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ARTICLE TYPE

Facile and large-scale synthesis of poly(m-phenylenediamine) nanobelts with high surface area and superior dye adsorption ability

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Electronic Supplementary Information

Fig.S1 The synthesis sketch map of the PmPD.

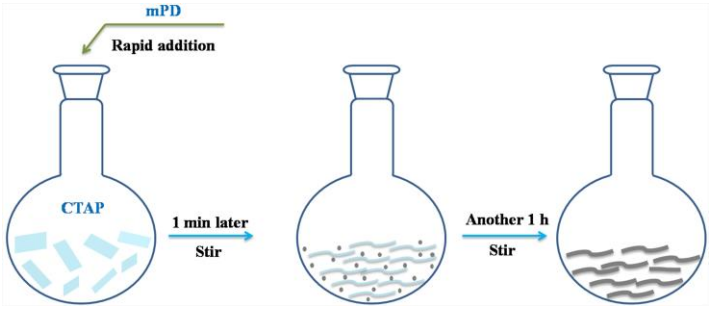
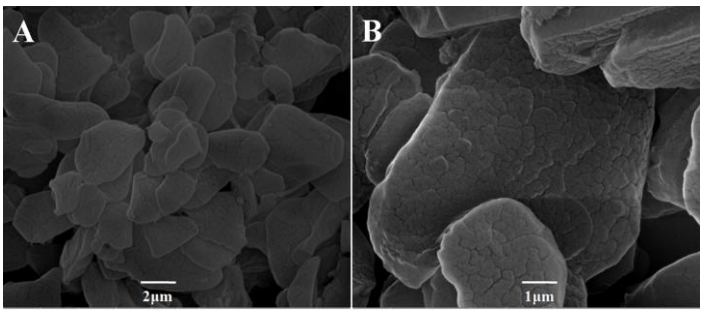
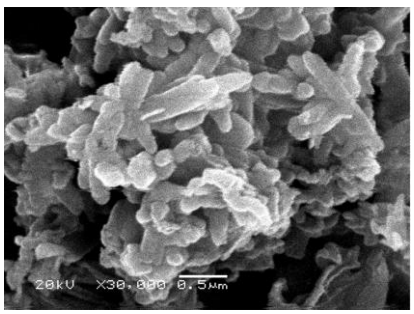


Fig.S2 The SEM images of precursor (white precipitates)



as soon as pouring the persulfate solution into CTAB solution, abundant white precipitates form. Based on SEM measureent, the white precipitates look like crystals with flat surface. It is believed that CTAB can combine with the negatively charged persulfate oxidant through electrostatic interaction, and persulfate acts as a link and leads to the closely packing of the CTAB bilayers, finally formation plate structure.

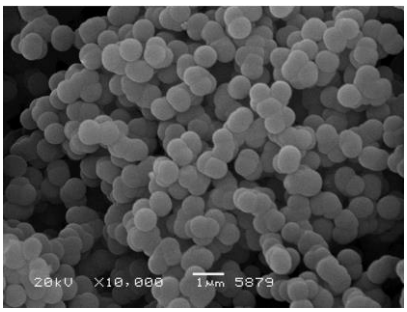
Fig.S3 TEM images of PmPD synthesized with the organic solvents (Methanol)



In our previous researches, rod-like morphology of poly(m-phenylenediamine) was achieved, by using organic solvents to mediate the morphology evolution. Briefly, m-phenylenediamine was dissolved in MeOH. By gradually adding the persulfate oxidant solution

