Supporting Information

Highly Selective Adsorption of Hg^{2+} by Polypyrrole-Reduced Graphene Oxide Composite

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Chemicals: graphite **(**300 mesh, Alfa Aesar), sodium nitrate (Aldrich), potassium permanganate (Aldrich), hydrogen peroxide (30% wt, Aldrich), sulphuric acid, hydrochloric acid, hydrazine (80%, Aldrich) Ammonium persulphate (Aldrich), pyrrole (Aldrich), distilled Water (H_2O, M = 18), mercury (II) nitrate monohydrate (Across Organics), zinc (II) nitrate hexahydrate (Sigma Aldrich), Copper (II) nitrate hemipentahydrate (Aldrich), Cadmium (II) nitrate terahydrate (Sigma Aldrich), Lead (II) nitrate (Aldrich).

Synthesis of Graphene Oxide (GO).

Graphene oxide was synthesized by Hummers method through oxidation of graphite [1]. Graphite (5 g) and $NaNO_3$ (5g) were mixed in 125mL of H_2SO_4 (95%) in a 1000 mL flask at ice temperature (0-5°C). The mixture was stirred for 30 min at this temperature and potassium permanganate (15g) was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15° C. The ice bath was then removed, and the mixture was stirred at 35°C until it became pasty brownish and then diluted with slow addition of 250 ml water. The reaction temperature was rapidly increased to 98° C with effervescence, and the color changed to brown color. Further this solution was diluted by adding 500 ml water and finally treated with 10 ml H_2O_2 (30wt.%). For purification, the mixture was washed by rinsing and centrifugation with 10% HCl and then deionized (DI) water several times. After filtration and drying under vacuum at room temperature, the graphene oxide (GO) was obtained as a powder.

Synthesis of reduced graphene oxide (RGO)

Chemical reduction of graphene oxide to reduced graphene oxide was done according to earlier reports [2]. In a typical experiment, 100 mg of graphene oxide was dispersed in 50 mL of distilled water for 3 h using a Barson sonication bath. The pH of the solution was adjusted to 10 by adding KOH and 1 mL of hydrazine monohydrate was added, to the solution at 95^{o}C and stirred for 24 h. Once the reaction is completed, the reduced graphene oxide was collected by filtration (0.22 μm, Millipore filter paper) as a black powder. The obtained powder was washed with distilled water several times to remove the excess hydrazine, and the final product was dried in a vacuum oven at 80^{o}C.

Synthesis of Polypyrrole

Polypyrrole was synthesized by chemical polymerization using ammonium persulphate as oxidant. 1 g of freshly distilled pyrrole was dispersed in 75 ml of distilled water in a sonication bath. A solution of ammonium per sulphate (4.0 g/25 ml) was added in the pyrrole solution with constant stirring at ice temperature (0-5^{o}C) for 10 hour. The product was washed with distilled water and methanol and vacuum dried at 40 °C for 24 h.

Synthesis of Polypyrrole–reduced graphene oxide (PPy-RGO) composite

The required amount of graphene oxide (wt. %) and pyrrole (**Table S1**) were dispersed in water. A pre-cooled solution of ammonium per sulphate (APS) was added to GO-pyrrole solution at 0-5 ^{o}C with constant stirring for 10 h [3-5]. The product formed washed with copious amount of water and dispersed in 75 ml distilled water. At 90^{o}C the required amount of hydrazine hydrate was added and reduced for 12 h which results in formation of PPy-RGO composites.

Table S1. Synthesis condition PPy and PPy-RGO composite.

