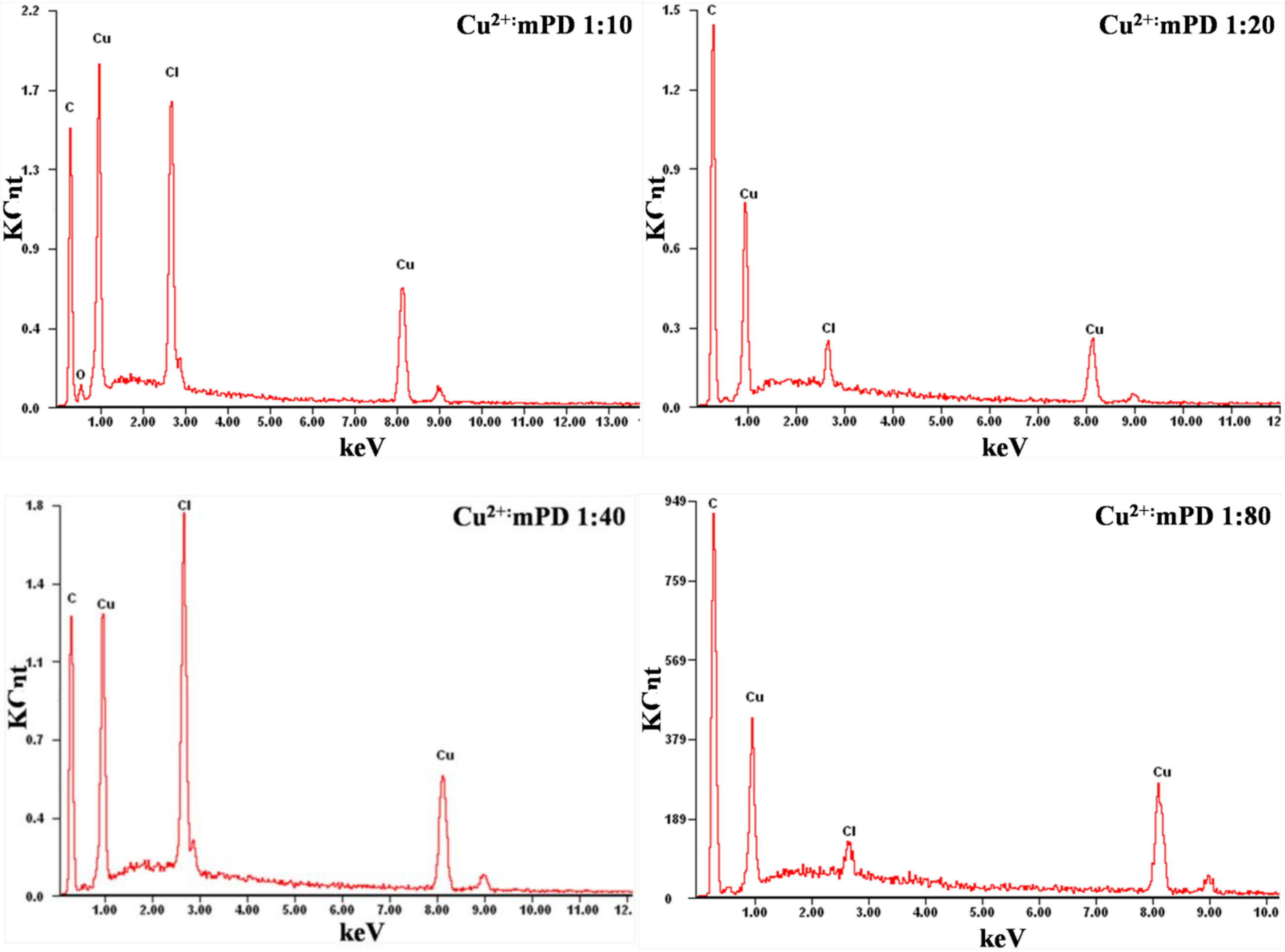