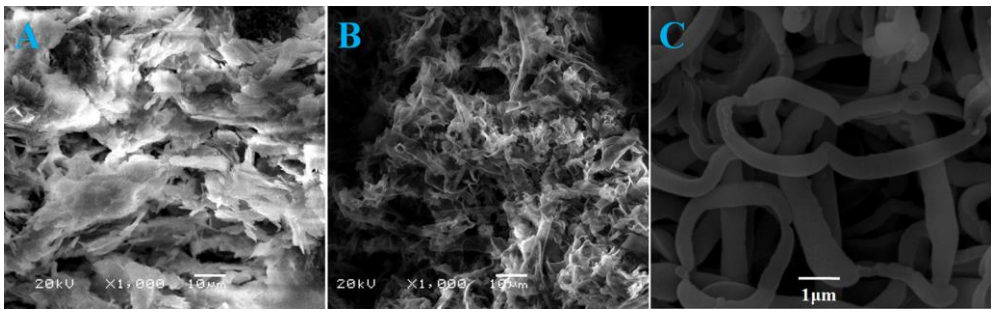
(dissolved in MeOH, too) into the monomer solution, PmPD nanorods were obtained. But the surface area of the nanorods are in the range from 10.0 ~32.6 $m^2 g^{-1}$, lower than Current study(185.50~284.55 $m^2 g^{-1}$).

Fig.S4 TEM images of PmPD prepared in aqueous medium with traditional oxidation polymerization



In our previous researches, we also achieved the PmPD nanoparticles with the Traditional chemical oxidative polymerization by Cu^{2+}-assisted, the PmPD nanoparticles possess a surface area in the range from 20.05~47.65 $m^2 g^{-1}$, still lower than Current study.

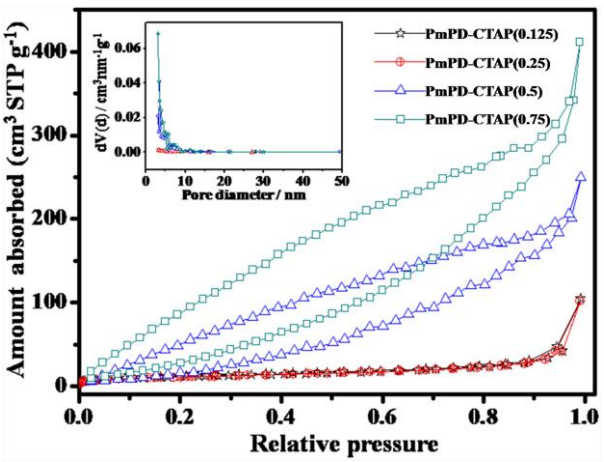
Fig.S5 The morphology evolution from CTAB bilayers to PmPD nanobelts



A : precursor (CTAB bilayers anchored by persulfate); B : PmPD(mPD : CTAP molar ratio = 0.025: 1), reaction time for 10 s; C : PmPD-CTAP(0.25).

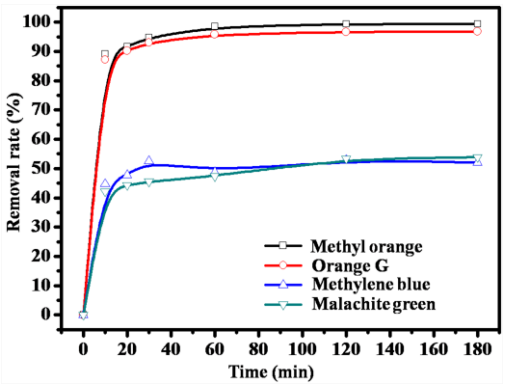
From SEM images in Fig. S5, we can acquire the morphology evolution process of poly (m-phenylenediamine). When the oxidant is poured into CTAB solution, negatively charged persulfate is anchored on the CTAB bilayers through electrostatic interaction, abundant white plate precipitates form (Fig.S5 A). as soon as adding a bit of mPD, the redox reaction is triggered and the polymerisation occurs on the surface of the plates, leading to the plate structure rapidly divide and transform into the belt structure (Fig.S5B). as the reaction progress, more and more mPD monomer polymerise and the belts gradually become curly and tenuous (Fig.S5C).

Fig.S6 N^2 adsorption-desorption isotherm of poly (m-phenylenediamine).



