

Supporting Information

Conductive copolymer of graphene oxide/poly (1-(3-aminopropyl) pyrrole) and the adsorption of metal ions

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Preparation of graphene oxide (GO)

GO was synthesized from natural graphite flakes by the modified Hummer method. 3 g of graphite (Alfa Aesar, 325 mesh, 99.8%), 2.5 g of NaNO₃, and 185 g of H₂SO₄ (purity 95%) were added to a beaker containing a stirrer. After 1 hour cooling in an ice water bath, 12 g of KMnO₄ was slowly added into the mixture. The mixture was stirred at room temperature until it became a highly viscous liquid. 300 ml of 5 wt% H₂SO₄ aqueous solution was added to the above solution and stirred for 1 hour. Then, 30 wt% H₂O₂ aqueous solution was slowly added until it become yellow and stirred for 1 hour. Then, the products were washed 20 times using centrifugation and DI water to obtain an aqueous solution of GO. The concentration of the resulting GO aqueous solution was about 20 mg/mL. And then, the GO solution was diluted by N-Methyl-2-pyrrolidone (NMP) solvent to 8 mg/mL for the subsequent synthesis. For comparison, solid graphene oxide paper was prepared by vacuum filtration and dried in an oven at 50°C.

Synthesis of poly (1-(3-aminopropyl) pyrrole) (poly (APP))

The synthesis of poly (APP) is similar with poly (GO-APP). Ammonium peroxy

disulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS) and APP monomer were mixed into a NMP solution. The molar ratio of APP to APS was APP:APS=5. The mixture solution was kept at 4°C in a refrigerator for 72 h. And after filtration and drying, the poly (APP) was obtained. The process was shown in Figure S2.

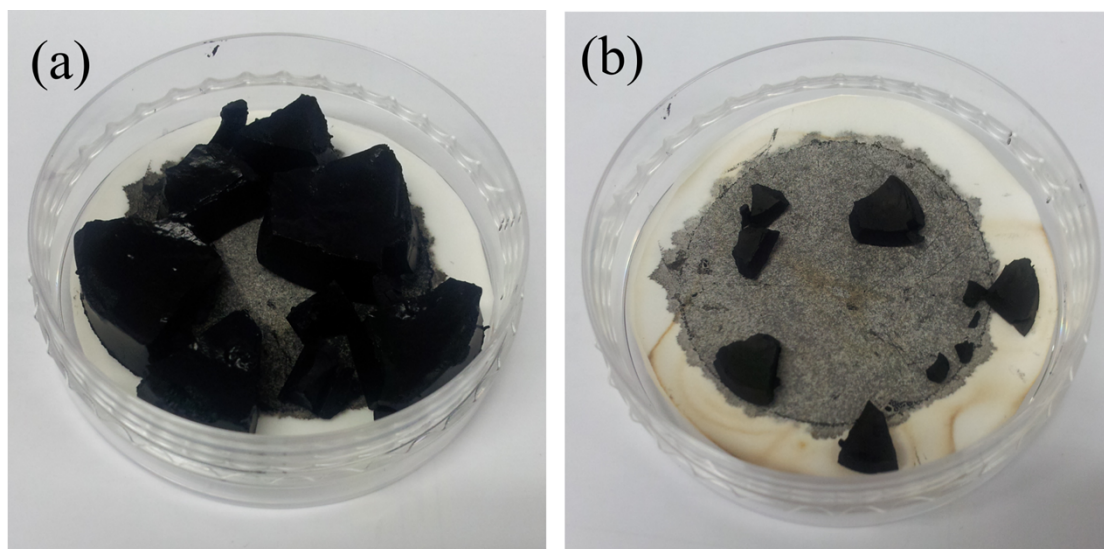


Figure S1 The photos of (a) gelatinous poly (GO-APP) before drying and (b) final solid poly (GO-APP) after drying.

