Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Rapid Characterization of Arsenic Adsorption on Single Magnetite Nanoparticles by Collisions at Microelectrodes

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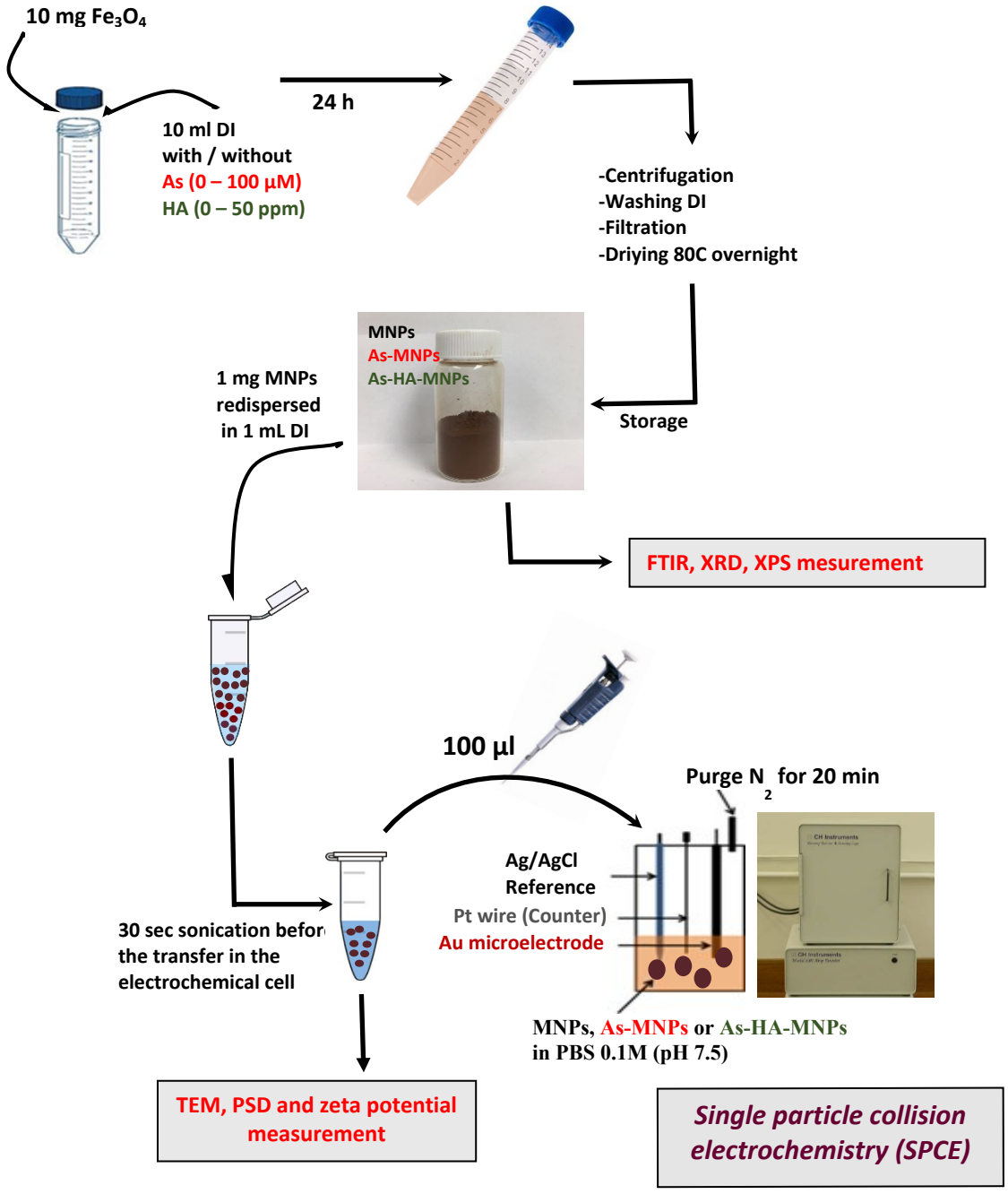

Scheme S1. Preparation and experimental collision measurements of MNPs, As-NPs and As-HA-MNPs.