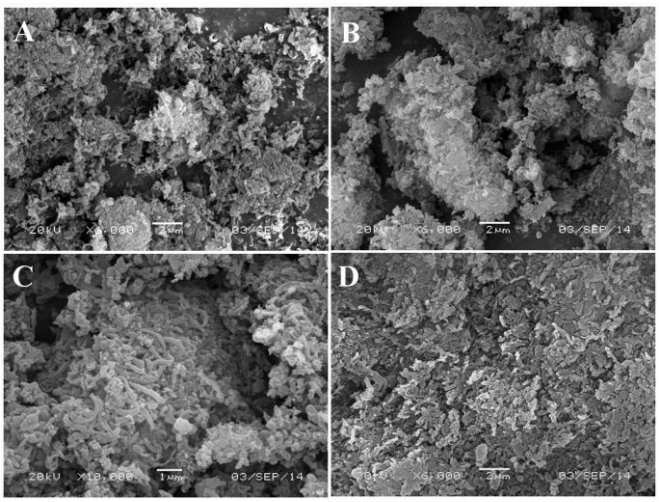
The N^2 adsorption-desorption isotherm of poly(m-phenylenediamine) was tested. As illustrated in Figure.S6, the maximum N^2 amount absorbed is similar for PmPD-CTAP(0.125) and PmPD-CTAP(0.25). But when the concentration of CTAP is larger than 0.25, the absorbed amount increases rapidly. The pore distribution indicates that many mesopores with diameter around 5 nm was contained within the poly(m-phenylenediamine) nanobelts. The pore volume calculated is more than 0.18 cm g^{-1}. These characteristics are all beneficial for the adsorption applications.

Fig.S7 Selectivity adsorption of the acid doping poly(m-phenylenediamine) towards different types of dye.



In order to detect the selection adsorption performance of adsorbent , the 200mg/L concentration of methyl orange (MO), malachite green (MG), methylene blue (MB) and Orange G (OG) solution were prepared respectively. 20mL adsorption solution was mixture with 0.02g of adsorbent, magnetic stirring under 25 ºC for different time intervals from 10min to 180min. The results as shown in Figure S6, acid doping poly (m-phenylenediamine) has good adsorption performance for anionic dye such as Orange G and methyl orange, removal rate for OG and MO are more than 98%, but the removal rate for cationic dyes such as malachite green (MG) and methylene blue (MB) are less than 50%. Their results demonstrate that the acid doping poly(m-phenylenediamine) has the adsorption selectivity and is more suitable for the adsorption of anionic dyes.

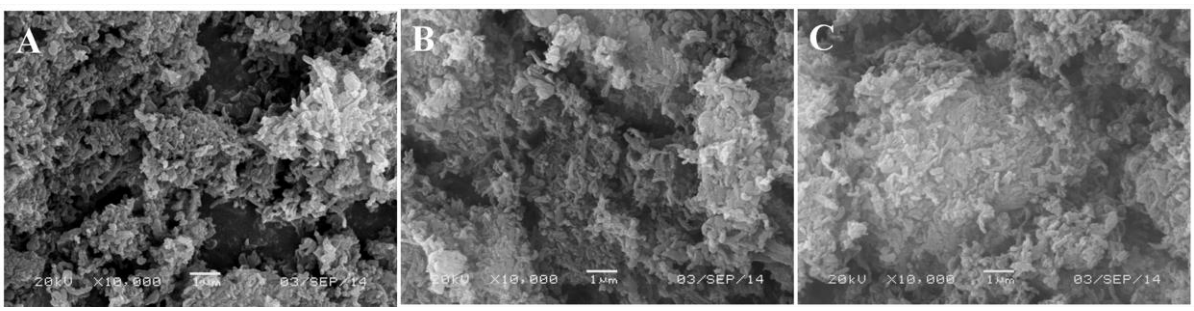
Fig.S8 SEM images of PmPD synthesized with the different reaction time.



A : PmPD-CTAP(0.5)-2h; B : PmPD-CTAP(0.5)-3h; C : PmPD-CTAP(0.5)-5h; D : PmPD-CTAP(0.5)-10h.