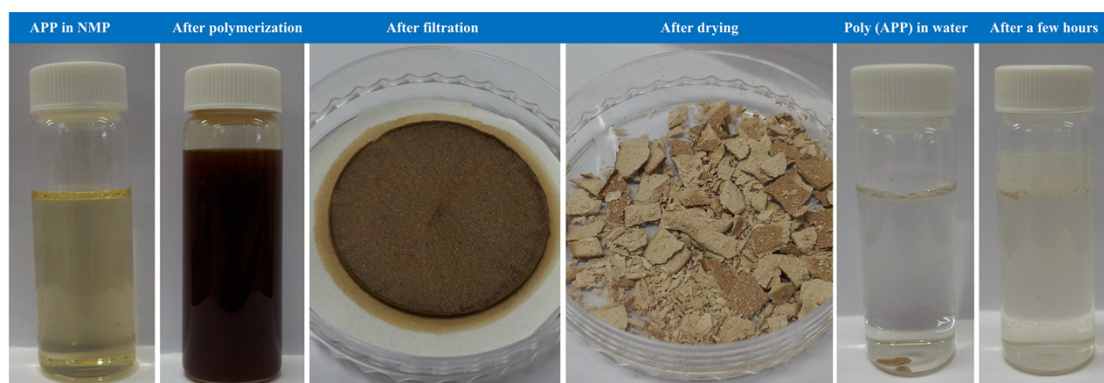


Figure S2 The process of poly (APP) preparation (from left to right), and parts of poly (APP) was soluble in water after a few hours.

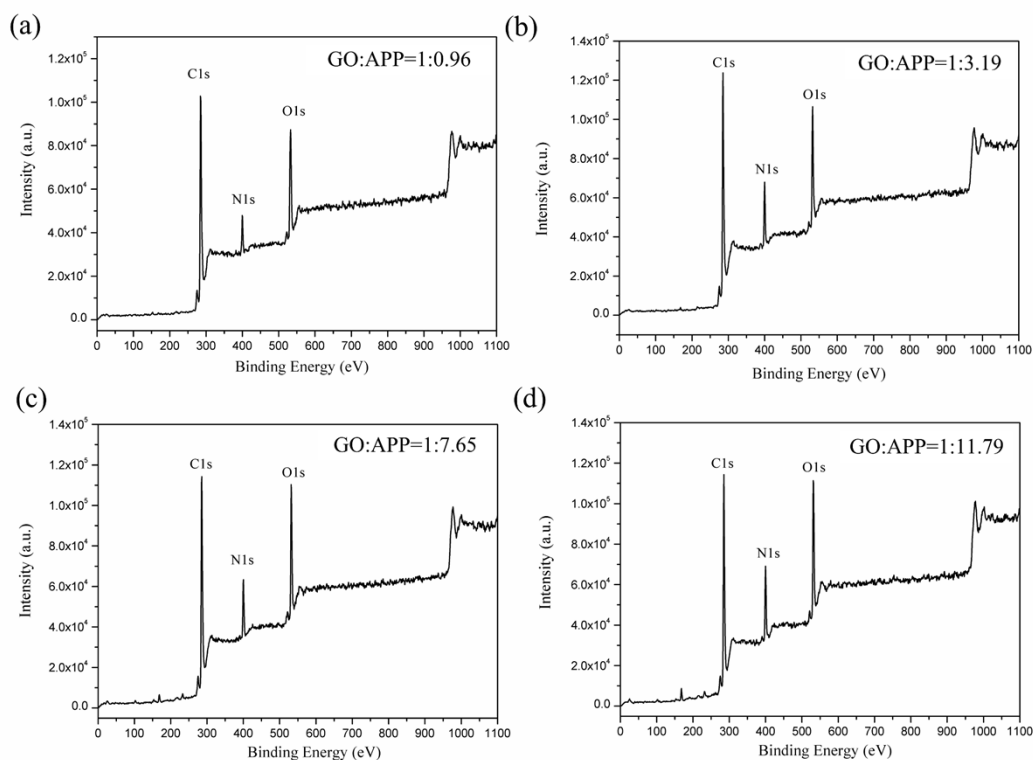


Figure S3 XPS spectra of all poly (GO-APP) copolymer containing different APP monomer content, (a) GO:APP=1:0.96, (b) GO:APP=1:3.19, (c) GO:APP=1:7.65 and (d) GO:APP=1:11.79.