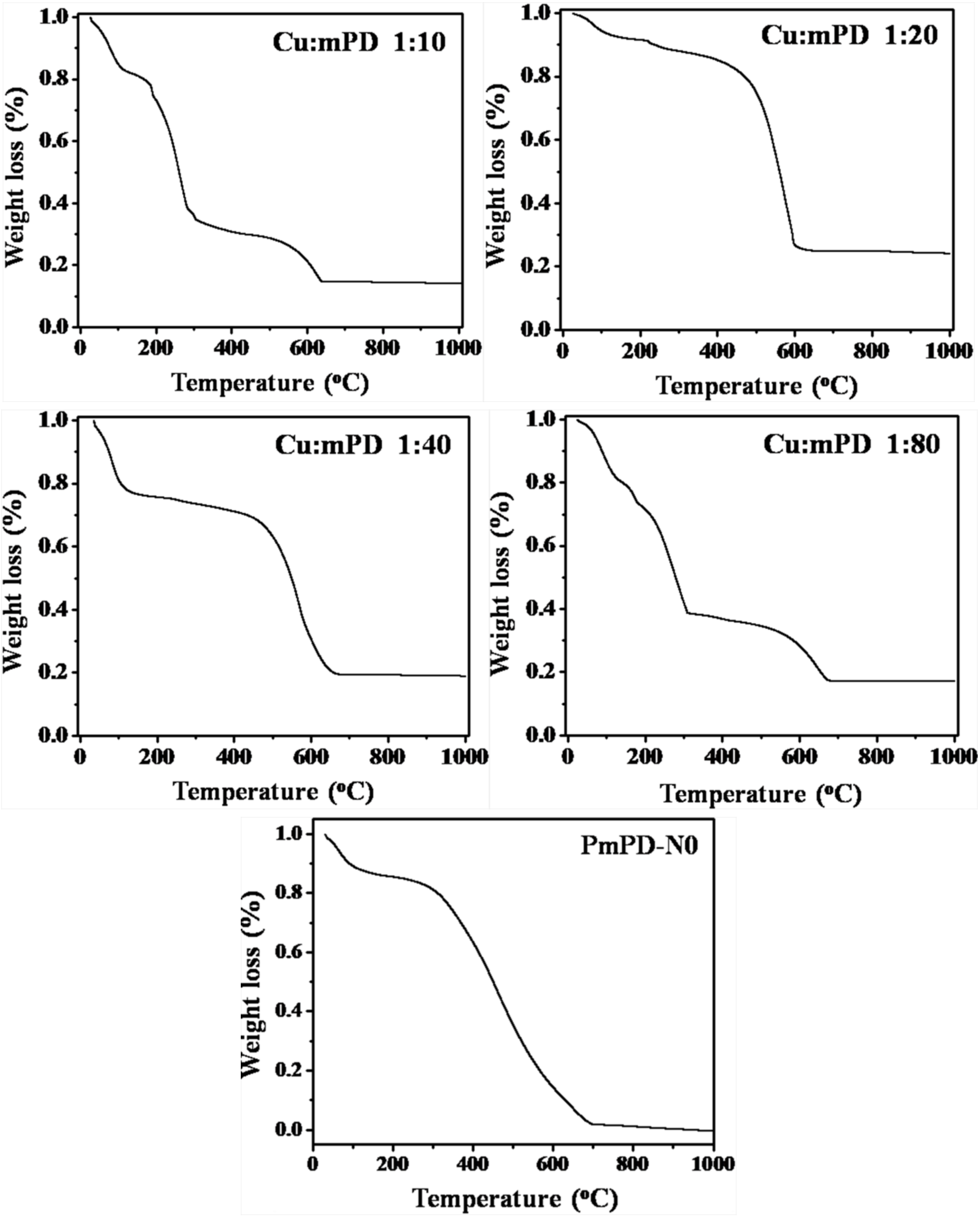


