Supporting Information

Effective Adsorption/Reduction of Cr(VI) Oxyanion by Halloysite@Polyaniline Hybrid Nanotubes

Tianzhu Zhou, Cuiping Li,* Huiling Jin, Yangyang Lian and Wenmei Han

School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming 650091, China.

Corresponding Author: Cuiping Li (E-mail: licp830@iccas.ac.cn).

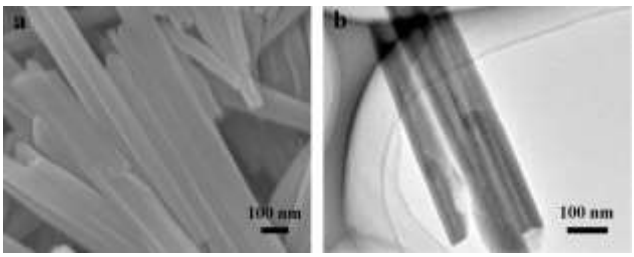

Figure S1. SEM (a) and TEM (b) images of the halloysite (HA) nanotubes.

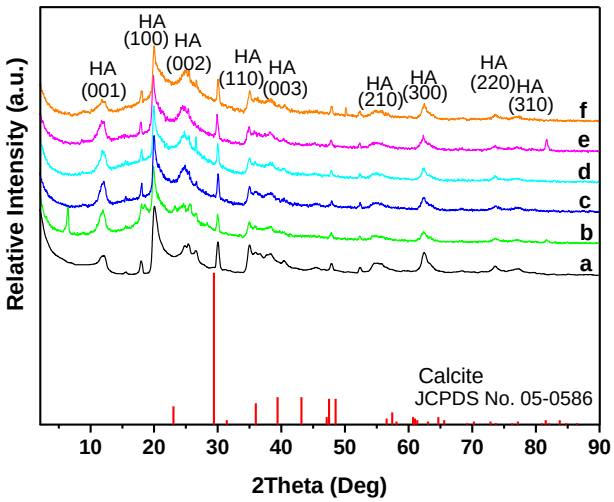

Figure S2. XRD of the HA@PANI hybrid nanotubes fabricated with 204% apparent weight proportion for ANI and HA and the standard XRD of calcite: (a) HA, (b) HP/6.57/204%-H_2O, (c) HP/0.5/204%-HCl, (d) HP/0.5/204%-H_2SO_4, (e) HP/0.5/204%-HNO_3 and (f) HP/0.5/204%- H_3PO_4.

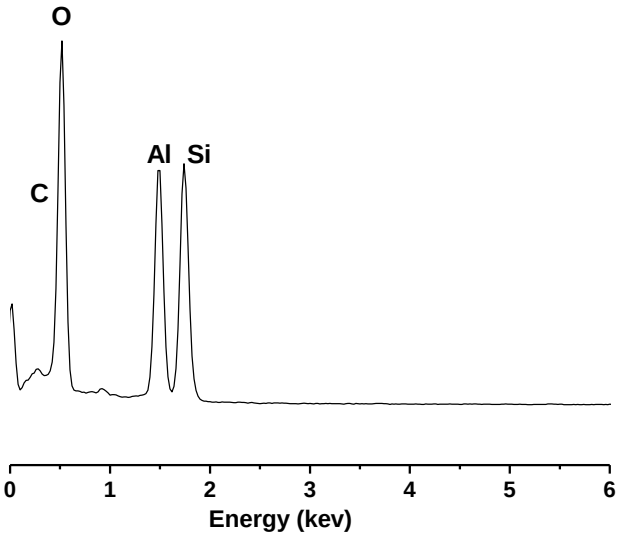

Figure S3. The energy-dispersive X-ray spectroscopy (EDX) of HA. The EDX shows that HA is composed of the elements Al, Si and O (C peak from the carbon-coated copper grids).