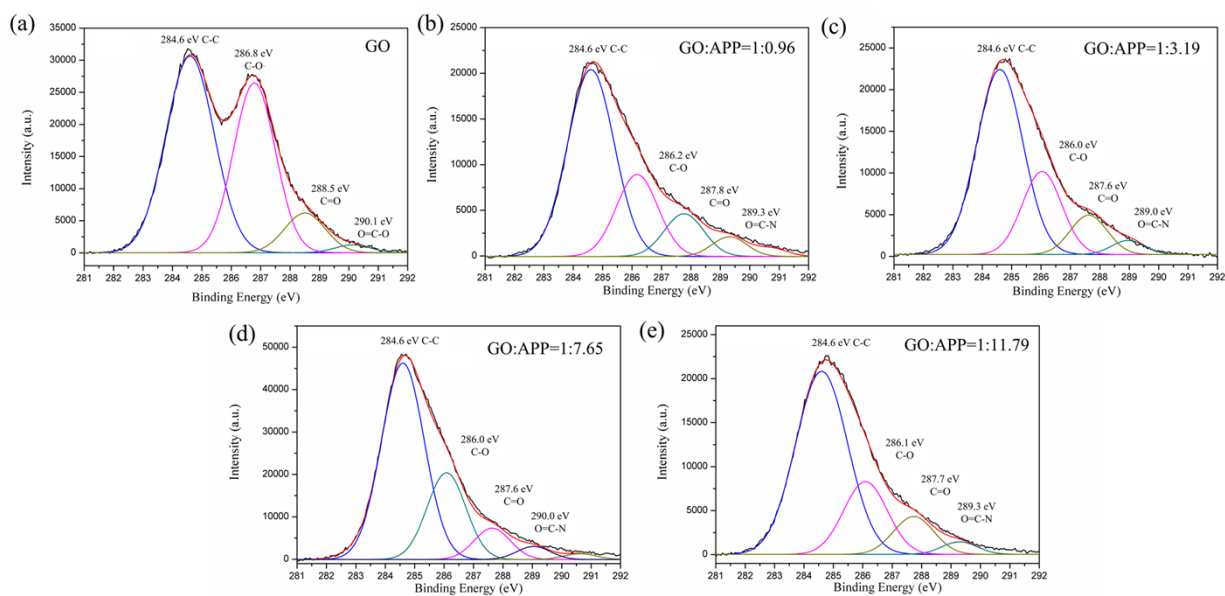


Figure S4 High resolution C1s XPS spectra of (a) GO and all poly (GO-APP) containing different APP monomer content, (b) GO:APP=1:0.96, (c) GO:APP=1:3.19, (d) GO:APP=1:7.65 and (e) GO:APP=1:11.79.