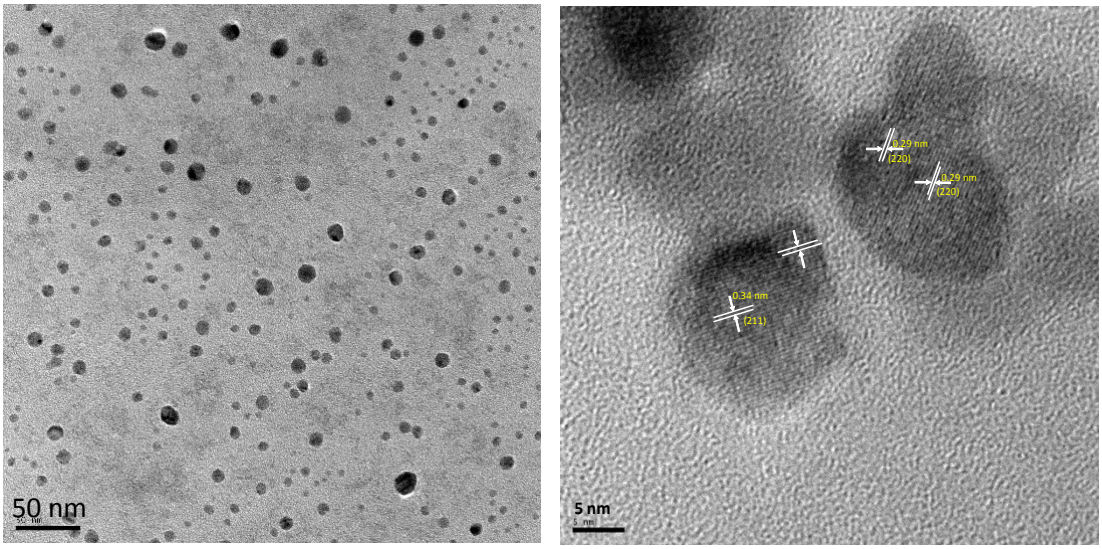

Figure S1. The HRTEM images of Fe_3O_4 nanoparticles.

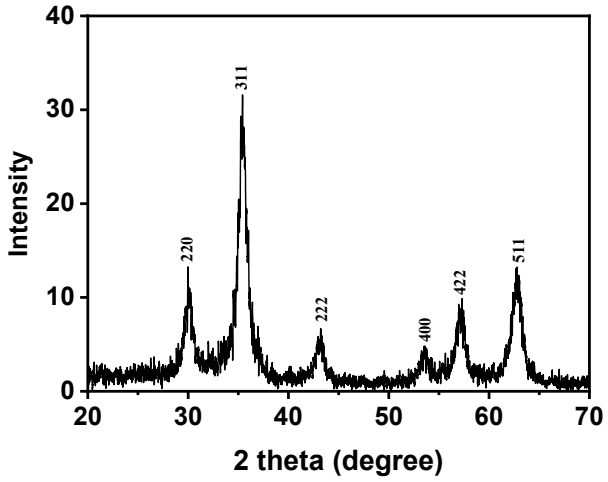

Figure S2. X-ray diffraction patterns of Fe_3O_4 nanoparticles.

Table S1. Arsenic removal efficiency by bare Fe_3O_4 and HA- Fe_3O_4 NPs (1 mg/ml) evaluated by AAS.

NPs type	Initial As concentration (µM)	Residual As concentration in supernatant (µM)	As removal (%)
Fe_3O_4	1	-	> 99
	10	**0.55**	**94.5**
HA-Fe_3O_4 (5 ppm HA)	10	0.3	97
	100	**5.7**	**94.3**
HA-Fe_3O_4 (50 ppm HA)	10	0.99	90.1
	100	10.7	89.3

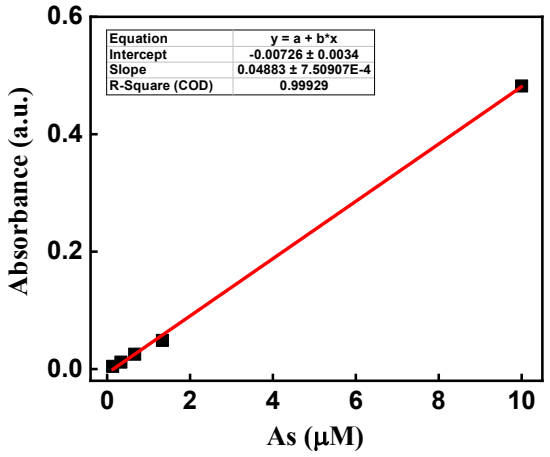

Figure S3. Arsenic atomic absorption standard calibration curve.

