Nitrogen-functionalised carbon nanotubes as a novel adsorbent for the removal of Cu(II) from aqueous solution

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Supplementary Information

Determination of point of zero charge (pH_{PZC})

Aliquots of 50 cm^3 of 0.01 mol dm^{-3} NaCl solutions were placed into bottles and adjusted with the addition of appropriate amounts of 0.1 mol dm^{-3} HCl or NaOH to obtain an initial pH in the range of 1-10. A mass of 100 mg of adsorbent was added into each bottle and the suspension left to equilibrate on an orbital shaker for 48 h at room temperature. The solutions were filtered and the final pH of the filtrate determined. A plot of $pH_{initial} - pH_{final}$ *vs.* $pH_{initial}$ was obtained and the point of intersection of the curves gave the pH_{PZC} of the adsorbent.

Boehm titration

The basic and acidic properties of the adsorbents were quantitatively determined by the Boehm titration. This analysis method gives quantitative information on the amount of total basic and acidic groups on the adsorbents. As reported by Boehm *et al.*, the determination of acidic groups (carboxyl, lactonic, phenolic) on the adsorbents was performed by weighing 100 mg of each sorbent into a 50 cm^3 polypropylene bottle and mixed with 20 cm^3 of either 0.05 mol dm^{-3} $NaHCO_3$, NaOH or 0.1 mol dm^{-3} Na_2CO_3 solutions. The suspensions were agitated in a thermostated water bath at room temperature for 24 h. The resulting solutions were filtered by

gravity, and the amount of excess base determined quantitatively by back-titration against 0.05 mol dm^{-3} HCl solution. For the determination of the basic groups, 100 mg of adsorbents were mixed with 0.05 mol dm^{-3} HCl solution and agitated on a thermostated water bath at room temperature for 24 h. After agitation, the suspension was filtered by gravity and the amount of basic groups in the adsorbent was determined by titrating the filtrate against 0.05 mol dm^{-3} NaOH solution. The Boehm titration is based on the assumption that NaOH gives information on the amount of carboxylic, lactonic and phenolic groups, Na_2CO_3, on the carboxylic and lactonic groups, $NaHCO_3$, on the carboxylic groups on each adsorbent and HCl gives the amount of basic groups on the adsorbent. Results were expressed as H^+/OH^- millimoles per gram of adsorbent.

Table S1: Kinetics models investigated for the adsorption of Cu^{2+}

Model	**Equation**[a]	**Parameters**
Pseudo-first order	$q_t = q_{eq}\left(1 - e^{-k_1 t}\right)$	q_{eq}, k_1
Pseudo-second order	$q_t = \frac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t}$	k_2, q_{eq}
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	α, β
Intraparticle diffusion	$q_t = k_{id}\sqrt{t} + l$	k_{id}, l

[a] q_t, quantity of adsorbate adsorbed at time t (mg g^{-1}); q_{eq}, quantity of adsorbate adsorbed at equilibrium (mg g^{-1}); α, adsorption rate constant (mg g^{-1} min^{-1}); β, desorption rate constant (g mg^{-1}); k_1, pseudo-first order rate constant (min^{-1}); k_2, pseudo-second order rate constant (g mg^{-1} min^{-1}); k_{id}, intraparticle diffusion rate constant (mg g^{-1} $min^{0.5}$), l, is a constant related to the boundary layer thickness (mg g^{-1}).

Table S2: Isotherm models investigated for the adsorption of Cu^{2+}

Isotherm model	Equation[a]	Parameters
Langmuir	$q_{eq} = \frac{q_m C_{eq} b}{1 + bC_{eq}}$	q_m, b
Freundlich	$q_{eq} = K_F C_{eq}^{1/n}$	K_F, n
Temkin	$q_{eq} = \frac{RT}{b_T} ln(A_T C_{eq})$	b_T, A_T
Dubinin-Radushkevich	$q_{eq} = q_m e^{-\beta\varepsilon 2}$ $\varepsilon = RTln\left(1 + \frac{1}{C_{eq}}\right)$	q_m, β
Sips	$q_{eq} = \frac{bq_m C_{eq}^{1/n}}{1 + bC_{eq}^{1/n}}$	q_m, b, n
Toth	$q_{eq} = \frac{q_m C_{eq}}{\left(\frac{1}{K_T} + C_{eq}^{n_T}\right)^{1/n_T}}$	q_m, K_T, n_T
Redlich-Peterson	$q_{eq} = \frac{K_{RP} C_{eq}}{1 + \alpha_{RP} C_{eq}^{g}}$	K_{RP}, a_{RP}, g
Khan	$q_{eq} = \frac{q_m b_K C_{eq}}{\left(1 + b_K C_{eq}\right)^{a_K}}$	q_m, a_K, b_K