Fig. S7 TG of suspended intermediate formed before the polymerization.



As can be seen from Fig. S7, the suspended intermediate formed before the polymerization degraded rapidly with increasing temperature from 30 ℃ to 650 ℃. When the temperature went up to 700 ℃, the four samples did not lose weight, which remain ~20 % of the original weight. However, in the same conditions, the remained mass of PmPD-N0 is only ~1.8 %. As a matter of fact, the raw materials for constituting the suspended intermediate is m-phenylenediamine and Cu^{2+}. The organic species in air should be decomposed to relevant gas. But in such condition, Cu species are still in the solid form. So the remaining mass should be the Cu species. This proves that the suspended intermediate contains abundant Cu ions.

Fig. S8 UV-vis spectra of suspended intermediate formed before the polymerization.

The suspended intermediate was dissolved in DMF.

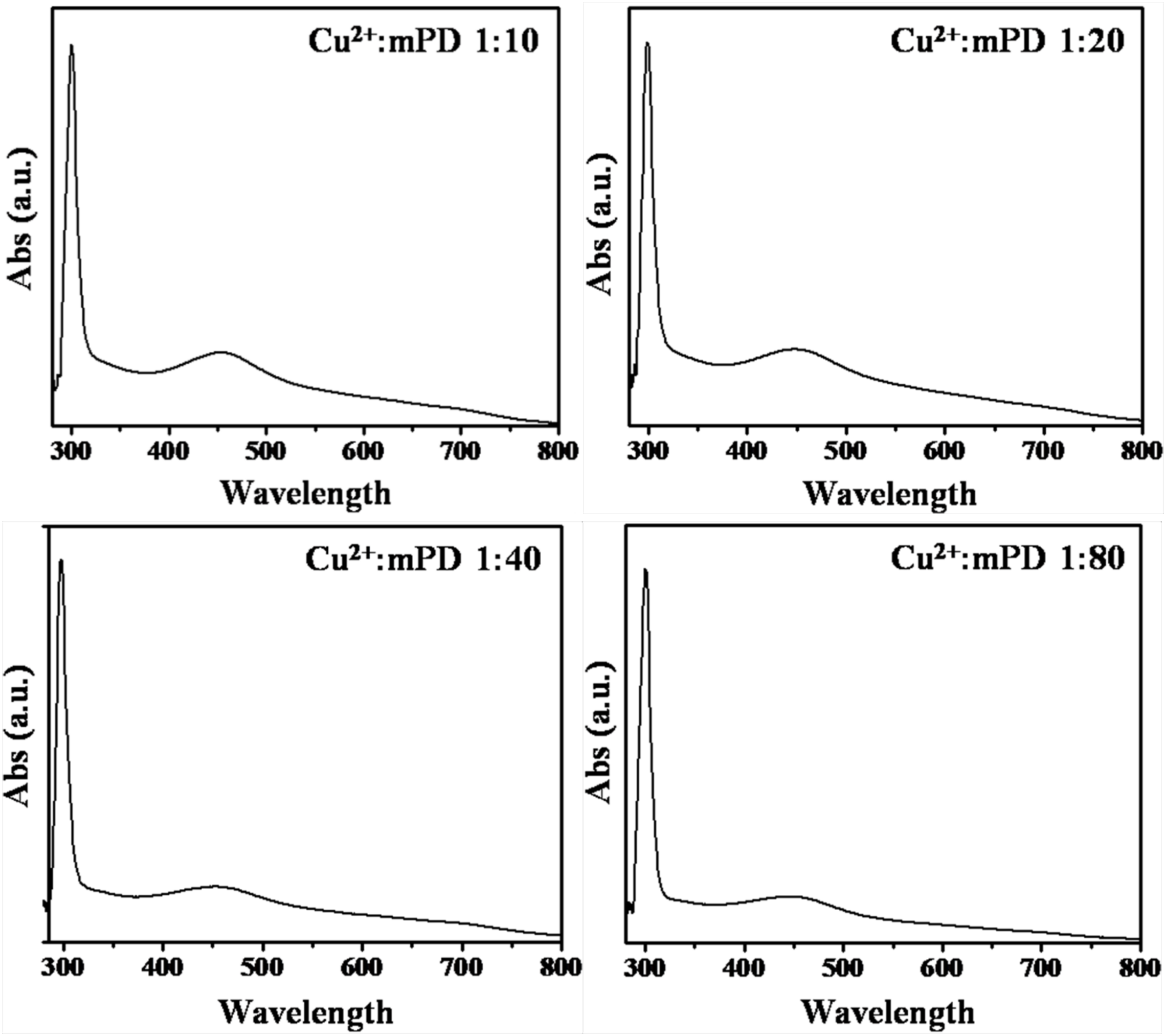


Fig. S9 UV-vis spectrum of mPD.

The mPD monomer was dissolved in DMF.

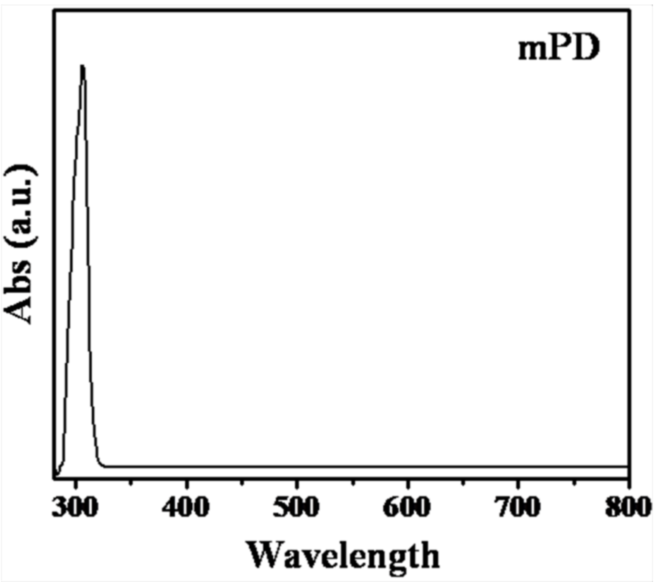


Fig. S10 TEM images of complex precipitate.

A: Cu^{2+}:mPD of 1:10; *B*: Cu^{2+}:mPD of 1:20; *C*: Cu^{2+}:mPD of 1:40; *D*: Cu^{2+}:mPD of 1:80.