Sample Name	Pyrrole (g)	GO	APS	Hydrazine
PPy	1g / 75 ml	0	4g	0
5% GO	1g / 75 ml	50 mg	4g	0.5ml
10 % GO	1g / 75 ml	100 mg	4g	1.0 ml
15% GO	1g / 75 ml	150 mg	4g	1.5ml
20% GO	1g / 75 ml	200 mg	4g	2.0 ml

Adsorption experiments

Hg^{2+} ions adsorption experiments on PPy and PPy-RGO composites were done to study the effect of pH, temperature, time of adsorption, and initial concentration of mercury (II) ions on the mercury removal. $HgNO_3.H_2O$ (Across Organics) was used to prepare solution and the adsorbent (0.2 g/ lit) was dispersed using ultrasonic bath. After three hour stirring the solutions were filtered using 0.22 μm filter paper (Millipore, 47 mm diameter). The mercury (II) ion concentration before and after adsorption was measured with the *Millennium Merlin* system (P. S. Analytical). The pH of the solution was maintained with HNO_3 and NaOH solutions.

Adsorption isotherms were studied by monitoring Hg^{2+} solution of 50 ppm – 250 ppm under a similar condition of temperature $20^{o}C$, pH 3 and adsorption time 3 hour. The data of mercury adsorption was fitted using *Freundlich* [6] and *Langmuir isotherm* models [7].

The Langmuir isotherm is expressed as

$q_e = abC_e / (1+ bC_e)$ …………………..S1

and Freundlich isotherm is represented by

$q_e = k (C_e)^{1/n}$ …………………………S2

where q_e is the amount of mercury adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of mercury (mg/l), b is the constant related to the free energy of adsorption (l/mg), and a is the maximum adsorption capacity (mg/g). Freundlich constant (k) is indicative of the relative adsorption capacity of the adsorbent (mg/g), and ($1/n$) is the adsorption intensity.

Table S2. Langmuir and Freundlich Adsorption Isotherm parameters for mercury removal on PPy and PPy-RGO composite.

Isotherm Type	Isotherm Cons.	PPy	PPy-RGO
Langmuir	a (mg/g)	400.11	979.54
	b (l/mg)	0.029	0.011
	R^2	0.99	0.99
Freundlich	k	95.13	55.4
	n	4.1	2.16
	R^2	0.99	0.98

The adsorption kinetics was done for 50 ppm Hg^{2+} ion solution at pH 3, T=20°C. The kinetic data were fitted for pseudo second-order kinetic model to describe Hg (II) adsorption on the PPy and PPy-RGO composite. The equation is expressed as

$t/q_t = 1/q_e^2\, k_2 + 1/q_e\, t$ ……………………S3

Where q_t and q_e are the amounts (mg/g) of Hg (II) adsorbed at time t and at equilibrium, respectively, and k_2 (g/mg · min) is the equilibrium rate constant of pseudo second-order adsorption. The initial adsorption rate $V_o = k_2\, q_e^2$, and q_e for mercury adsorption parameters were calculated.

Table S3. Parameters of a Pseudo-Second-Order Kinetic Model.

Adsorbent	Isotherm Constant	Hg(II)	R^2
PPy	q_e	204.768	0.98
	k_2	1.69×10^{-6}	
	V_0	7.04	
PPy-RGO	q_e	226.244	0.99
	k_2	3.1×10^{-3}	
	V_0	157.72	

The pH and temperature dependent adsorption experiments were carried out at Hg^{2+} concentration of 130 ppm, temperature 20°C, and adsorption time 3 h. The pH of the solution was maintained using NaOH and HNO_3.

For recyclability testing, adsorbent was dispersed in 50 ml HCl aqueous solution (pH 3, 2, 1). After 3 h stirring at 20°C, the solutions were filtered and tested for mercury (II) concentration. For selective adsorption experiment, a mixed solution of metal ions was prepared by dissolving 35 mg Hg^{2+}, 33mg Pb^{2+}, 56 mg Cd^{2+}, 90 mg Zn^{2+}, 92 mg Cu^{2+} in 150 ml water (pH 3, HNO_3) at 20°C. 10 mg of adsorbents were dispersed in 50 ml of solution and the mixture was stirred for 3 h at 20°C. The mixture was filtered through Millipore (0.22 μm) filter paper and filtrate was tested via Millennium Merlin System (P. S. Analytical) and ICP for different metal ions concentration before and after adsorption.