[a]q_{eq}, adsorption capacity (mg g^{-1}); C_{eq}, equilibrium concentration of adsorbate in solution (mg dm^{-3}); q_m, maximum monolayer capacity (mg g^{-1}); b, Langmuir isotherm constant (dm^3 mg^{-1}); K_F, Freundlich isotherm constant (mg g^{-1})(dm^3 $mg^{-1})^n$; n, adsorption intensity; b_T, Temkin isotherm constant; A_T, Temkin isotherm equilibrium binding constant (dm^3 g^{-1}); β, Dubinin-Radushkevich isotherm constant (mol^2 kJ^{-2}); K_T, Toth isotherm constant (mg g^{-1}); n_T, Toth isotherm constant; K_{RP}, Redlich-Peterson isotherm constant (dm^3 g^{-1}); a_{RP}, Redlich-Peterson isotherm constant; g, Redlich-Peterson isotherm exponent; a_k, Khan isotherm exponent; b_k, Khan isotherm constant.

Table S3: Elemental analysis of P-MWCNT, MWCNT-COOH and MWCNT-ttpy

Adsorbents	%C	%H	%O	%N	Relative ratio				General formula
					C	H	O	N	$C_aH_bO_cN_d$
P-MWCNT	97.34	-	2.656	-	1.000	-	0.021	-	$(C_{48}O)_n$
MWCNT-COOH	94.20	-	5.880	-	1.000	-	0.047	-	$(C_{21}O)_n$
MWCNT-ttpy	77.40	2.573	13.98	6.053	1.000	0.396	0.136	0.067	$(C_{15}H_6O_2N)_n$

Table S4: Analysis of real water samples

Sample Code	C_i Pb	C_i Zn	C_i Cu	C_f Pb	C_f Zn	C_f Cu	% Pb	% Zn	% Cu
Tributary	8.137	12.36	3.442	0.058	0.134	0.000	99.29	98.92	100.0
Blu Lagoon	5.087	6.112	6.114	0.216	0.000	0.005	95.75	100.0	99.92
Ethwekini	10.34	4.332	8.114	0.123	0.100	0.127	98.81	97.69	98.43