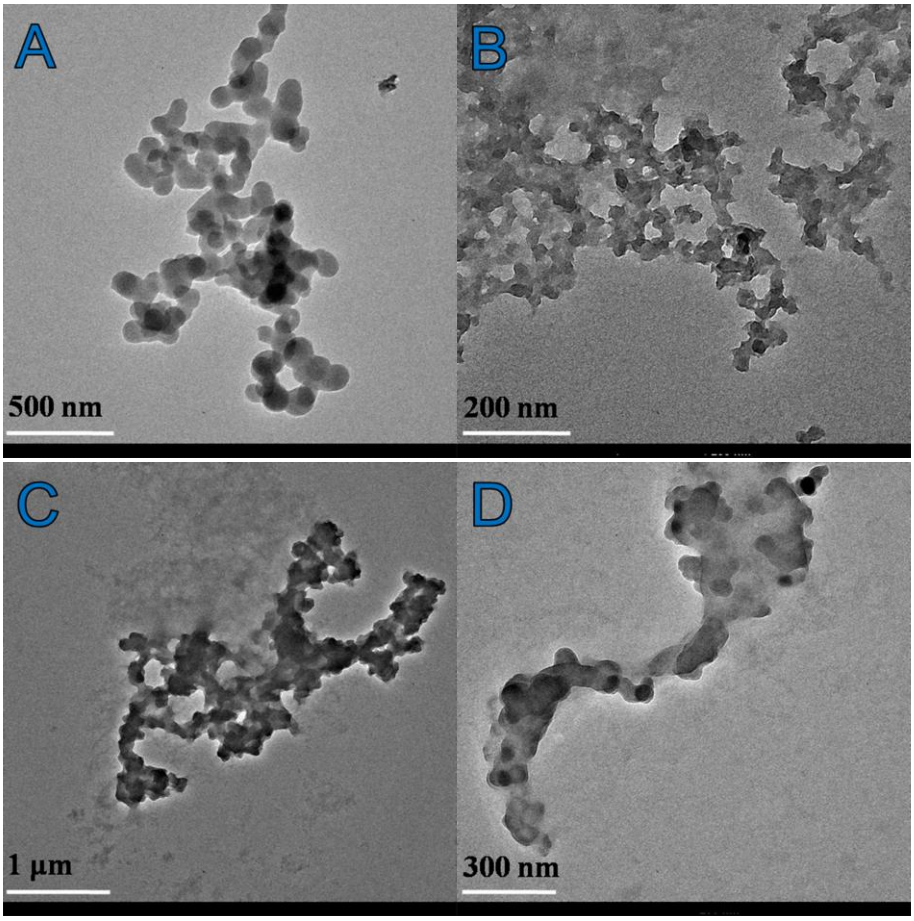
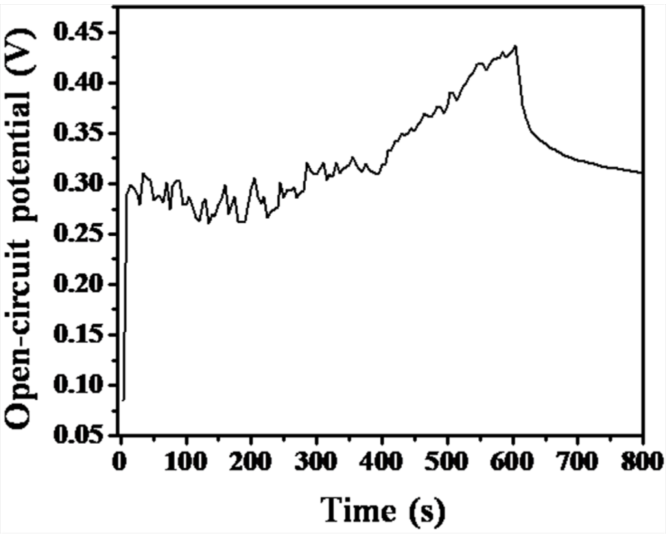


Fig. S11 The polymerization replacing the Cu^{2+} with the complex nanoparticle structure (0.1 g).

The complex nanoparticle structure were synthesized with condition of Cu^{2+}:mPD ratio of 1:20.



SEM image of the PmPDs prepared with using 0.1 g of the complex nanoparticle structure.

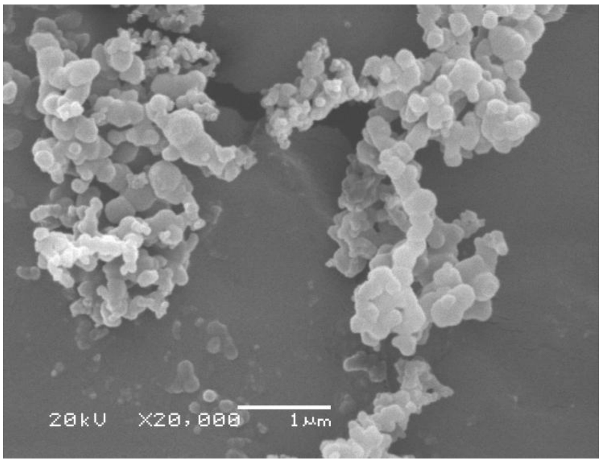
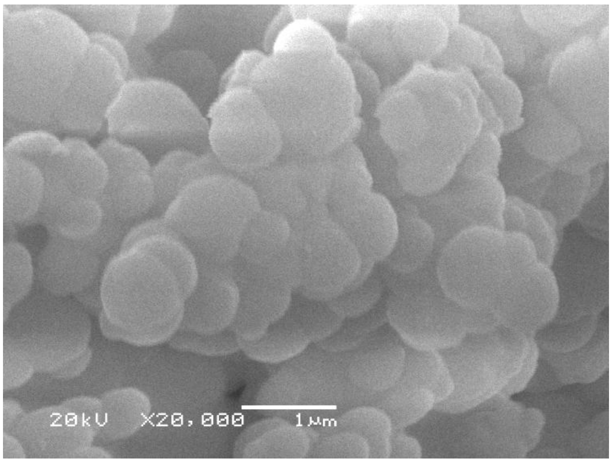


Fig. S12 SEM image and yield of the PmPD synthesized with HCl solution as solvent at the presence of Cu^{2+}.