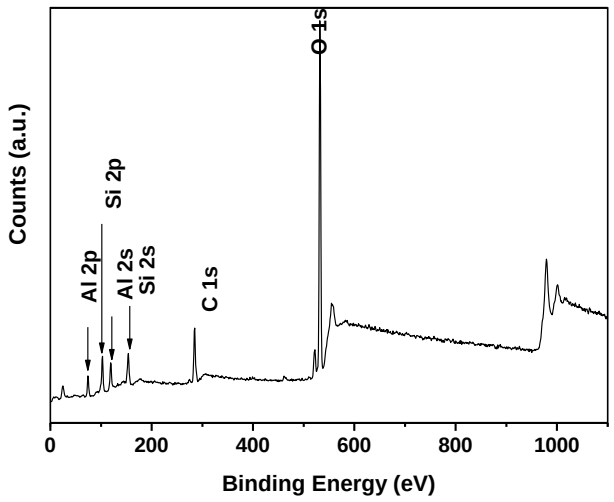

Figure S4. XPS survey spectra of HA (C peak from the adventitious elemental carbon).

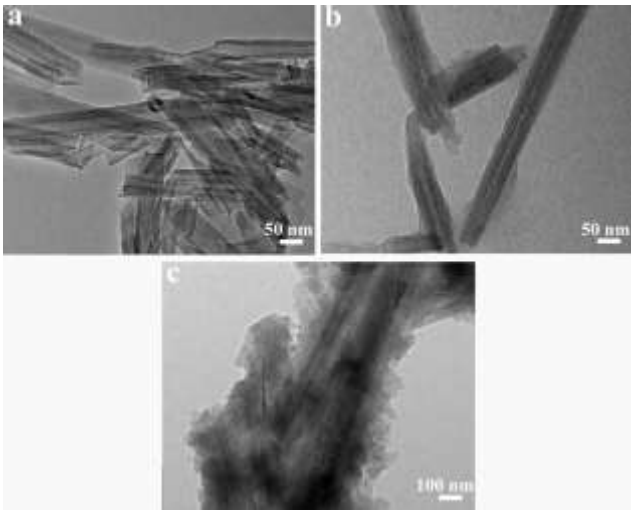

Figure S5. TEM images of the HA@PANI hybrid nanotubes fabricated at pH 0.5 with different

apparent weight proportion for ANI and HA: (a) 2.04%, (b) 40.8% and (c) 204%. The pH of the starting solution is tuned by 2 M HCl solution.

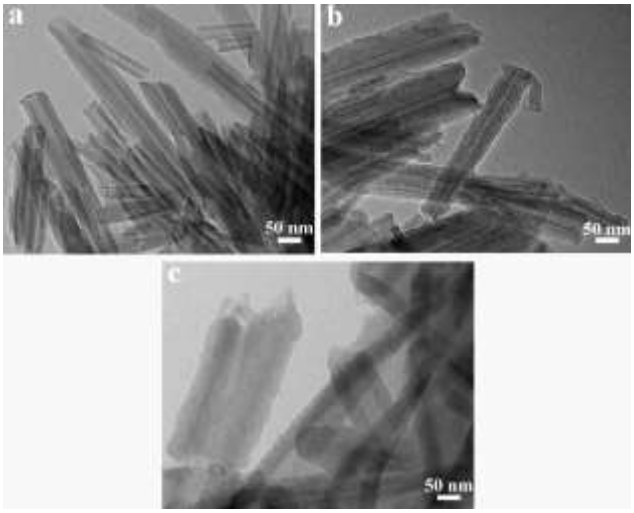

Figure S6. TEM images of the HA@PANI hybrid nanotubes fabricated at pH 1.5 with different apparent weight proportion for ANI and HA: (a) 2.04%, (b) 40.8% and (c) 204%. The pH of the starting solution is tuned by 2 M HCl solution.