C_i: initial concentration, C_f: final concentrations

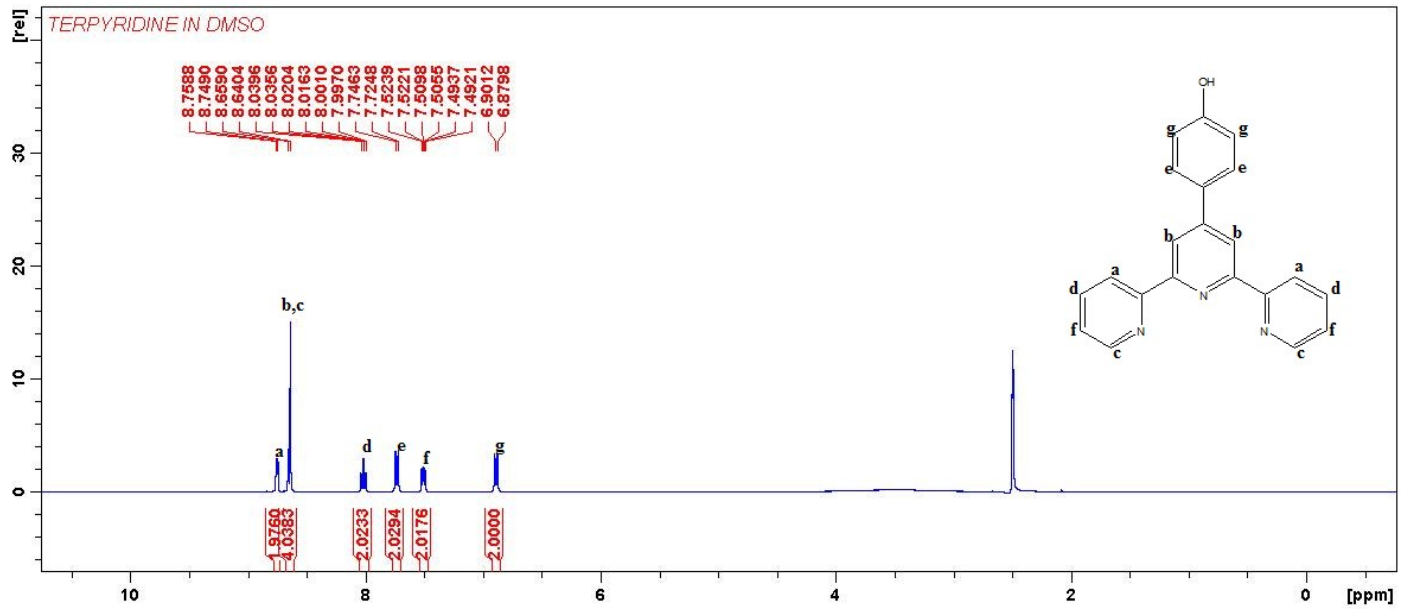

Fig S1: ^{1}H NMR spectrum of HO-Phttpy.

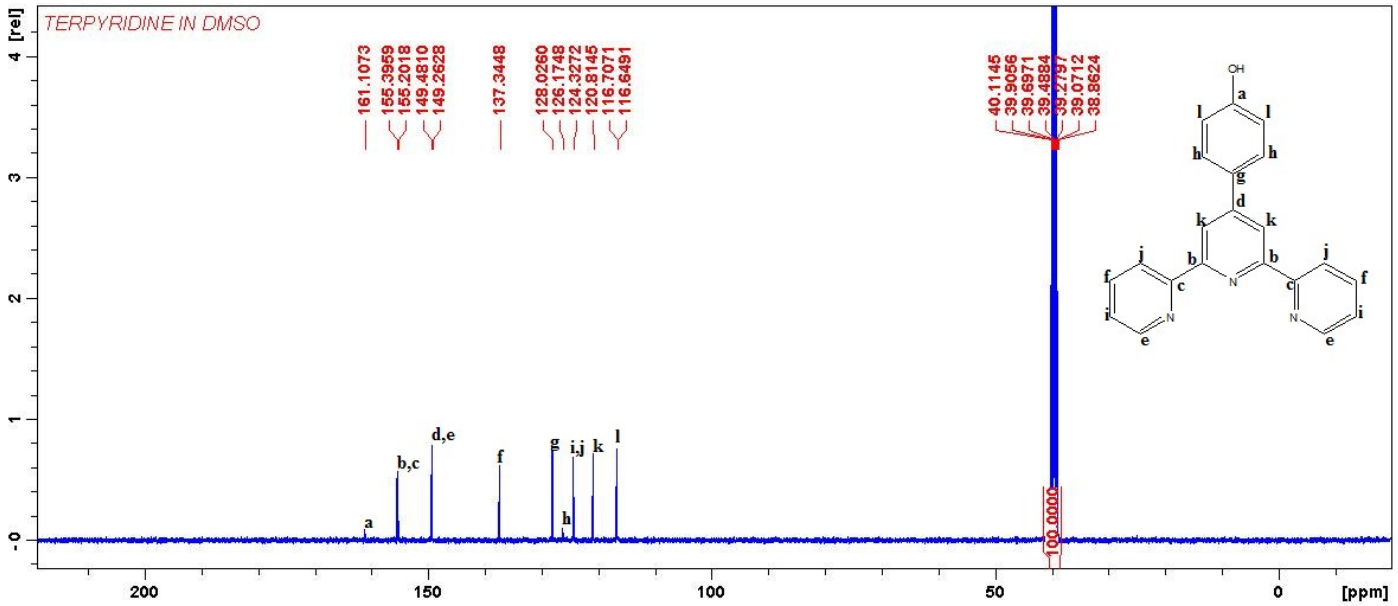

Fig S2: ^{13}C NMR spectrum of HO-Phttpy.

