Methanol-induced formation of 1D poly(*m*-phenylenediamine) by conventional chemical oxidative polymerization exhibiting superior Ag$^+$ adsorption ability

Zhen Su,[a,c] Liyuan Zhang,[a,c] Liyuan Chai,[a,b] Wanting Yu,[a] Haiying Wang,[*a,b] Yu Shi[a]

[a]Department of Environmental Engineering, School of Metallurgical Science and Engineering, Central South University, Changsha 410017, China; [b]National Engineering Research Center for Heavy Metals Pollution Control and Treatment, Changsha 410017, China and [c]Zhen Su and Liyuan Zhang share the first author.

Electronic Supplementary Information

* Corresponding author: Tel.: +86-0731-88836804; fax: +86-0731-88710171. E-mail address: haiyw25@yahoo.com (H.W).

Experiment-S1

1. Synthetic Procedures.

Briefly, 3.0 g of mPD was dissolved in 100 mL of mixture of methanol and water with different volume ratio at 30 °C. 6.6 g of sodium persulfate (oxidant/monomer ratio is 1) was added to 20 mL of distilled water as an oxidant solution. The reaction mixture was initiated by gradually adding oxidant solution at a rate of 2 mL min^{-1} and then stirred for another 3 h at 30 °C. The final products were collected by filtration, rinsed with distilled water, ammonia-water (1:1, v/v), and absolute ethanol respectively. Finally, the product was dried at 45 °C under vacuum for 12 h. The yield of the product was calculated by the equation (1):

$$Y = \frac{m}{M} \times 100\% \qquad\qquad (1)$$

where Y represents the yield (%), m is the mass (g) of the product; M is the mass (g) of the monomer.

2. Characterization.

Scanning electron microscope (SEM JSM6360) and transmission electron microscope (TEM TECNAI G2) were used to investigate the size and morphology of PmPD-Mx ($x=0,50,80,100$). FTIR spectra were conducted on a pressed pellet with KBr using Nicolet IS10 infrared spectrometer at 4 cm^{-1} resolution. Surface area of PmPD was measured by Brunauer-Emmett-Teller (BET) method with the Quanta-chrome Instruments. Thermal stability of the product was tested by the SETSYS Evolution thermo analyzer under air atmosphere at a heating rate of 20 °C min^{-1}. The X-ray diffraction (XRD) pattern was collected on a D/Max 2500 VB+X X-ray diffractometer using Cu (40 kV, 300 mA) radiation.

The solubility was investigated semiquantitatively as follows: 10 mg of sample was added into 1 ml of the specific solvent and the solution was shaken for 24 h at room temperature. Then the solution was filtered to acquire the filtrate for calculation. In this study, all products are insoluble or slightly soluble in the organic solvents.

3. Ag^+ adsorption.

Kinetics. 25 mg of PmPD was added into 20 mL of $AgNO_3$ aqueous solution with an initial concentration of 46 mM at 30 °C for a specific time (0-36 h). The Ag^+ concentration in the filtrate was detected by the Volhard titration method. The Ag^+ adsorbance of PmPD-Mx was calculated by equation (2). The kinetic process of adsorption was tested by pseudo-first (3) and -second (4) equations.

$$Q = \frac{(C_0 - C_1)}{M} \times V \qquad (2)$$

$$\log(Q_e - Q_t) = \log Q_e{}' - \frac{kt}{2.303} \qquad (3)$$

$$\frac{t}{Q_t} = \frac{1}{hQ_e{}'^2} + \frac{t}{Q_e{}'} \qquad (4)$$

where Q (mg g^{-1}) is the Ag^+ adsorbance of PmPD, C_0 is the initial concentration and C_1 is the final concentration of Ag^+ solution. M (mg) is the dosage of PmPD and V (mL) is the volume of Ag^+ solution, Q_e and Q_e' (mg g^{-1}) are the equilibrium and calculated Ag^+ adsorbance of the PmPD, Q_t is the adsorbance of the PmPD at certain time (t, h), k and h are the rate constants of first and second order equations, respectively.

Isotherm. The adsorption manipulation is similar to that of kinetics but the adsorption time is fixed at 24 h. Langmuir (5) and Freundlich (6) models were used to study the isotherm adsorption behavior of the

PmPD-Mx.