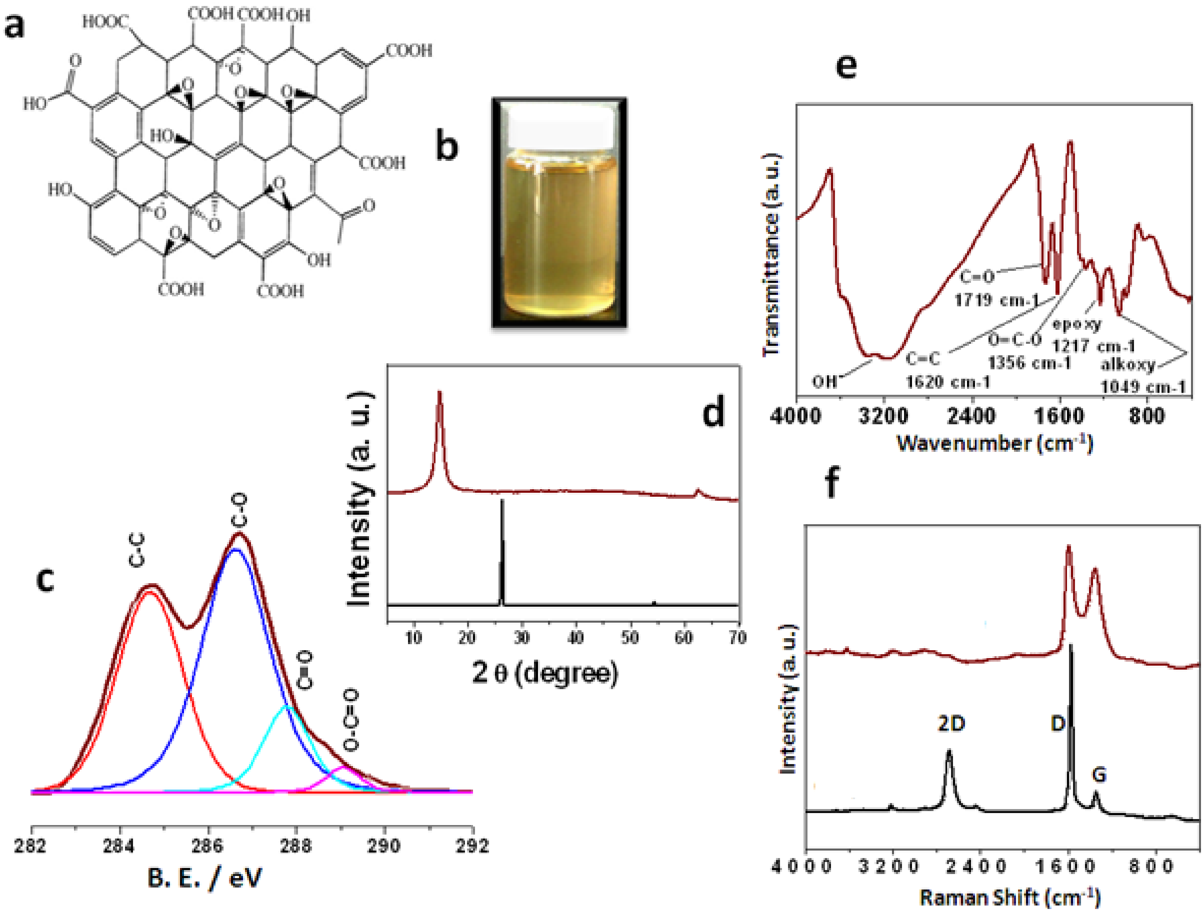