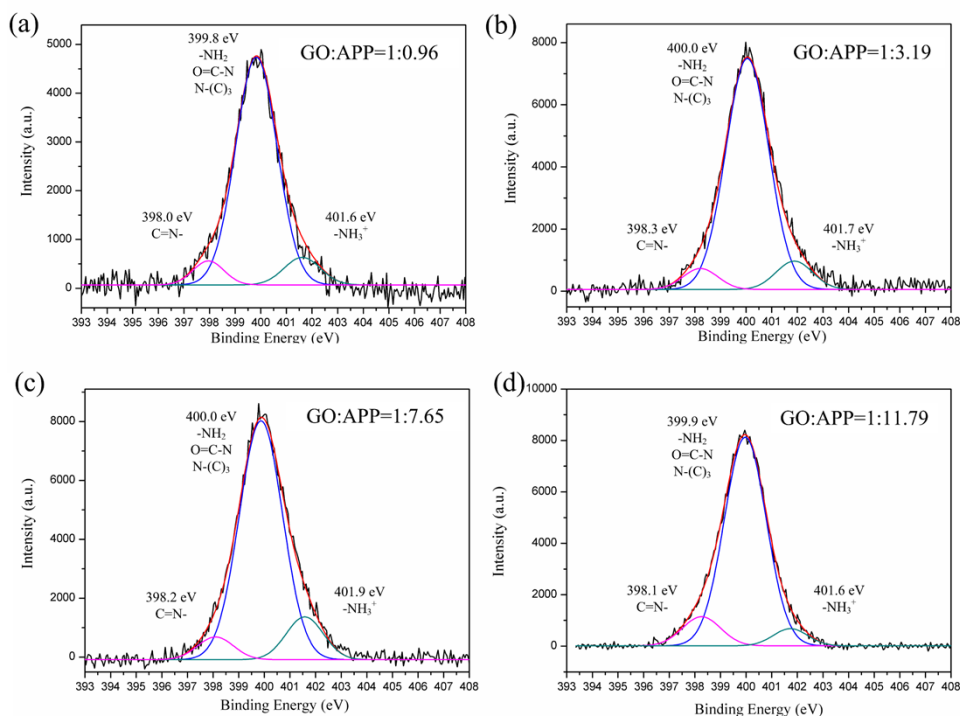


Figure S5 High resolution N1s XPS spectra of all poly (GO-APP) containing different APP monomer content, (a) GO:APP=1:0.96, (b) GO:APP=1:3.19, (c) GO:APP=1:7.65 and (d) GO:APP=1:11.79.

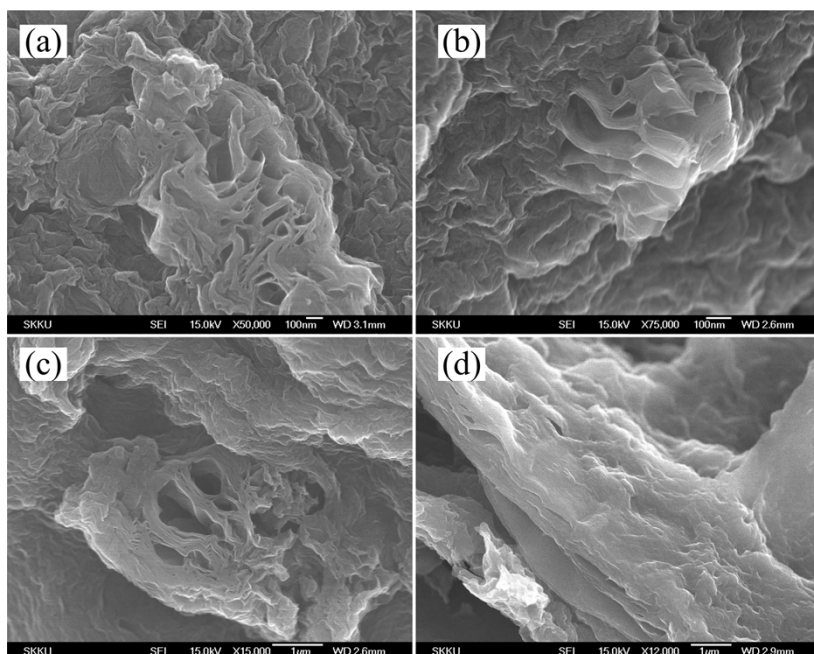


Figure S6 Surface SEM images of all poly (GO-APP) containing different APP monomer content, (a) GO:APP=1:0.96, (b) GO:APP=1:3.19, (c) GO:APP=1:7.65 and (d) GO:APP=1:11.79.