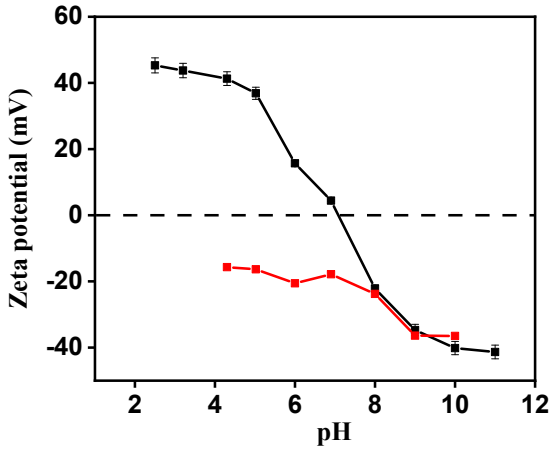

Figure S4. Zeta potential of magnetite NPs (black) and As-MNPs (red) function of pH.

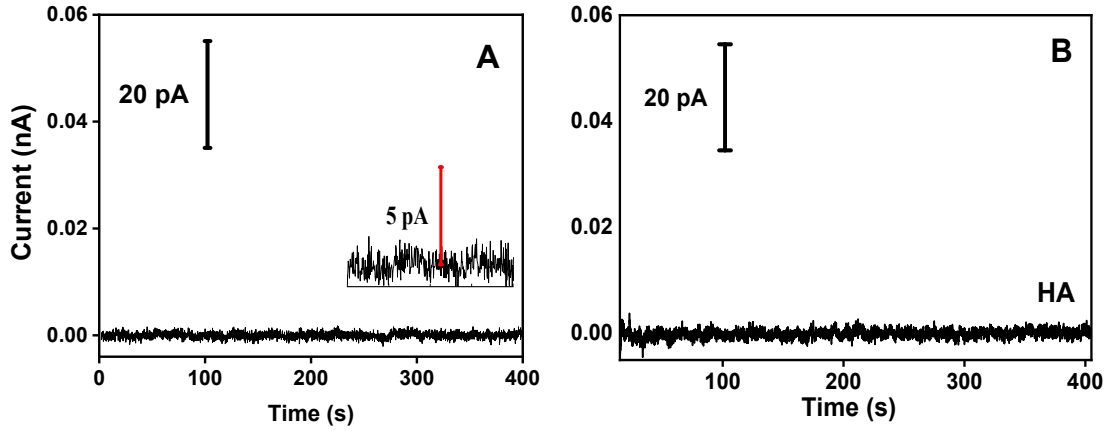

Figure S5. Chronoamperometric profile of oxidation spikes of bare Fe_3O_4 (A) and HA- Fe_3O_4 NPs at +0.4 V in PB (pH 7.5) for 400 s.

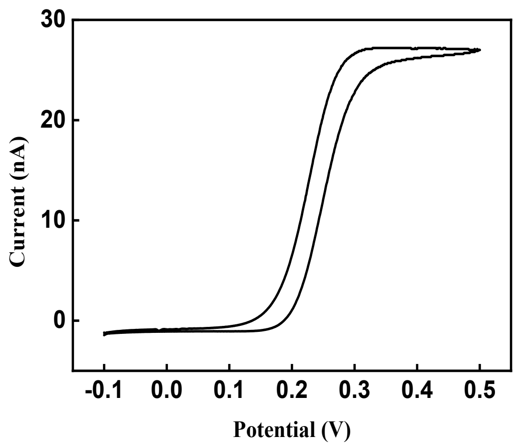

Figure S6. CV of AuME in 2 mM FcMeOH with 0.1M Na_2SO_4 and 25 mV/s scan rate.