From the SEM images of PmPD synthesized with the different reaction time, we can see that the poly(m-phenylenediamine) nanobelts become shorter and irregular with the increase of reaction time, the best reaction time is still 1 hour in Fig.1 and Fig.2.

Fig.S9 SEM images of PmPD synthesized with the different stirring rate.

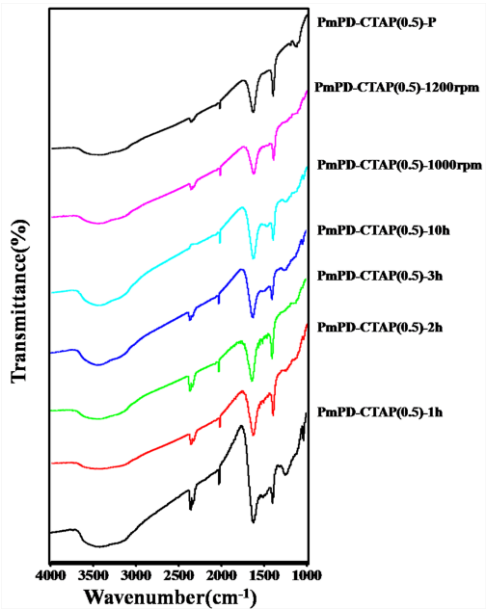


A : PmPD-CTAP(0.5)-800rpm; B : PmPD-CTAP(0.5)-1000rpm; C : PmPD-CTAP(0.5)-1200rpm.

From the SEM images of PmPD synthesized with the different stirring rate, we can see that the poly(m-phenylenediamine) nanobelts

become shorter and unite with the increase of stirring rate, the benefit stirring rate is still 600 rpm.

Fig.S10 FTIR spectra of poly(m-phenylenediamine) synthesized with the different reaction time and stirring rate.



As shown in Fig. S10, the peaks between 3000-3600 cm^{-1}, ~1620,~1500, ~1250 cm^{-1} ,~1350, ~1200 and ~150 cm^{-1} have no obvious variation, indicating that the change of reaction time and stirring rate does not influence the molecular structure. In addition, There is no damage for poly(m-phenylenediamine) molecular structure after acid doping

Table.S1 Isotherm model equations for Orange G adsorption onto the poly(m-phenylenediamine).

Models	PmPD-name	Equations	Correlation efficiency	Standard deviation	Qm [mg·g^{-1}]
Langmuir	PmPD-CTAP(0.125)	Ce/Qe=0.03926+0.00249Ce	0.99919	0.03973	401.61
	PmPD-CTAP(0.25)	Ce/Qe=0.03586+0.00242Ce	0.99949	0.03024	413.22
	PmPD-CTAP(0.5)	Ce/Qe=0.02851+0.0023Ce	0.99955	0.02635	434.78
	PmPD-CTAP(0.75)	Ce/Qe=0.02885+0.00213Ce	0.99939	0.02669	469.48
Freundlich	PmPD-CTAP(0.125)	logQe=0.23823logCe+1.92747	0.76536	0.25121	
	PmPD-CTAP(0.25)	logQe=0.25755logCe+1.90387	0.7976	0.23894	
	PmPD-CTAP(0.5)	logQe=0.24628logCe+1.9533	0.74768	0.27117	
	PmPD-CTAP(0.75)	logQe=0.25006logCe+1.96754	0.73968	0.28238	

Table.S2 Kinetics model equation for Orange G adsorption onto the poly(m-phenylenediamine).