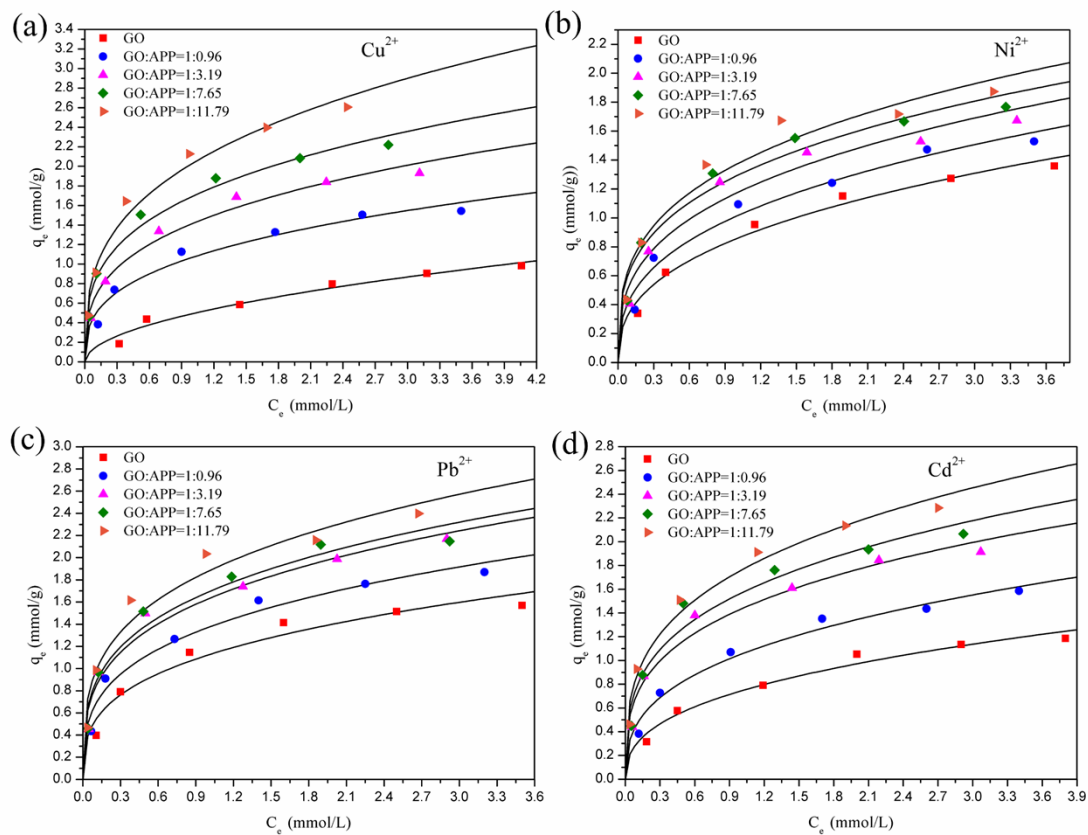


Figure S7 Freundlich adsorption isotherms of GO and all poly (GO-APP) for 4 kinds of metal ion, (a) Cu^{2+} , (b) Ni^{2+} , (c) Pb^{2+} and (d) Cd^{2+} .

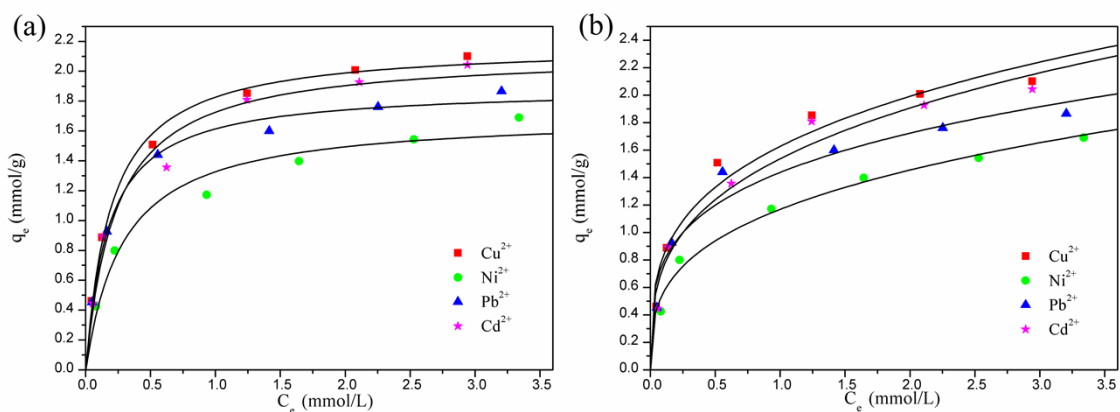


Figure S8 Langmuir (a) and Freundlich (b) adsorption isotherms of poly (APP) for 4 kinds of metal ion, Cu^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+} .