Table S2 Collision characteristics of MNPs exposed to As^{3+} (10µM) at different pH values.

pH	The number of oxidation peaks	Average current intensity (pA)	Average charge per spike (pC)	Total charge for 400 s (pC)	As conc / MNP (fM)
4	4	5	2.74	11.0	0.014
5	8	10.8	3.48	27.9	0.018
6	15	15.7	5.52	82.8	0.029
7	10	20.7	6.22	62.2	0.032
8	13	12.5	6.54	84.0	0.034
9	11	10	4.37	48.0	0.024

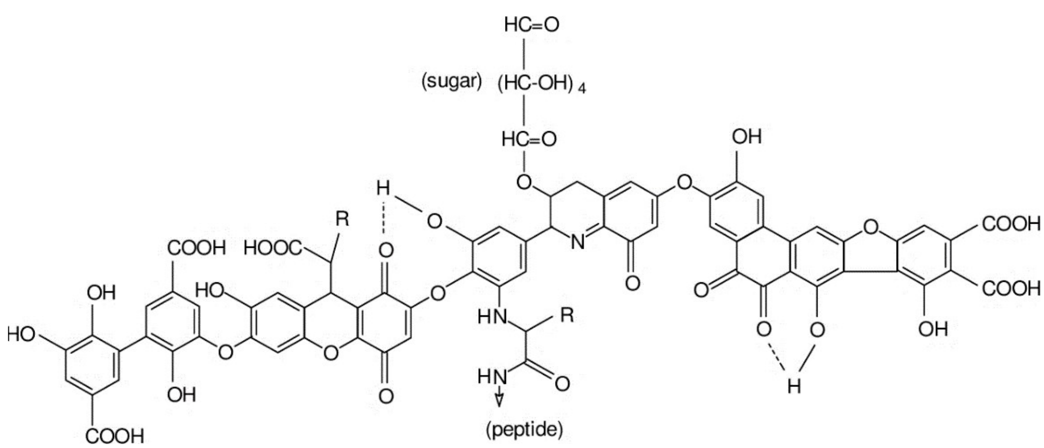

Figure S7. Humic acid structure (Pena-Menez, E.M.; Havel, J.; Potocka, J., *J. Appl. Biomed.*, 2005, 3, 13-24).+

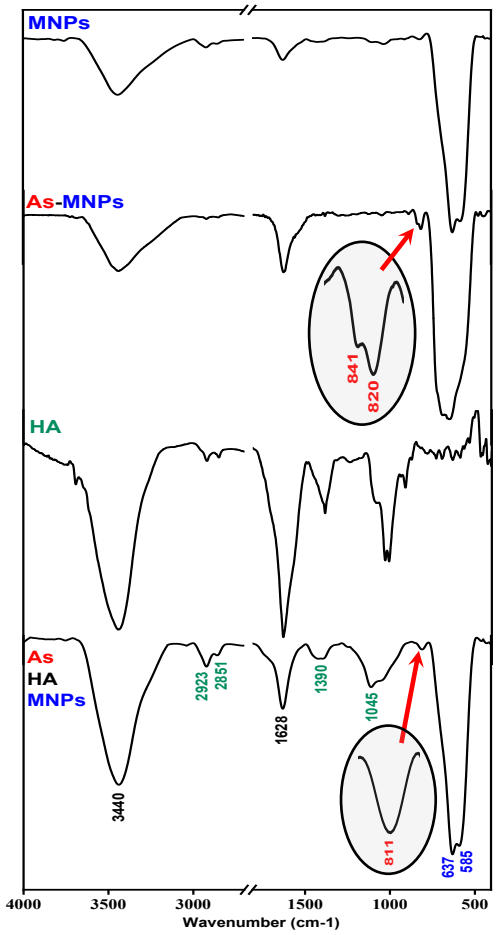

Figure S8. The FTIR spectra of MNPs, As-MNPs, HA and AS-HA-MNPs.