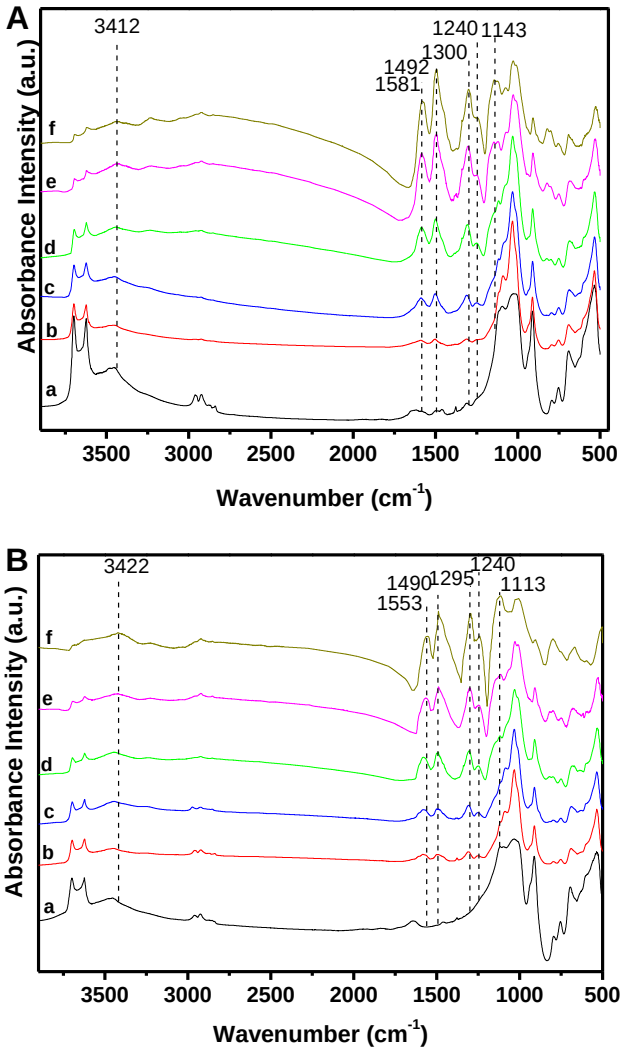

Figure S7. FT-IR spectra of HA@PANI hybrid nanotubes fabricated with different apparent weight proportion for ANI and HA at pH 1.5 (A) and 0.5 (B) of the starting solution: (a) 2.04%, (b) 10.2%, (c) 20.4%, (d) 40.8%, (e) 102% and (f) 204%. The pH of the starting solution is tuned by 2 M HCl solution.

Table S1. The mass ratio, PANI doped degree and conductivity of HA@PANI hybrid nanotubes (HP/A/B-C).

Sample	The acidity tuned by	Mass ratio of PANI in HP/A/B-C (%)	Doped degree of PANI in HP/A/B-C (%)	Conductivity (S/cm^{-1})
HP/0.5/2.04%-HCl	HCl	-	-	1.20×10^{-7}
HP/1.5/2.04%-HCl	HCl	-	-	3.89×10^{-9}
HP/0.5/10.2%-HCl	HCl	-	-	1.23×10^{-7}
HP/1.5/10.2%-HCl	HCl	-	-	4.65×10^{-9}
HP/0.5/20.4%-HCl	HCl	-	-	2.04×10^{-7}
HP/1.5/20.4%-HCl	HCl	-	-	1.02×10^{-8}
HP/0.5/40.8%-HCl	HCl	-	-	2.32×10^{-6}
HP/1.5/40.8%-HCl	HCl	-	-	3.32×10^{-8}
HP/0.5/102%-HCl	HCl	-	-	3.30×10^{-6}
HP/1.5/102%-HCl	HCl	-	-	7.24×10^{-8}
HP/0.5/204%-HCl	HCl	35.24 (34.79)[a]	33.61	8.89×10^{-6}
HP/1.5/204%-HCl	HCl	34.65	-	8.16×10^{-7}
HP/0.5 M/204%-HCl	HCl	-	-	9.00×10^{-6}
HP/1 M/204%-HCl	HCl	-	-	9.39×10^{-6}
HP/2 M/204%-HCl	HCl	-	-	1.32×10^{-5}
HP/0.5/204%-H_2SO_4	H_2SO_4	34.98	28.97	7.48×10^{-6}
HP/1.5/204%-H_2SO_4	H_2SO_4	30.39	-	1.33×10^{-7}
HP/0.5/204%-HNO_3	HNO_3	36.35	27.97	3.37×10^{-6}
HP/1.5/204%-HNO_3	HNO_3	38.13	-	6.96×10^{-7}
HP/0.5/204%-H_3PO_4	H_3PO_4	36.54	25.45	1.49×10^{-6}
HP/1.5/204%-H_3PO_4	H_3PO_4	36.10	-	1.01×10^{-7}
PANI/1.5-HCl	HCl	-	-	1.06×10^{-6}
PANI/0.5-HCl	HCl	-	-	1.23×10^{-5}
PANI/0.5 M-HCl	HCl	-	-	1.76×10^{-5}
PANI/1 M-HCl	HCl	-	-	2.89×10^{-5}
PANI/2 M-HCl	HCl	-	-	4.66×10^{-5}