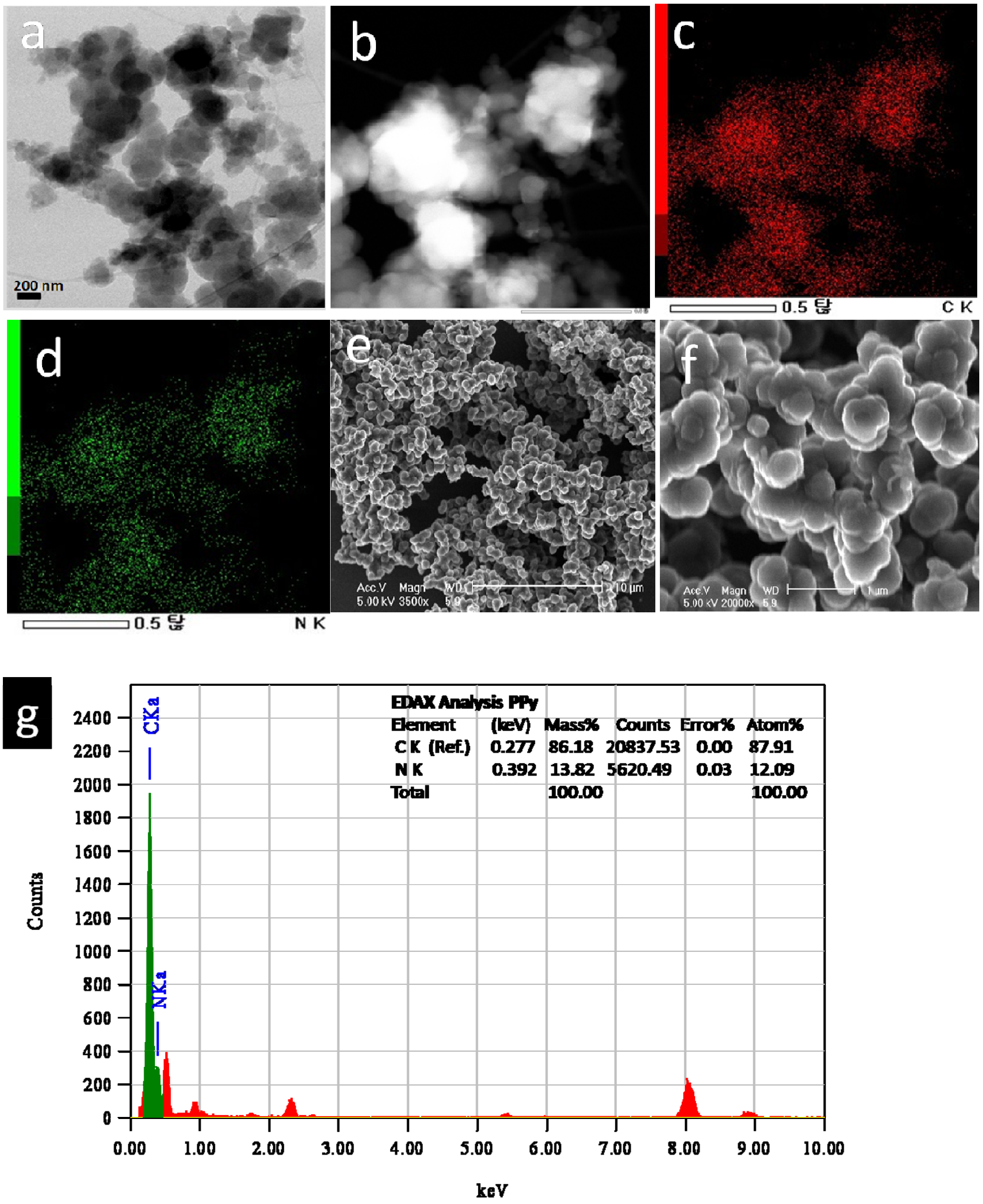