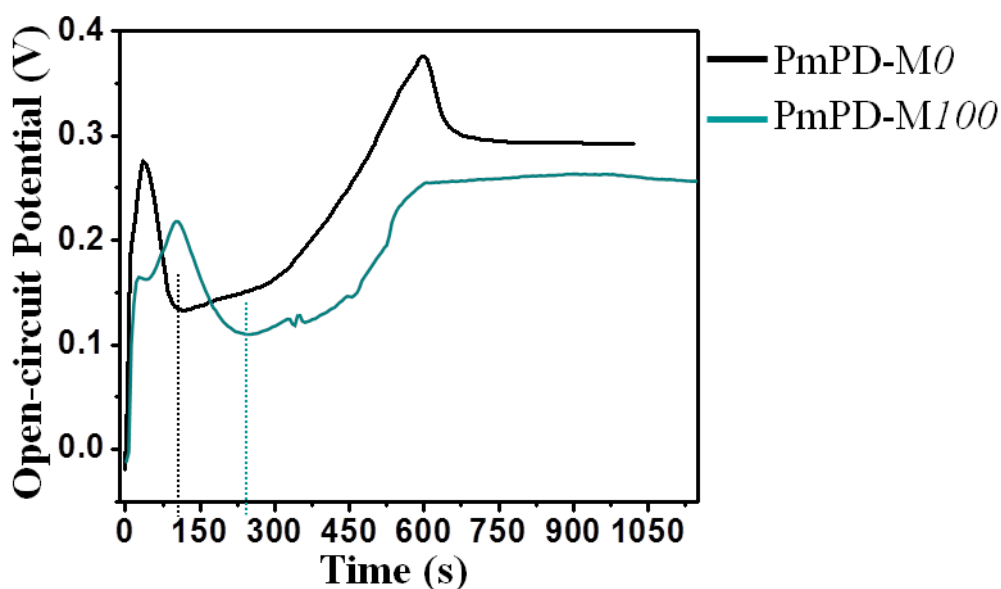$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_a Q_m} \qquad (5)$$

$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \qquad (6)$$

where Q_m (mg g^{-1}) represents the maximum adsorption capability, C_e (mg L^{-1}) is the equilibrium concentration of Ag$^+$, K_a (L mg^{-1}) is the adsorption coefficient, K_f and n are the equilibrium constants.

Competitive adsorption was carried out with identical conditions as above besides introducing coexisting metal ions. The initial concentration of the metal ions is 10 mM. The concentration of metal ions was measured with inductively coupled plasma.

Adsorption for different forms of Ag$^+$ with the initial concentration of 90 mM was conducted at the similar conditions. The final Ag$^+$ concentration after adsorption was detected by the Volhard titration method.

Fig. S1 Open-circuit potential versus time for mPD polymerization.

The OCP first rise sharply and then decrease rapidly to a minimum value. After that, the OCP again increase slowly until the oxidant solution added up. These three stages could be attributed to the sudden addition of oxidant, the formation of oligomer, and chain propagation to polymer. It is obvious that the time to form oligomer is longer in methanol than in water media. This is consistent with the color changes of the reaction solution. In the water, by dropwise adding oxidant solution, the colorless mixture became red immediately, while in the methanol reaction system, the colorless solution changed into blue, purple, and then the characteristic red color. This phenomenon also implies that the initial polymerization rate in methanol is slower than the rate in water media.

Fig. S2 SEM (left) and TEM (right) images of PmPD-M*100* after adsorbing AgNO$_3$ solution (Scale bar: 500 nm).
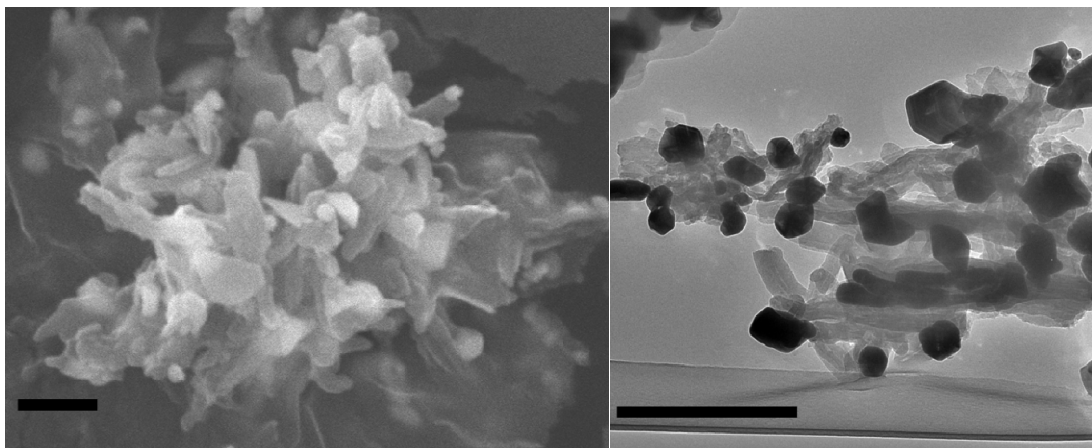
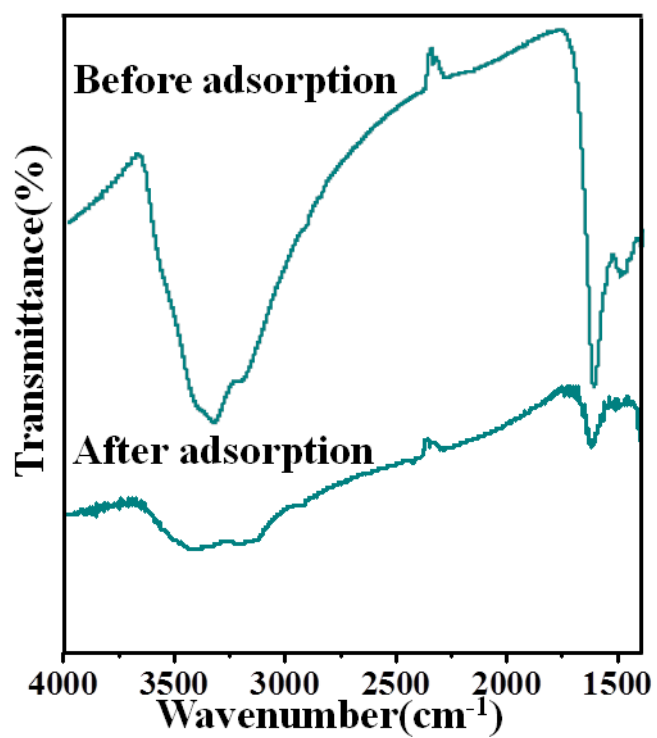**Fig. S3 FTIR of PmPD-M*100* nanorods before and after adsorbing AgNO$_3$ solution.**