The HCl concentration is 0.6 M. Other procedures are the same as that in Experiment Section in main text.

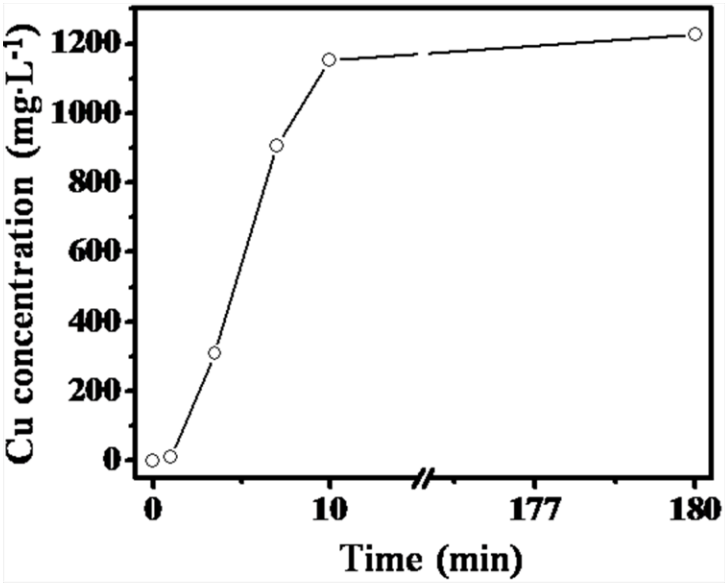


The yield of this product is only 42 %. For one thing, the absence of complex nanoparticle structure should be one of the key reasons. For another, the protonation of monomer by H^+ should be another key reason. This is because the protonation of monomer restricts its oxidation and subsequently the polymerization.

Fig. S13 Cu concentration in solution before, during and after the polymerization.

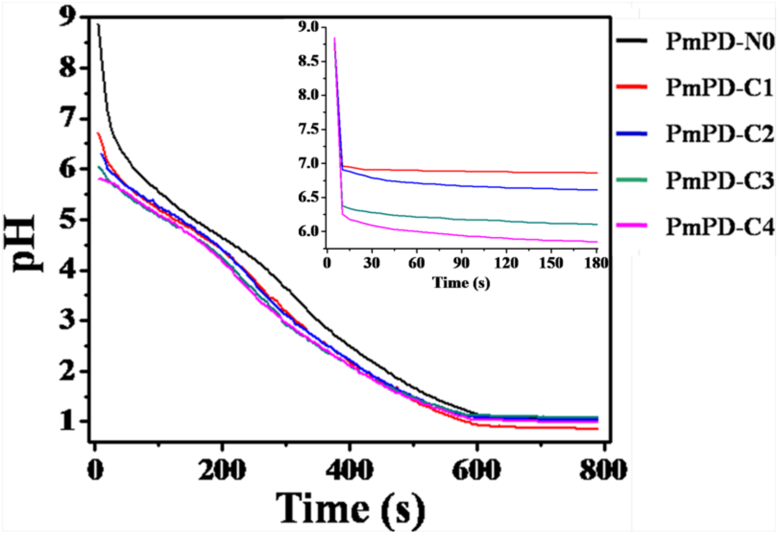
We detected the Cu concentration of the polymerization with Cu^{2+}:mPD ratio of 1:10.