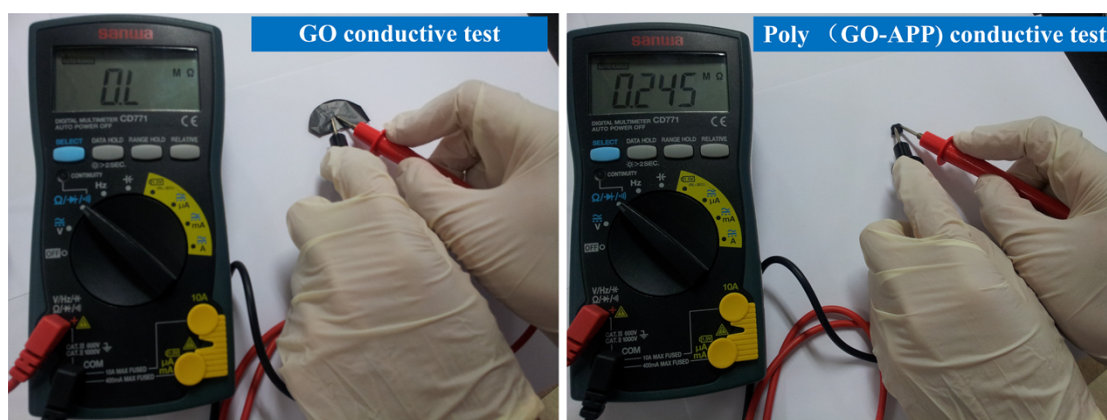


Figure S9 Conductive tests of GO (left) and poly (GO-APP) copolymer (right).

Table S1 All the initial concentrations C_i , equilibrium concentrations C_e and adsorption capacities q_e in the adsorption experiment. “GO:APP” represent the poly (GO-APP) containing different APP content.

Metal Ions	C_i	GO		Poly (APP)		GO:APP							
		C_e	q_e	C_e	q_e	1:0.96		1:3.19		1:7.65		1:11.79	
						C_e	q_e	C_e	q_e	C_e	q_e	C_e	q_e
Cu²⁺	0.505	0.321	0.184	0.045	0.460	0.122	0.383	0.057	0.448	0.041	0.464	0.030	0.475
	1.013	0.576	0.437	0.126	0.887	0.276	0.737	0.192	0.821	0.110	0.904	0.103	0.910
	2.025	1.440	0.585	0.517	1.508	0.903	1.122	0.689	1.336	0.520	1.505	0.382	1.643
	3.097	2.301	0.796	1.244	1.853	1.770	1.327	1.409	1.688	1.218	1.879	0.970	2.127
	4.084	3.180	0.904	2.076	2.008	2.580	1.504	2.245	1.839	2.012	2.072	1.689	2.395
	5.043	4.061	0.982	2.942	2.101	3.502	1.541	3.112	1.931	2.823	2.220	2.438	2.605
Ni²⁺	0.505	0.166	0.339	0.079	0.425	0.140	0.365	0.098	0.407	0.078	0.427	0.070	0.435
	1.023	0.401	0.622	0.224	0.799	0.300	0.723	0.255	0.768	0.195	0.828	0.195	0.828
	2.103	1.150	0.953	0.932	1.171	1.010	1.093	0.857	1.247	0.796	1.307	0.736	1.367
	3.041	1.891	1.150	1.644	1.397	1.799	1.242	1.589	1.452	1.489	1.552	1.369	1.672
	4.073	2.799	1.274	2.529	1.544	2.603	1.470	2.545	1.528	2.405	1.668	2.355	1.718
	5.029	3.671	1.358	3.339	1.689	3.505	1.524	3.355	1.674	3.262	1.767	3.155	1.874
Pb²⁺	0.502	0.106	0.396	0.049	0.452	0.067	0.435	0.047	0.455	0.042	0.460	0.035	0.467
	1.090	0.302	0.788	0.164	0.926	0.180	0.910	0.124	0.966	0.124	0.966	0.104	0.986
	1.996	0.850	1.146	0.555	1.441	0.730	1.266	0.498	1.498	0.482	1.514	0.380	1.616
	3.014	1.602	1.412	1.415	1.599	1.403	1.611	1.276	1.739	1.186	1.828	0.980	2.034
	4.014	2.501	1.513	2.252	1.762	2.250	1.764	2.026	1.988	1.896	2.118	1.856	2.158
	5.070	3.499	1.571	3.204	1.866	3.198	1.872	2.900	2.170	2.923	2.147	2.673	2.397
Cd²⁺	0.500	0.185	0.315	0.056	0.444	0.117	0.383	0.061	0.439	0.052	0.448	0.038	0.462
	1.028	0.450	0.578	0.135	0.893	0.300	0.728	0.160	0.868	0.150	0.878	0.090	0.938
	1.980	1.190	0.790	0.624	1.356	0.910	1.070	0.603	1.377	0.503	1.477	0.470	1.510
	3.051	2.010	1.041	1.242	1.809	1.698	1.353	1.441	1.610	1.290	1.761	1.140	1.911
	4.035	2.902	1.133	2.108	1.927	2.602	1.433	2.190	1.845	2.105	1.930	1.903	2.132
	4.985	3.803	1.182	2.942	2.043	3.406	1.579	3.069	1.916	2.919	2.066	2.698	2.287