[a]The value in bracket is the mass ratio of PANI in HP/0.5/204%-HCl fabricated with the distilled ANI.

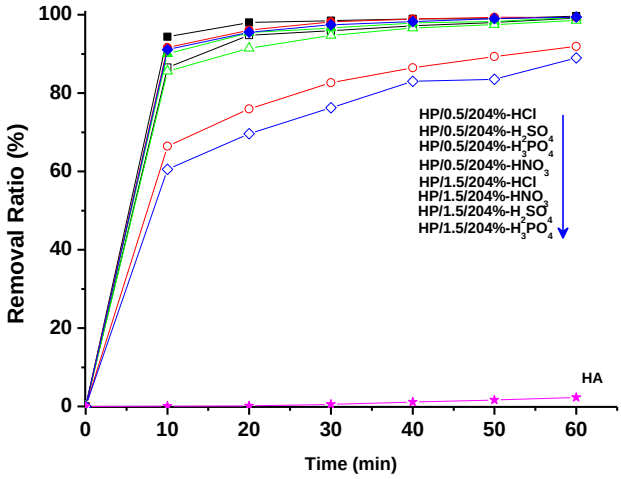

Figure S8. The removal ratio of HA@PANI hybrid nanotubes fabricated under different dopant acid with 204% apparent weight proportion for ANI and HA (HP/A/204%-C) for 10 mg/L Cr(VI) oxyanion solution.

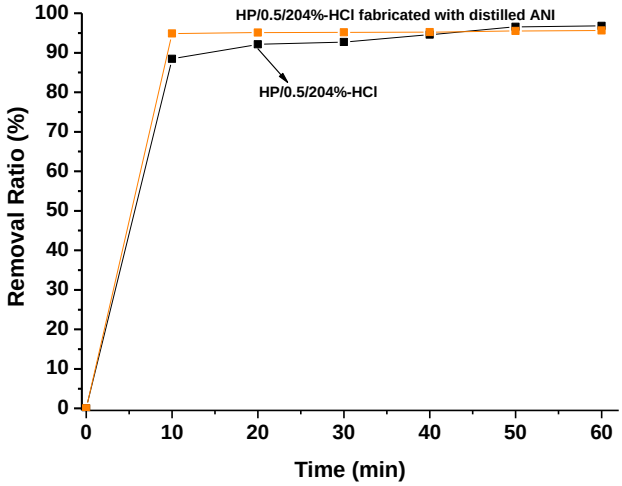

Figure S9. The comparison of removal ratio of HP/0.5/204%-HCl fabricated with distilled and parent ANI for 20 mg/L Cr(VI) oxyanion solution.

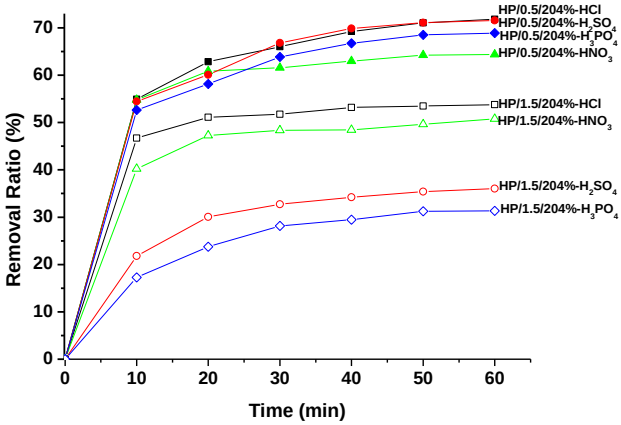

Figure S10. The removal ratio of HA@PANI hybrid nanotubes fabricated under different dopant acid with 204% apparent weight proportion for ANI and HA (HP/A/204%-C) for 40 mg/L Cr(VI) oxyanion solution.