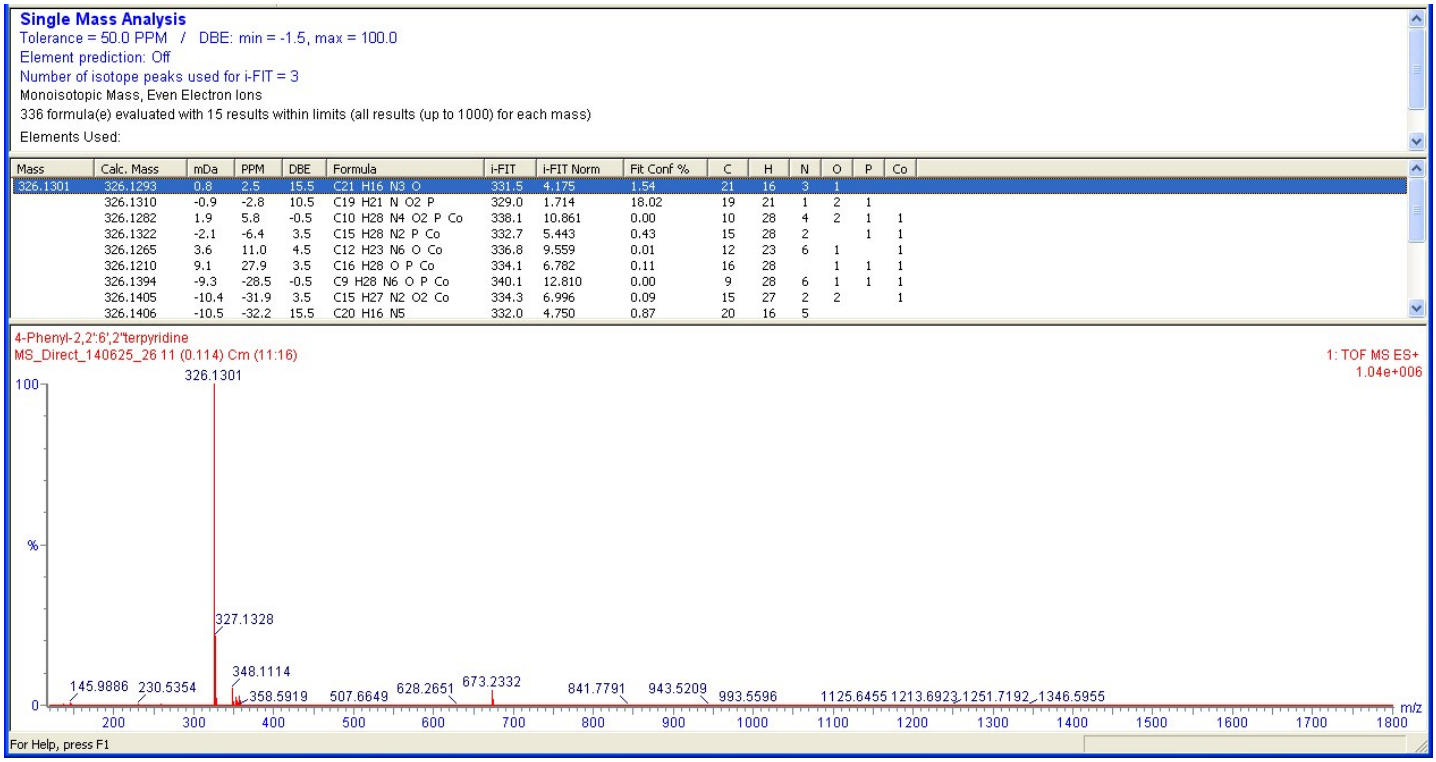

Fig S3: Mass spectrum of HO-Phttpy

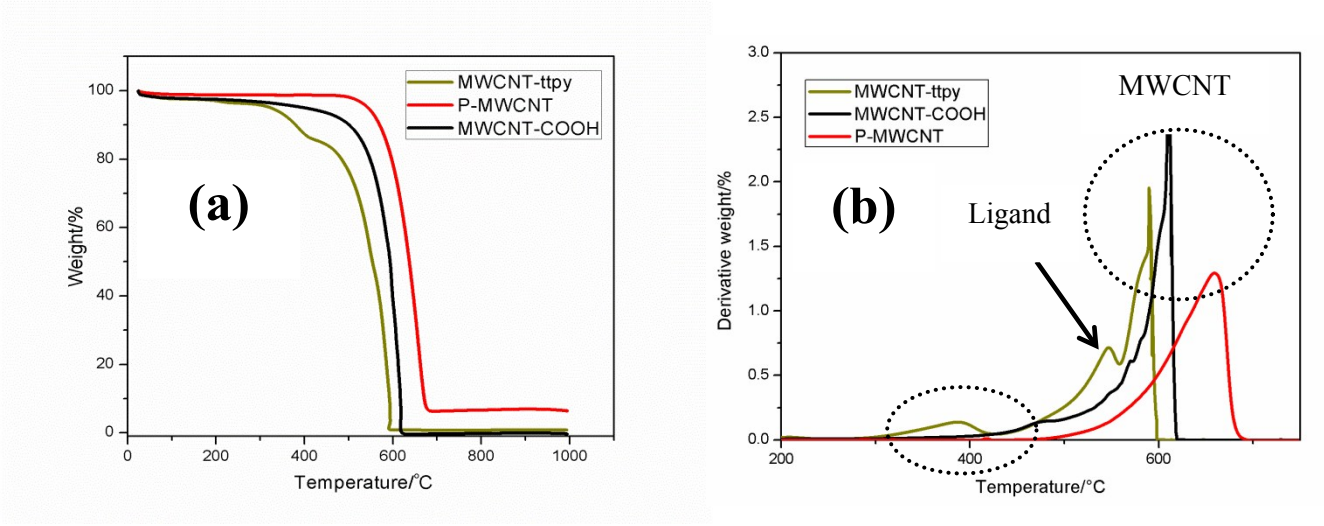

Fig S4: (a) Thermograms and (b) derivative thermograms of P-MWCNT, MWCNT-COOH and MWCNT-ttpy.

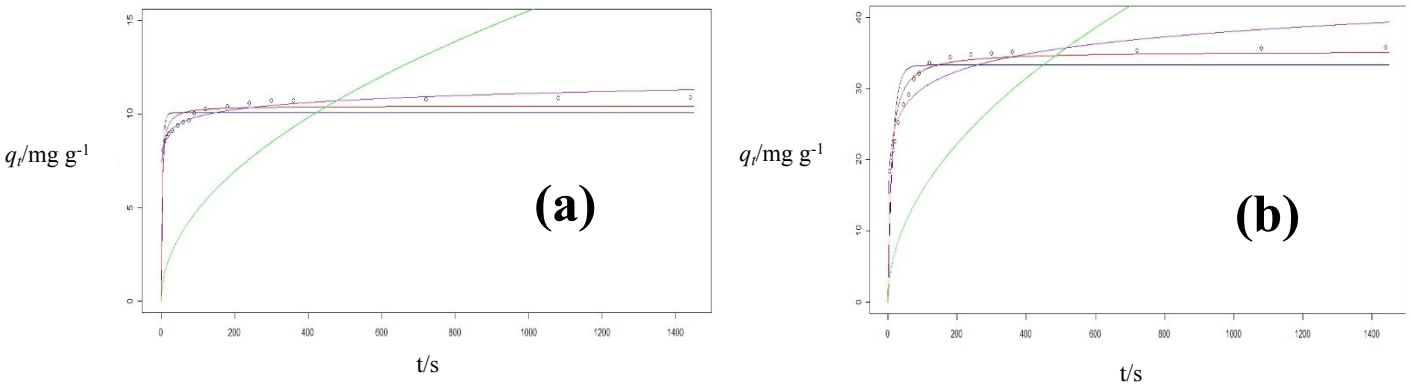

Fig S5: Comparison of kinetics models fitted to the experimental data for the adsorption of Cu^{2+} onto (a) MWCNT-COOH and (b) MWCNT-ttpy (pseudo-first order ——, pseudo-second order ——, intraparticle diffusion —— and Elovich model ——).