Figure S1: (a) Structure of graphene oxide, (b) aqueous solution of graphene oxide (0.5mg/mL), (c) C1s spectra of graphene oxide, (d) X-ray diffraction of graphene oxide (brown) and graphite (black) (e) FTIR spectra of graphene oxide (f) Raman spectra of graphene oxide (brown) and graphite (black).



EDAX Analysis PPy

Element	(keV)	Mass%	Counts	Error%	Atom%
C K (Ref.)	0.277	86.18	20837.53	0.00	87.91
N K	0.392	13.82	5620.49	0.03	12.09
Total		100.00			100.00

Figure S2. Surface morphology of Polypyrrole (a) TEM image (b) scanning transmission electron microscopy (STEM) image (c) carbon mapping, (d) nitrogen mapping and (g) EDAX analysis of PPY corresponding to the STEM image which shows 12 % atomic nitrogen.

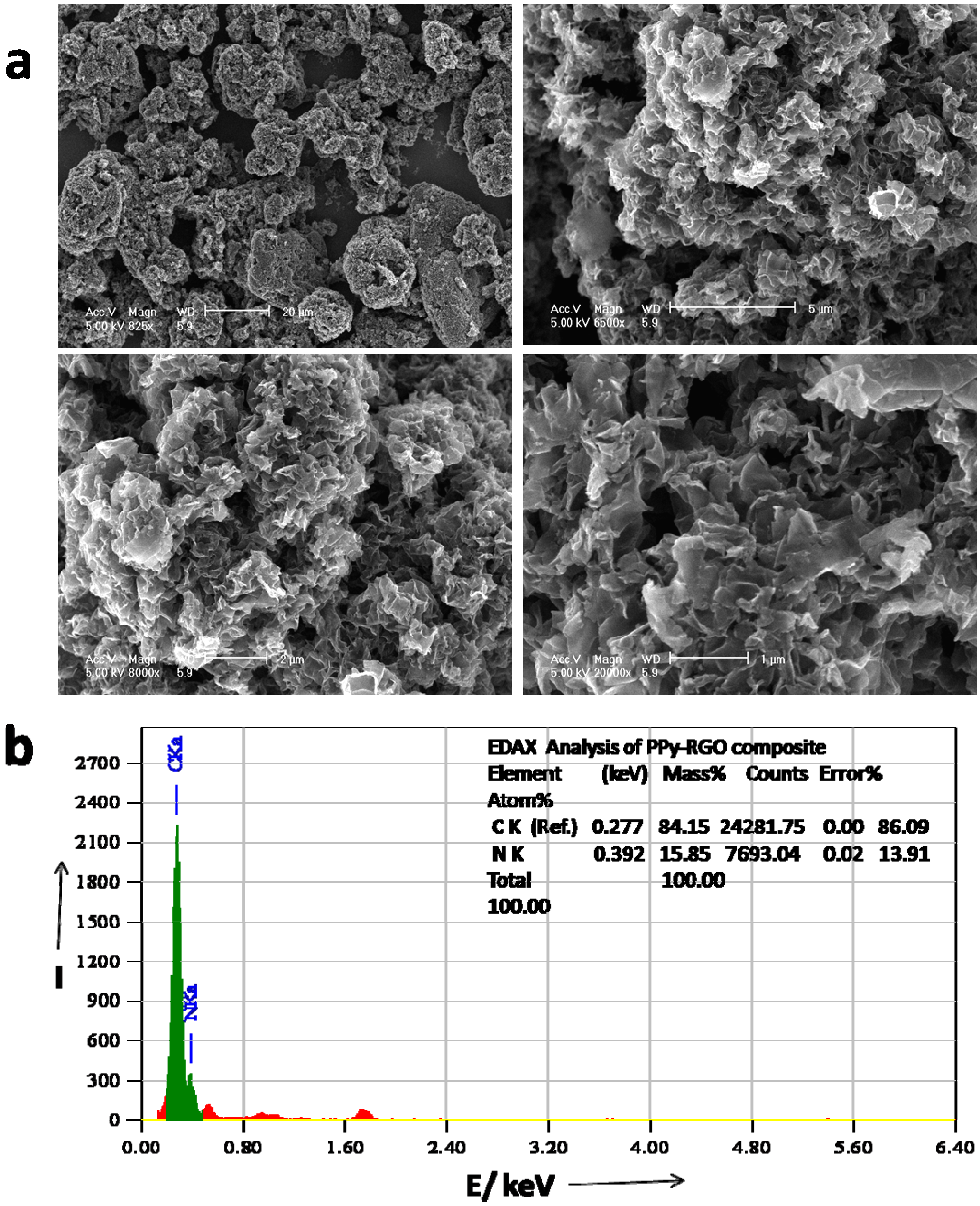


Figure S3. (a) SEM images of PPy-RGO composites for 15 % (wt) graphene oxide loaded in PPy. Note that there are no granular particles of PPy visible on the graphene sheets indicative of PPy growing along sheets in PPy-RGO composite. (b) EDAX analysis of PPy-RGO composite shows the presence of 14% N.