Models	PmPD-name	Equations	Correlation efficiency	Standard deviation	Rate constant (k) [min^{-1}] / Initial adsorption rate (h) [mg g^{-1} min $^{-1}$]
Pseudo-first-order	PmPD-CTAP(0.125)	log(Qe-Qt)=1.99096-0.0099t	-0.95845	0.06162	k=0.0227997
	PmPD-CTAP(0.25)	log(Q_e-Q_t)=2.12337-0.00104t	-0.97047	0.10399	k=0.00239512
	PmPD-CTAP(0.5)	log(Q_e-Q_t)=2.01354-0.00126t	-0.91633	0.14844	k=0.00290178
	PmPD-CTAP(0.75)	log(Q_e-Q_t)=2.1097-0.00246t	-0.99603	0.06617	k=0.00566538
Pseudo-second-order	PmPD-CTAP(0.125)	t/Qt=0.11199+0.0033t	0.99874	0.06865	h=0.00001089
	PmPD-CTAP(0.25)	t/Q_t =0.10979+0.00328t	0.99896	0.06804	h=0.0000107589
	PmPD-CTAP(0.5)	t/Q_t =0.07972+0.00327t	0.9996	0.03809	h=0.0000106929
	PmPD-CTAP(0.75)	t/Q_t =0.08215+0.00338t	0.99972	0.03547	h=0.0000114242

Table.S3 the relationship between adsorbance and surface area of different adsorbtents.

Materials	Surface area (m^{2}g^{-1})	Adsorbance(mg g^{-1})	References
PmPD-N0	4.86	160	Previous study
PmPD-C3	26.19	320	Previous study
PmPD-CTAB(0.125)	40.931	401.61	Current study
PmPD-CTAB(0.25)	39.816	413.22	Current study
PmPD-CTAB(0.5)	185.498	434.78	Current study
PmPD-CTAB(0.75)	284.545	469.48	Current study

Table.S4 Isotherm model equations for Orange G adsorption onto the acid doping poly(m-phenylenediamine).

Models	PmPD-name	Equations	Correlation efficiency	Standard deviation	Qm [mg·g^{-1}]
Langmuir	PmPD-CTAP(0.125)-P	Ce/Qe=0.01925+0.00242Ce	0.99972	0.02292	413.22
	PmPD-CTAP(0.25)-P	Ce/Qe=0.01837+0.0024Ce	0.99966	0.02487	416.67
	PmPD-CTAP(0.5)-P	Ce/Qe=0.0224+0.0023Ce	0.99972	0.0212	434.78
	PmPD-CTAP(0.75)-P	Ce/Qe=0.02376+0.00201Ce	0.99944	0.02432	497.51
Freundlich	PmPD-CTAP(0.125)-P	logQe=0.21697logCe+2.01165	0.69968	0.28054	
	PmPD-CTAP(0.25)-P	logQe=0.23906logCe+1.97851	0.74404	0.26299	
	PmPD-CTAP(0.5)-P	logQe=0.22979logCe+2.00119	0.71868	0.27615	
	PmPD-CTAP(0.75)-P	logQe=0.24492logCe+2.011	0.70897	0.29466	

Table.S5 Kinetics model equation for Orange G adsorption onto the acid doping poly(m-phenylenediamine).

Models	PmPD-name	Equations	Correlation efficiency	Standard deviation	Rate constant (k) [min^{-1}] / Initial adsorption rate (h) [mg g^{-1} min $^{-1}$]
Pseudo-first-order	PmPD-CTAP(0.125)-P	log(Qe-Qt)=2.21775-0.01924t	-0.98926	0.12659	k=0.04430972
	PmPD-CTAP(0.25)-P	log(Qe-Qt)=1.76447-0.0057t	-0.95047	0.08295	k=0.0131271
	PmPD-CTAP(0.5)-P	log(Qe-Qt)=1.69284-0.00678t	-0.85373	0.18425	k=0.01561434
	PmPD-CTAP(0.75)-P	log(Qe-Qt)=1.73427-0.00862t	-0.95865	0.05681	k=0.01985186
Pseudo-second-order	PmPD-CTAP(0.125)-P	t/Qt=0.01343+0.00277t	0.99994	0.00209	h=0.0000076729
	PmPD-CTAP(0.25)-P	t/Qt=0.00962+0.00268t	0.99975	0.00411	h=0.0000071824
	PmPD-CTAP(0.5)-P	t/Qt=0.00875+0.00291t	0.99988	0.00309	h=0.0000084681
	PmPD-CTAP(0.75)-P	t/Qt=0.00846+0.00284t	0.99987	0.00308	h=0.0000080656