Table S2 Peak position, area and concentration of C1s and N1s for the GO and poly (GO-APP) composites, “GO:APP” represent the poly (GO-APP) containing different APP content.

Samples	C1s			N1s		
	Position /eV	Area	Conc. %	Position /eV	Area	Conc. %
GO	284.6	62932.66	36.630			
	286.786	47022.58	27.370			
	288.506	10658.38	6.204			
			Sum=70.204			
GO:APP=1:0.96	284.601	40559.3	55.022	397.957	745.664	0.562
	286.169	15872.27	21.532	399.825	9496.21	7.157
	287.764	7844.906	10.642	401.617	1005.831	0.758
	289.31	3189.131	4.326			
		Sum=91.522			Sum=8.477	
GO:APP=1:3.19	284.599	47863.58	51.850	398.261	2128.035	1.280
	286.109	20934.51	22.678	399.968	16660.55	10.027
	287.738	8982.624	9.731	401.73	1129.236	0.680
	289.031	3464.766	3.754			
		Sum=88.013			Sum=11.987	
GO:APP=1:7.65	284.601	43498.79	54.243	398.217	1148.608	0.796
	286.033	16680.94	20.801	400.049	15648.91	10.841
	287.622	7416.32	9.248	401.881	1628.643	1.128
	288.966	2359.364	2.942			
		Sum=87.234			Sum=12.765	
GO:APP=1:11.79	284.601	46078.18	55.693	398.096	1346.719	0.904
	286.09	15339.81	18.541	399.869	17208.65	11.555
	287.73	7387.913	8.93	401.578	2633.989	1.769
	289.29	2157.865	2.608			
		Sum=85.772			Sum=14.228	

Table S3 Langmuir and Freundlich isotherm parameters for Cu²⁺, Ni²⁺, Pb²⁺ and Cd²⁺, which were obtained from the fitted Langmuir and Freundlich isotherms, “GO:APP” represent the poly (GO-APP) containing different APP content.