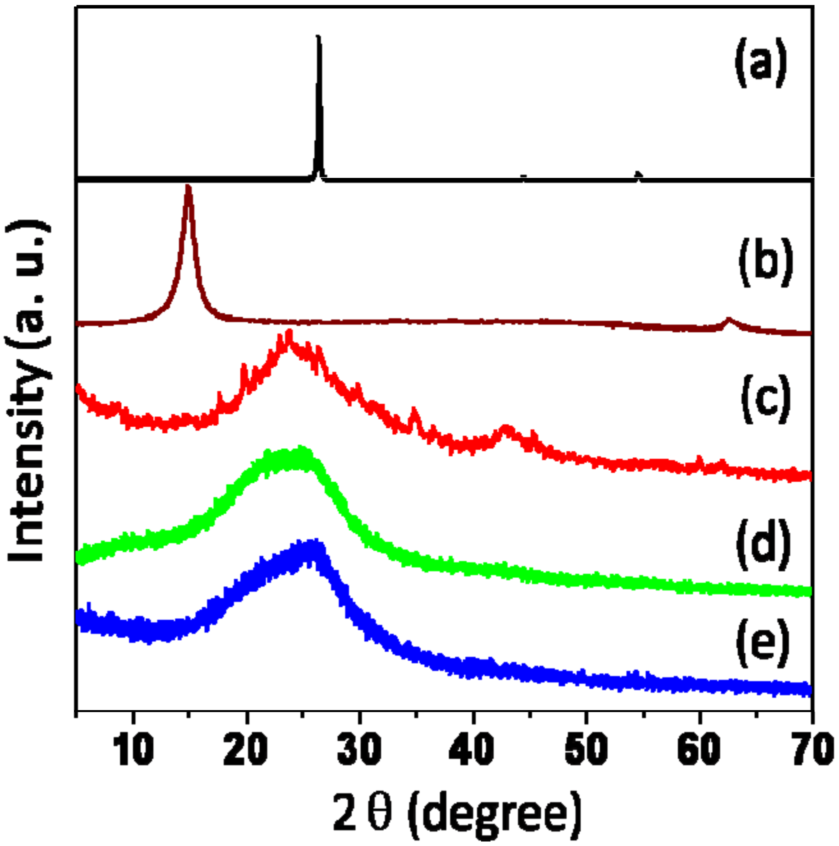


Figure S4. X-ray diffraction pattern of (a) graphite, (b) graphene oxide, (c) reduced graphene oxide, (d) polypyrrole, and (e) PPy-RGO composite.