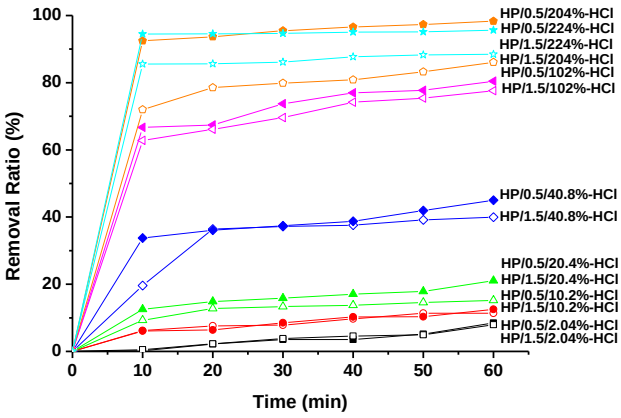

Figure S11. The removal ratio of HP/A/B-HCl fabricated with different apparent weight proportion for ANI and HA for 20 mg/L Cr(VI) oxyanion solution.

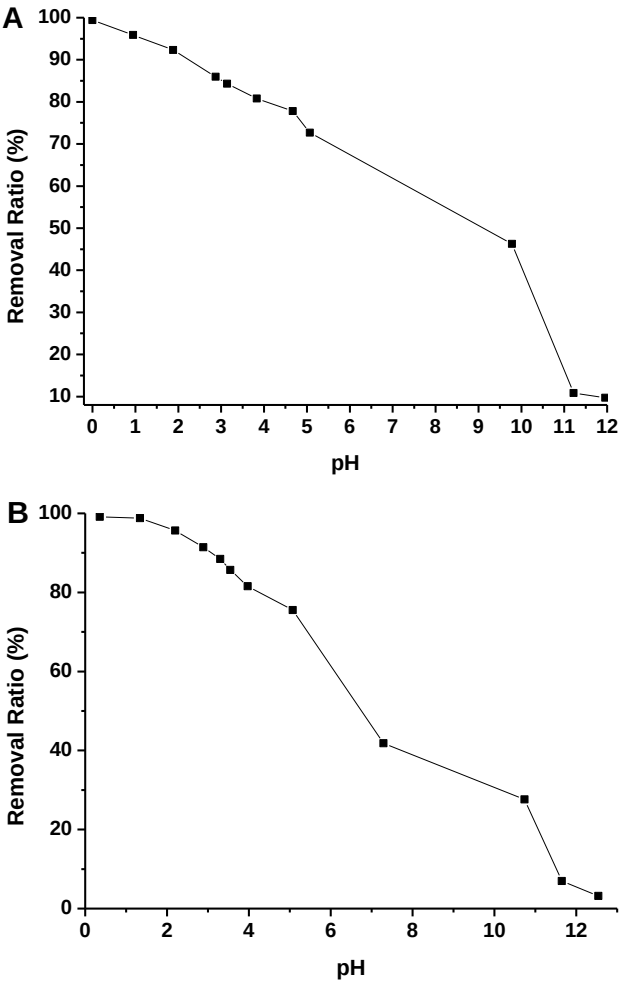

Figure S12. Effect of the initial pH of Cr(VI) oxyanion solution on Cr(VI) oxyanion removal efficiency of HP/0.5/204%-HCl (A) (30 mg/L Cr(VI) oxyanion solution, treating time: 60 min) and HP/1.5/204%-HNO_3 (B) (20 mg/L Cr(VI) oxyanion solution, treating time: 60 min).