Metal Ions	Samples	Langmuir			Freundlich		
		q_{\max} (mmol/L)	K_L (L/mmol)	R	K_F	n	R
Cu ²⁺	GO	1.359	0.6167	0.969	0.4927	1.9378	0.959
	GO:APP=1:0.96	1.695	2.4669	0.988	1.0688	2.9681	0.951
	GO:APP=1:3.19	2.059	3.3819	0.980	1.4144	3.1236	0.970
	GO:APP=1:7.65	2.253	5.2613	0.975	1.6924	3.3143	0.967
	GO:APP=1:11.79	2.708	4.6625	0.982	2.0294	3.0788	0.971
	Poly (APP)	2.181	5.1459	0.992	1.6278	3.4365	0.945
Ni ²⁺	GO	1.565	1.5419	0.993	0.8570	2.5967	0.973
	GO:APP=1:0.96	1.687	2.0825	0.974	1.0132	2.7697	0.958
	GO:APP=1:3.19	1.783	2.8831	0.994	1.1734	3.0101	0.944
	GO:APP=1:7.65	1.852	3.7362	0.989	1.2919	3.2746	0.949
	GO:APP=1:11.79	1.975	3.6029	0.990	1.3721	3.2311	0.938
	Poly (APP)	1.708	3.4780	0.956	1.1690	3.1685	0.981
Pb ²⁺	GO	1.731	2.6622	0.995	1.1222	3.1192	0.939
	GO:APP=1:0.96	1.924	4.0661	0.961	1.3709	3.2835	0.956
	GO:APP=1:3.19	2.148	5.5745	0.966	1.6284	3.4390	0.951
	GO:APP=1:7.65	2.226	5.4854	0.980	1.6900	3.4756	0.943
	GO:APP=1:11.79	2.417	6.0855	0.987	1.8772	3.4977	0.936
	Poly (APP)	1.889	5.8542	0.989	1.4378	3.8238	0.922
Cd ²⁺	GO	1.394	1.4187	0.979	0.7438	2.5872	0.966
	GO:APP=1:0.96	1.720	2.2052	0.983	1.0529	2.8338	0.969
	GO:APP=1:3.19	1.985	4.3859	0.983	1.4333	3.3307	0.951
	GO:APP=1:7.65	2.145	4.5597	0.993	1.5672	3.3417	0.941
	GO:APP=1:11.79	2.308	5.5637	0.970	1.7598	3.3086	0.968
	Poly (APP)	2.122	4.3580	0.965	1.5375	3.2207	0.952

Table S4 Dimensionless constant separation factor R_L for the Langmuir isotherm, which was calculated by equation $R_L = 1 / (1 + K_L C_i)$. K_L was from Table S3 and C_i was from Table S1. “GO:APP” represent the poly (GO-APP) containing different APP content.

Metal Ions	C_i	$R_L = 1 / (1 + K_L C_i)$					
		GO	Poly (APP)	GO:APP			
				1:0.96	1:3.19	1:7.65	1:11.79
Cu²⁺	0.505	0.762	0.278	0.445	0.369	0.273	0.298
	1.013	0.615	0.161	0.286	0.226	0.158	0.175
	2.025	0.445	0.088	0.167	0.127	0.086	0.096
	3.097	0.344	0.059	0.116	0.087	0.058	0.065
	4.084	0.284	0.045	0.090	0.068	0.044	0.050
	5.043	0.243	0.037	0.074	0.055	0.036	0.041
Ni²⁺	0.505	0.562	0.363	0.487	0.407	0.346	0.355
	1.023	0.388	0.219	0.319	0.253	0.207	0.213
	2.103	0.236	0.120	0.186	0.142	0.113	0.117
	3.041	0.176	0.086	0.136	0.102	0.081	0.084
	4.073	0.137	0.066	0.105	0.078	0.062	0.064
	5.029	0.114	0.054	0.087	0.065	0.051	0.052
Pb²⁺	0.502	0.428	0.254	0.329	0.263	0.266	0.247
	1.090	0.256	0.136	0.184	0.141	0.143	0.131
	1.996	0.158	0.079	0.110	0.082	0.084	0.076
	3.014	0.111	0.054	0.075	0.056	0.057	0.052
	4.014	0.086	0.041	0.058	0.043	0.043	0.039
	5.070	0.069	0.033	0.046	0.034	0.035	0.031
Cd²⁺	0.500	0.585	0.314	0.476	0.313	0.305	0.264
	1.028	0.407	0.183	0.306	0.182	0.176	0.149
	1.980	0.263	0.104	0.186	0.103	0.100	0.083
	3.051	0.188	0.069	0.129	0.070	0.067	0.056
	4.035	0.149	0.054	0.101	0.053	0.052	0.043
	4.985	0.124	0.044	0.083	0.044	0.042	0.035