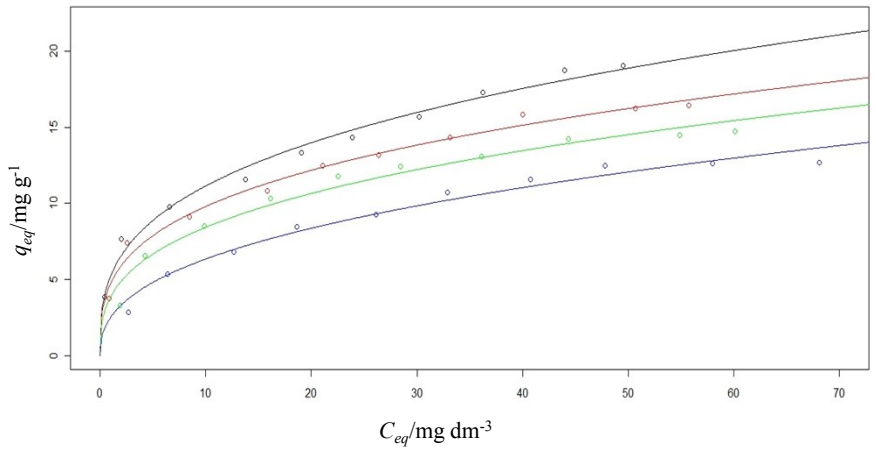

Fig S6: The Freundlich adsorption isotherm fitted to the experimental data for the adsorption of Cu^{2+} onto MWCNT-COOH at various temperatures (293 K ———, 303 K———— , 313 K———— and 318 K————).

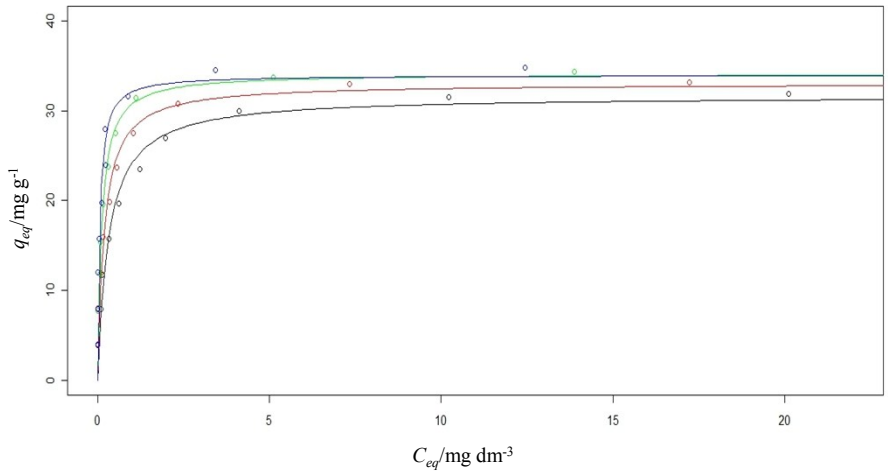

Fig S7: The Langmuir adsorption isotherm fitted to the experimental data for the adsorption of Cu^{2+} onto MWCNT-ttpy at various temperatures (293 K ———, 303 K———— , 313 K———— and 318 K————).

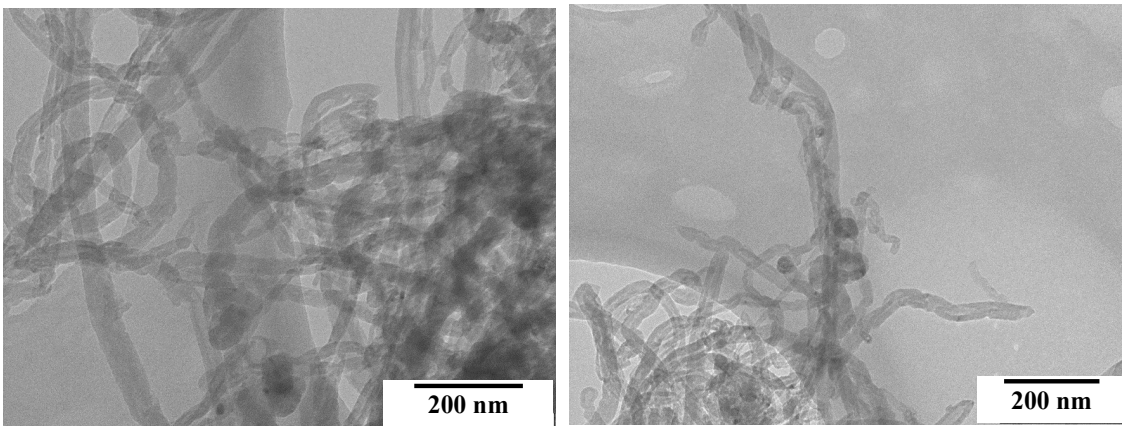

Fig S8: TEM images of (a) MWCNT-COOH and (b) MWCNT-ttpy after adsorption.