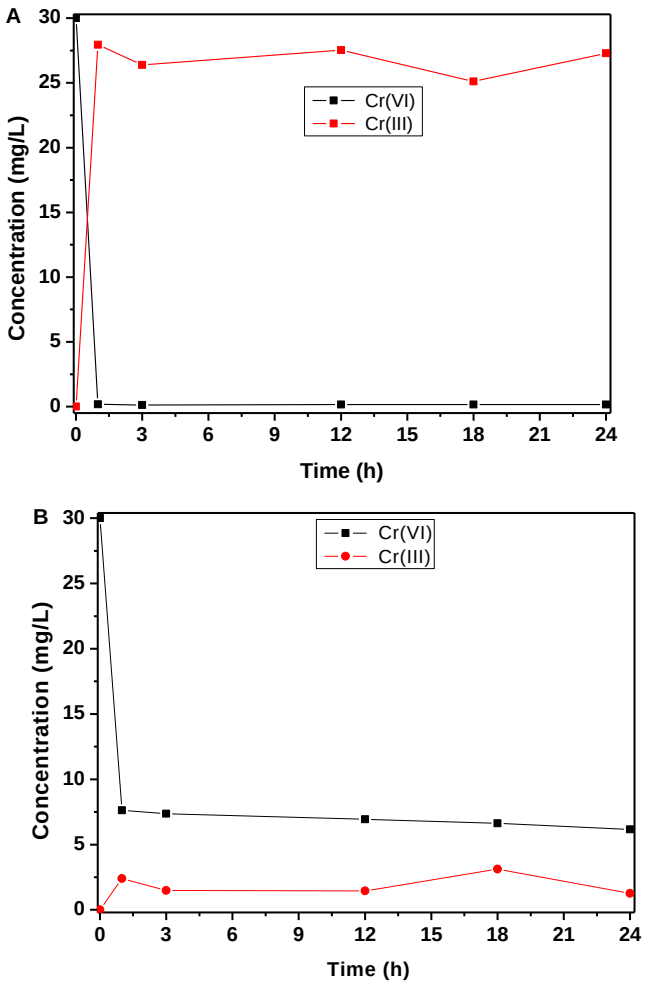

Figure S13. Cr(III) and Cr(VI) oxyanion concentrations in the adsorption solution over time for HP/0.5/204%-HCl adsorbing 30 mg/L pH 0 (A) and parent (pH 5.07) (B) Cr(VI) oxyanion solution.

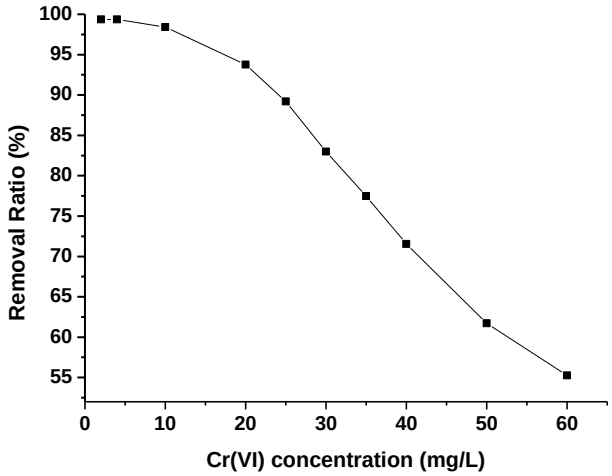

Figure S14. Effect of Cr(VI) oxyanion solution concentration on the Cr(VI) oxyanion removal efficiency of HP/0.5/204%-HCl (pH 5.07, treating time: 60 min).