Table S1 Isotherm model equations for Ag^{+} adsorption onto the PmPD-Mx (x=0,50,80,100).

Models	PmPD-Mx	Equations	Correlation efficiency	Standard deviation	Q$_m$ (mg g^{-1})
Langmuir	M0	$C_e/Q_e = 7.78846 \times 10^{-4} C_e + 0.0164$	0.9977	0.00672	1284.0
	M50	$C_e/Q_e = 5.98276 \times 10^{-4} C_e + 0.01986$	0.9961	0.00668	1671.5
	M80	$C_e/Q_e = 5.67255 \times 10^{-4} C_e + 0.02167$	0.9932	0.00835	1762.9
	M100	$C_e/Q_e = 4.82447 \times 10^{-4} C_e + 0.01742$	0.9939	0.00666	2072.8
Freundlich	M0	$logQe = 0.26368 logCe + 2.46301$	0.96443	0.04358	-
	M50	$logQ_e = 0.30782 logC_e + 2.44419$	0.9931	0.02211	-
	M80	$logQ_e = 0.29254 logC_e + 2.48351$	0.9886	0.02753	-
	M100	$logQ_e = 0.26540 logC_e + 2.60040$	0.9868	0.02760	-

Table S2 Effect of coexisting ions on the Ag^+ adsorption of PmPD-M100.[a]

Initial ion concentration (mM)				Adsorbance (mg g^{-1})			
Ag^+	Pb^{2+}	Zn^{2+}	Cu^{2+}	Ag^+	Pb^{2+}	Zn^{2+}	Cu^{2+}
10	0	0	0	331	-	-	-
10	10	10	10	329	25	16	13

[a] Adsorption conditions: 20 mL solution, 25 mg of PmPD-M100, 24 h, 30 °C.

Table S3 Kinetics model equations for Ag$^+$ adsorption onto the PmPD-Mx (x=0,50,80,100).

Models	PmPD-Mx	Equation	Correlation efficiency	Standard deviation	Rate constant(k) [min^{-1}]/ Initial adsorption rate (h)[mg·g^{-1}·min^{-1}]
Pseudo-first-order	M0	$\log(Q_e\text{-}Q_t)$= -0.03053t + 2.71695	0.98332	0.07973	k=0.07031059
	M50	$\log(Q_e\text{-}Q_t)$= -0.03206t + 2.68392	0.95676	0.13762	k=0.07383418
	M80	$\log(Q_e\text{-}Q_t)$= -0.03918t + 2.76346	0.98422	0.09945	k=0.09023154
	M100	$\log(Q_e\text{-}Q_t)$= -0.07591t + 2.92309	0.99553	0.06841	k=0.17482073
Pseudo-second-order	M0	t/Q_t=0.00137t+0.00428	0.99221	0.00254	h=0.00043853
	M50	t/Q_t=0.00129t+0.00277	0.99545	0.00184	h=0.00060076
	M80	t/Q_t=0.00115t+0.00302	0.99461	0.00178	h=0.00043791
	M100	t/Q_t=0.000962484t+0.00264	0.99645	0.00121	h=0.00035090