Table S3. The influence of HA concentration in SPCE characteristics of As-HA-MNPs (the average value of 3 electrodes)**.**

Humic acid (ppm)	Number of collisions	Charge Transferred (pC)	As content / particle (fM)
1	11 ± 3	1.66	0.008
2.5	13 ± 4	4.59	0.024
5	13 ± 4	5.72	0.030
10	10 ± 5	3.63	0.022
25	5 ± 3	5.34	0.028
50	2-3	6.41	0.033

Table S4. Relative peak areas of peak components for Fe2p and As3d XPS spectra

NPs type	As solution conc. (mM)	Surface elemental mass (%) quantification					Electron shell				
							Fe 2p			As 3d	
		As	C	N	O	Fe	Fe^{2+} (%)	Fe^{3+} (%)	Fe^{3+}/Fe^{2+} ratio	As^{3+} (%)	As^{5+} (%)
(Fe_3O_4) MNPs	-	-	8.2	-	23.2	68.6	43.6	56.4	1.29	-	-
As-MNPs	0.1	-	9.2	-	22.7	68.1	45.7	54.3	1.16	-	-
As-HA*-MNPs	0.1	0.5	8.2	0.6	23	67.7	43.8	56.2	1.28	100	-
As-MNPs	10	3.7	8.6	-	22.4	65.3	43.2	56.8	1.31	81	19
As-HA*-MNPs	10	4.8	7.5	1.0	23	63.7	49.5	50.5	1.02	85	15

* the humic acid (HA) concentration was 5 ppm

Table S5. The influence of As concentration in SPCE characteristics of As-HA-MNPs collisions

As conc in solution (µM)	Number of collisions	Charge Transferred (pC)	As content / particle (fM)
0.001	7	2.46 ± 0.36	0.013
0.01	11	3.26 ± 0.78	0.017
0.1	12	3.95 ± 0.61	0.021
1	10	4.94 ± 0.87	0.026
10	17	7.02 ± 1.12	0.036

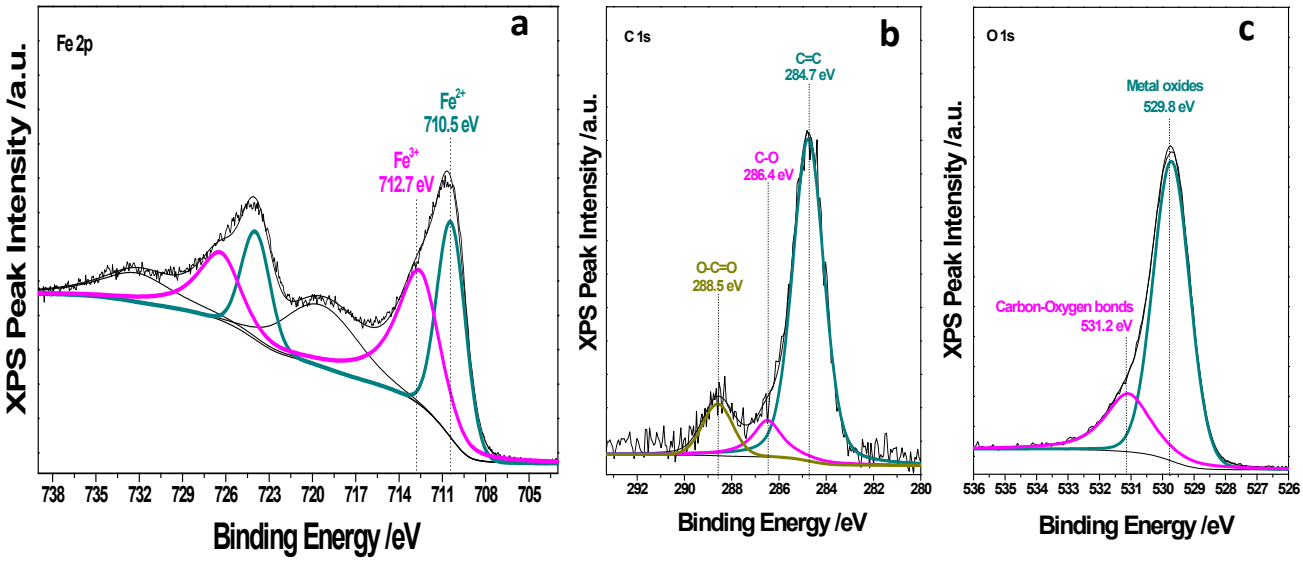

Figure S9. The Fe2p (a), C1s (b) and O1s (c) XPS spectra of bare Fe_3O_4 NPs.