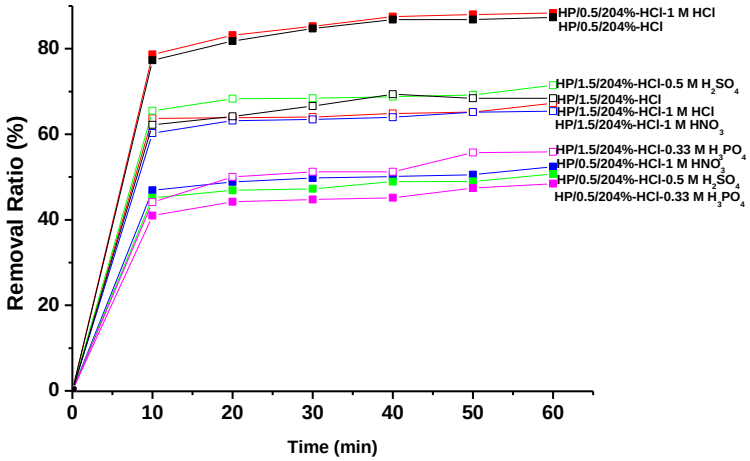

Figure S15. The removal ratio of HP/A/204%-HCl after being redoped by 1 M HCl, 1 M HNO_3, 0.5 M H_2SO_4, and 0.33 M H_3PO_4 solution for 30 mg/L Cr(VI) oxyanion solution.

Table S2. The PANI content (wt%), Al/Si (at%) of the regenerated HP/0.5/204%-HCl and the Cr concentrations in the desorption solutions for removal of 40 mg/L Cr(VI) oxyanion over the regenerated HP/0.5/204%-HCl and HP/0.5/204%-HNO_3.

Sample	Number of cycle desorption	PANI content (wt%)	Al/Si (at%)	Cr concentration in the desorption solutions (mg/L)
HP/0.5/204%-HCl	0	35.24	115	-
	1	-	-	19.43
	2	35.31	116	21.51
	4	35.20	115	18.19
HP/0.5/204%-HNO_3	1	-	-	18.80
	2	-	-	20.15
	4	-	-	18.90

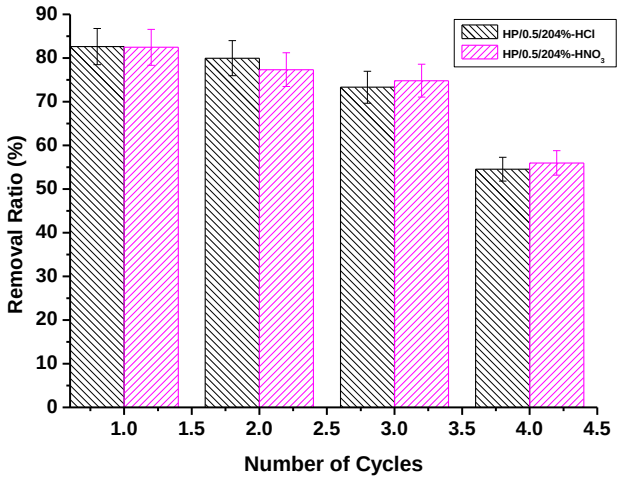

Figure S16. Effect of adsorption cycles on Cr(VI) oxyanion removal ratio for 40 mg/L Cr(VI) oxyanion solution over the regenerated HP/0.5/204%-HCl and HP/0.5/204%-HNO_3.