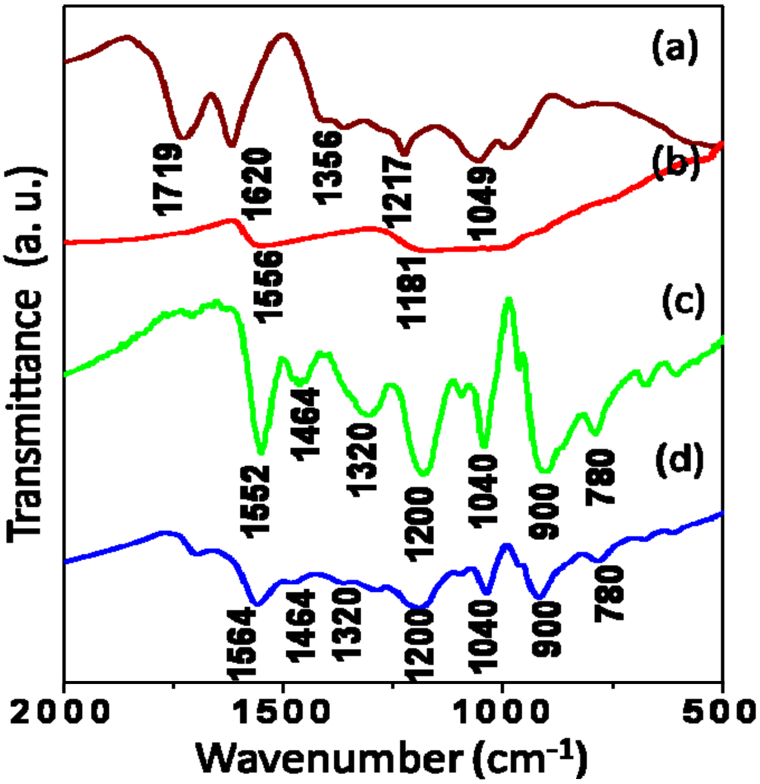


Figure S5. FTIR spectra of (a) graphene oxide, (b) reduced graphene oxide, (c) polypyrrole, and (d) PPy-RGO composite. The FTIR spectra of GO shows carbonyl C=O (1719 cm^{-1}), aromatic C=C (1620 cm^{-1}), carboxyl O=C-O (1356 cm^{-1}), epoxy C-O (1217 cm^{-1}), and alkoxy C-O (1049 cm^{-1}) stretching vibrational modes. The IR spectra of RGO show two broad peaks at 1556 cm^{-1} and 1181 cm^{-1} which correspond to the aromatic C=C stretch and C-O stretch, respectively. In FTIR of PPy, bands at 1552 cm^{-1} corresponds to the pyrrole ring vibration. The bands at 1464 cm^{-1} correspond to the =CH in-plane vibration and the peaks at 900 cm^{-1} and 780 cm^{-1} are due to the =CH out-of-plane vibration. The stretching vibration of C-N bonds shows a band at 1320 cm^{-1} and the band at 1200 cm^{-1} corresponds to the C-C stretching. A very intense band at 1040 cm^{-1} is assigned to in-plane deformation of C-H and N-H bonds of pyrrole ring. See the text for the description of the PPy–RGO composite

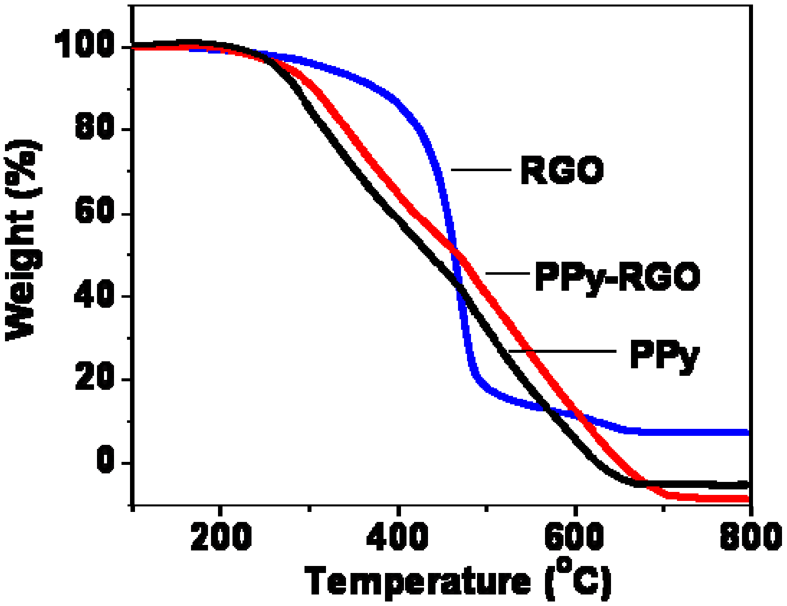


Figure S6. The thermal gravimetric analysis of RGO, PPy and PPy-RGO composite in N_2.