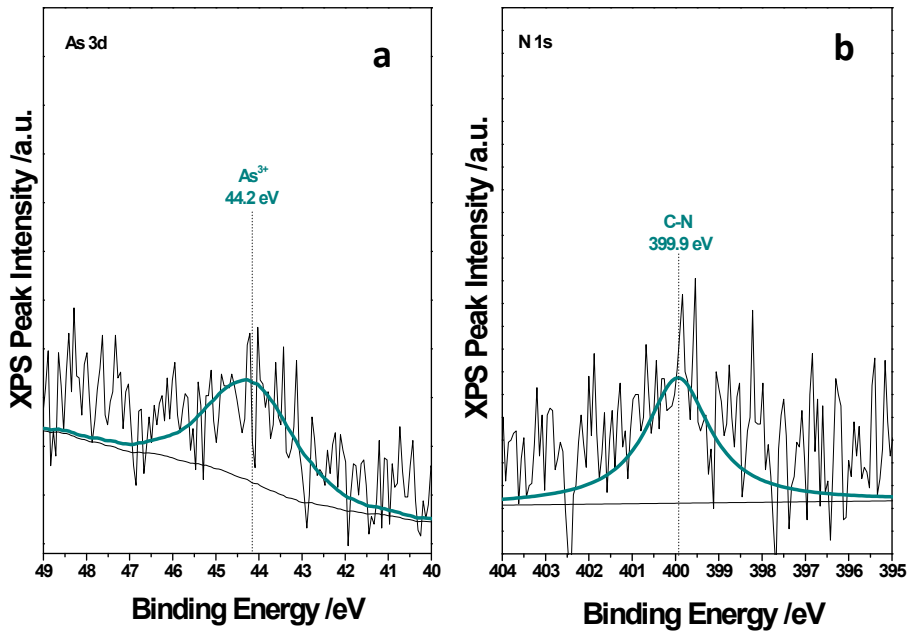

Figure S10. The As3d and N1s XPS spectra of As-HA-MNPs (prepared with 10 μM As and 5 ppm HA)

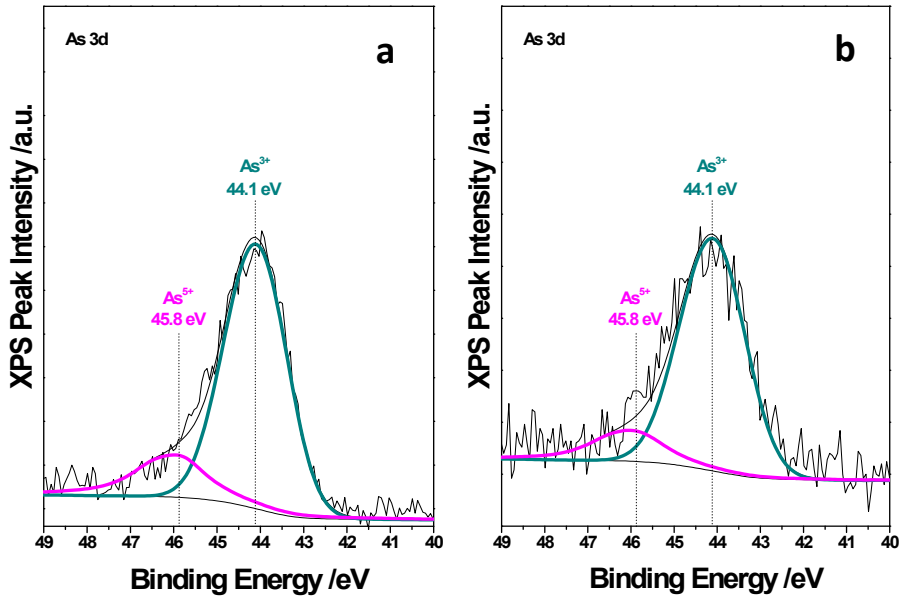

Figure S11. The As3d XPS spectra of As-HA-MNPs prepared with 100 μM As in the absence (a) and in the presence (b) of 5 ppm HA.