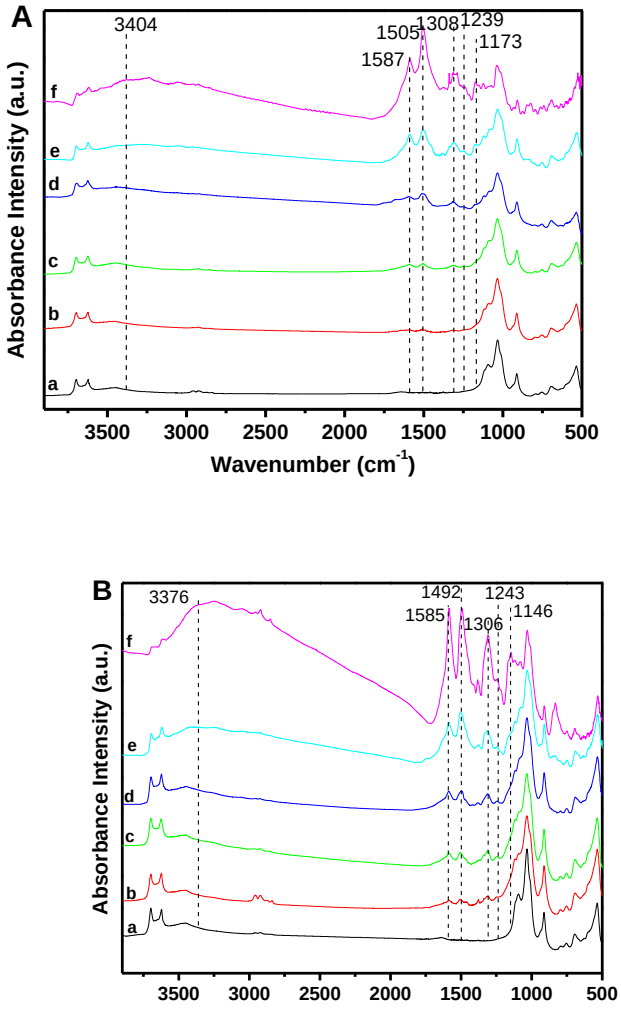

Figure S17. FT-IR spectra of HA@PANI hybrid nanotubes fabricated with different apparent weight proportion for ANI and HA at pH 1.5 (A) and 0.5 (B) after adsorption 30 ppm Cr(VI) oxyanion solution: (a) 2.04%, (b) 10.2%, (c) 20.4%, (d) 40.8%, (e) 102% and (f) 204%. The pH of the starting solution is tuned by 2 M HCl solution.

Table S3. Chemical composition of HA and HP/0.5/204%-HCl before and after Cr(VI) oxyanion adsorption.

Sample	Atomic concentration (%)						
	Si	Al	O	C	N	Cl	Cr
HA	13.72	10.12	55.51	20.65	-	-	-
HP/0.5/204%-HCl	1.61	1.86	16.57	73.05	6.37	0.54	-
HP/0.5/204%-HCl after Cr(VI) adsorption	1.57	1.72	20.77	64.25	5.80	0.25	5.64

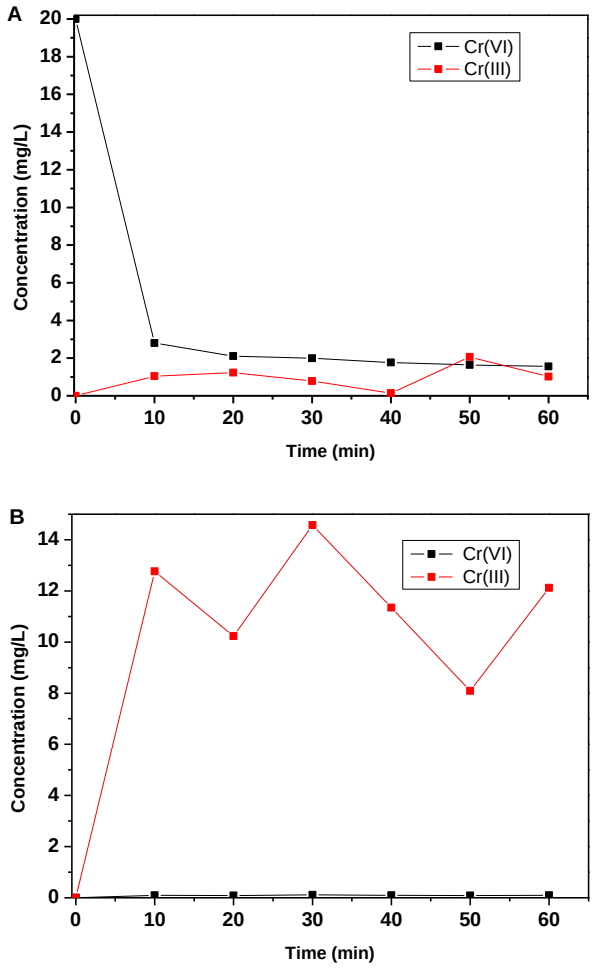

Figure S18. Cr(III) and Cr(VI) oxyanion concentrations in the adsorption solution (A) and desorption solution (B) over time after HP/0.5/204%-HCl adsorbing 20 mg/L Cr(VI) oxyanion solution.