Note: 0 min corresponds to "before the polymerization; 0-180 min corresponds to "during the polymerization"; within the range of 0-180 min, the 0-10 min corresponds to "initiating the polymerization by adding persulfate"; 180 min corresponds to "after the polymerization".



From Fig. S13, the Cu concentration is very low (~0.1 mg·L^{-1}: 0 min) before the polymerization. When adding persulfate to initiate the polymerization (0-10 min), the Cu concentration increases rapidly. After the addition of persulfate (10-180 min), the Cu concentration does not change much, which maintains at ~1230 mg·L^{-1}. This is very close to the Cu concentration of 1480 mg·L^{-1} calculated in ideal conditions.

Fig. S14 pH versus time for the polymerization.



As can be seen in Fig. S14, the solution pH declines very fast with adding persulfate oxidant. Noticeably, the initial solution pH for the polymerization of PmPD-N0 is higher than that of PmPD-Cx (x: 1 ,2, 3, 4). This should be due to the addition of Cu^{2+} prior to the persulfate, as shown in the inner image of Fig. S14.

Table S1. The molecular weight of complex precipitate.

PmPD-Cx	M_n	M_w	PD
1	372	386	1.0376
2	378	385	1.0185
3	424	452	1.0660
4	375	393	1.0480

Table S2. Kinetics model equation for Orange G adsorption onto the PmPD.

Models	**PmPD-*xx***	**Equations**	**Correlation efficiency**	**Standard deviation**	**Rate constant (*k*) [min^{-1}] / Initial adsorption rate (*h*) [mg·g^{-1}·min^{-1}]**
Pseudo-first-order	*N0*	$\log(Q_e-Q_t)= -0.00733t + 2.03598$	-0.93749	0.06697	k=0.01688099
	C1	$\log(Q_e-Q_t)= -0.00871t + 2.27206$	-0.81412	0.15290	k=0.02005913
	C2	$\log(Q_e-Q_t)= -0.00997t + 2.19271$	-0.78933	0.19081	k=0.02296091
	C3	$\log(Q_e-Q_t)= -0.01745t + 2.26844$	-0.94698	0.14565	k=0.04018735
	C4	$\log(Q_e-Q_t)= -0.01292t + 2.33049$	-0.93601	0.11948	k=0.02975476
Pseudo-second-order	*N0*	$t/Q_t= 0.00683t + 0.11860$	0.98532	0.08259	h=0.000393
	C1	$t/Q_t= 0.00296t + 0.02265$	0.99607	0.01837	h=0.000387
	C2	$t/Q_t= 0.00311t + 0.01577$	0.99796	0.01387	h=0.000613
	C3	$t/Q_t= 0.00313t + 0.01398$	0.99929	0.00825	h=0.000701
	C4	$t/Q_t= 0.00300t + 0.02136$	0.99815	0.01276	h=0.000421

Table S3. Isotherm model equations for Orange G adsorption onto the PmPD.

Models	**PmPD-*xx***	**Equations**	**Correlation efficiency**	**Standard deviation**	**Q_m [mg·g^{-1}]**
Langmuir	*N0*	C_e/Q_e=0.00610C_e + 0.000729	0.99998	0.00498	163.9
	C1	C_e/Q_e =0.00282C_e + 0.00558	0.99993	0.00463	354.6
	C2	C_e/Q_e = 0.00264C_e + 0.02249	0.99345	0.04085	378.8
	C3	C_e/Q_e = 0.00297C_e + 0.00321	0.99996	0.00403	336.7
	C4	C_e/Q_e y= 0.00258C_e + 0.0076	0.99979	0.00695	387.6
Freundlich	*N0*	logQ_e= 0.06194logC_e + 2.08965	0.8891	0.1218	
	C1	logQ_e= 0.16035logC_e + 2.18822	0.8595	0.1235	
	C2	logQ_e= 0.15899logC_e + 2.17154	0.8397	0.1331	
	C3	logQ_e= 0.15217logC_e + 2.18931	0.8520	0.1310	
	C4	logQ_e= 0.18019logC_e + 2.18346	0.7442	0.0729	