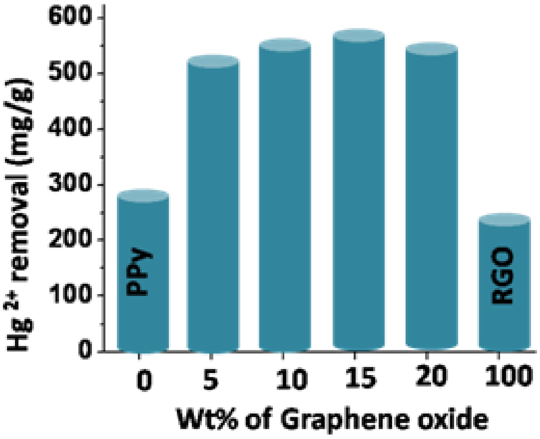


Figure S7. Optimization of graphene oxide loading in PPy (Hg^{2+} concentration: 130 ppm, pH 3 temperature 20°C and time for adsorption 3 hour),

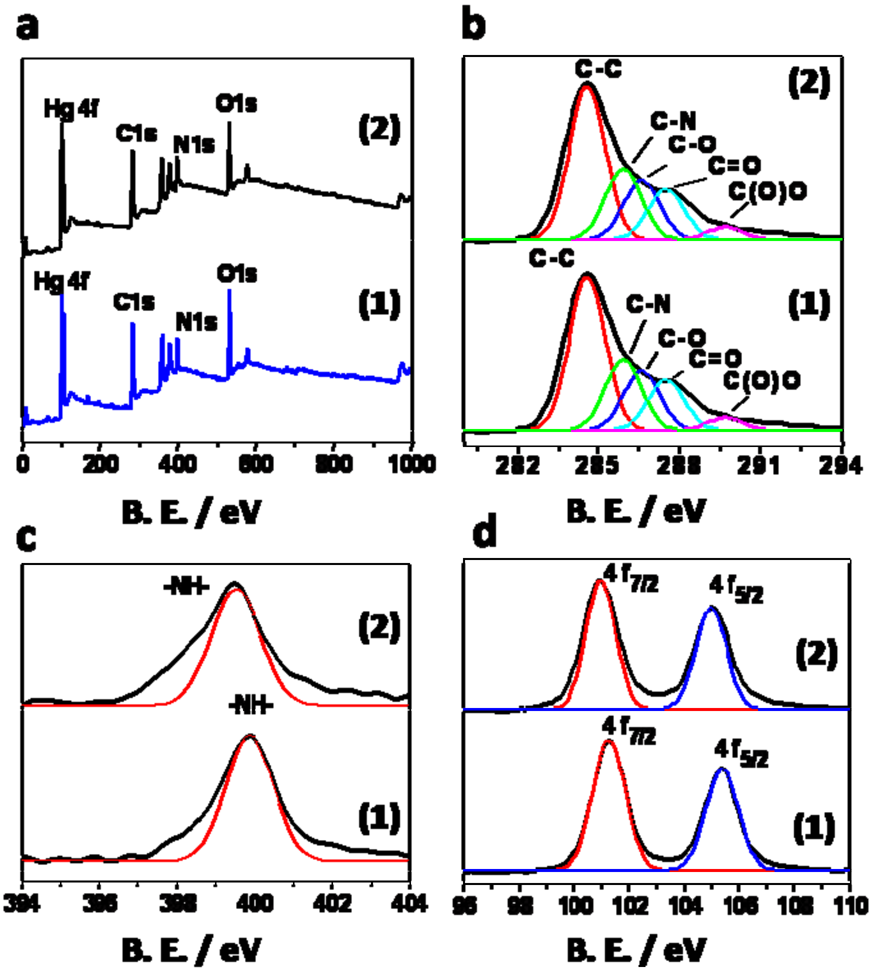


Figure 8. X-ray photoelectron spectrum after mercury ions adsorption on PPy (1) and PPy-RGO composite (2); (a) full spectrum, (b) C1s spectrum, (c) N1s spectrum, and (d) Hg 4f spectrum.

References

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