Supporting Information

Insights into the facet-dependent adsorption of phenylarsonic acid on hematite nanocrystals

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14 pages, 3 text, 13 figures, 7 tables

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Text S1. The ratio of {001} and {102} facets on HNPs

From the SEM and TEM images, the mean width, and the average thickness of the hexagonal HNPs were 79.3 and 15.5 nm. Both the upper and bottom surfaces exposed with {001} facet were regular hexagons with a width of 79.3 nm, and each area was calculated as $\frac{3\sqrt{3}\times79.3\times79.3}{2} = 16.3 \times 10^3$ nm^2. In the meantime, the six sides exposed with {102} were all rectangular, with the length 79.3 nm and the width 15.5 nm, so each area could be calculated as $79.3 \times 15.5 = 1230$ nm^2. From the data above, we could easily get the ratio of {001} and {102} facets.

The ratio of {001}: $\frac{2\times16300}{2\times16300+6\times1230} = 81.5\%$

The ratio of {102}: $\frac{6\times1230}{2\times16300+6\times1230} = 18.5\%$

Text S2. The density of adsorption sites and the utilization of these adsorption sites on HNPs and HNCs.

The PhAs adsorption capacity (q_m) of HNCs reached a maximum value of 1.49 mg/m^2, which was higher than that (0.72 mg/m^2) of HNPs (Figure S5a). So the PhAs sites of HNPs and HNCs could be calculated to be 2.15 As/nm^2 and 4.44 As/nm^2, respectively. Since one adsorbed PhAs molecule corresponded to one Fe atom on HNPs and two on HNCs, the occupied Fe sites were 2.15 Fe/nm^2 (HNPs) and 8.88 Fe/nm^2 (HNCs), respectively. Now, we would calculate the proportion of surface irons to the total irons over one hematite nanoplate (the thickness was 15.5 nm and the width was 79.3 nm) or hematite nanocube (the width was 30.3 nm). According to the cell model, there were two layers of iron atoms per 2.2867 Å on the {001} facet, and two layers of iron atoms per 3.6780 Å on the {012} facet. And there were also two layers of iron atoms per 2.4533 Å on the {102} facet. From above experimental and calculated results, the ratios of surface irons to total irons were

calculated to be 1.72% (for HNPs) and 7.30% (for HNCs), respectively. Since 50 mg of hematite was added into the solution, there were total 3.76×10^{20} iron atoms in both adsorption system. And the available surface iron atoms were calculated to be 6.47×10^{18} (for HNPs) and 2.75×10^{19} (for HNCs). Considering the actual surface area of hematite nanocrystals from BET data ($20.9 \text{ m}^2/\text{g}$ for HNPs, and $20.4 \text{ m}^2/\text{g}$ for HNCs), the available surface iron atoms could be calculated to be 2.64 Fe/nm^2 for HNPs and 11.17 Fe/nm^2 for HNCs, respectively. Combined with above results of occupied Fe sites, the practical utilizations of adsorption sites were estimated to be 81% for HNPs and 79% for HNCs, respectively.

Text S3. Adsorption isotherms

The Langmuir isotherm model and Freundlich isotherm model were used as the PhAs adsorption equilibrium.

The linear form of Langmuir equation is expressed as eq 1.

$$\frac{1}{q_e} = \frac{1}{C_e} \cdot \frac{1}{q_m K_L} + \frac{1}{q_m} \qquad (1)$$

Where q_e is the amount of PhAs adsorbed by the hematite nanomaterials and normalized to the specific surface area at equilibrium (mg/m^2). C_e is the equilibrium concentration of PhAs (mg/L), and q_m (mg/m^2) indicates the maximum adsorption capacity. K_L (L/mg) is the equilibrium constant.

The linear form of the Freundlich model represented as eq 2.

$$\log q_e = \ln K_F + \frac{1}{n} \log C_e \qquad (2)$$

Where $1/n$ and K_F ($(\text{mg/m}^2)(\text{mg/L})^n$) are correlated with adsorption intensity and adsorption capacity, respectively.
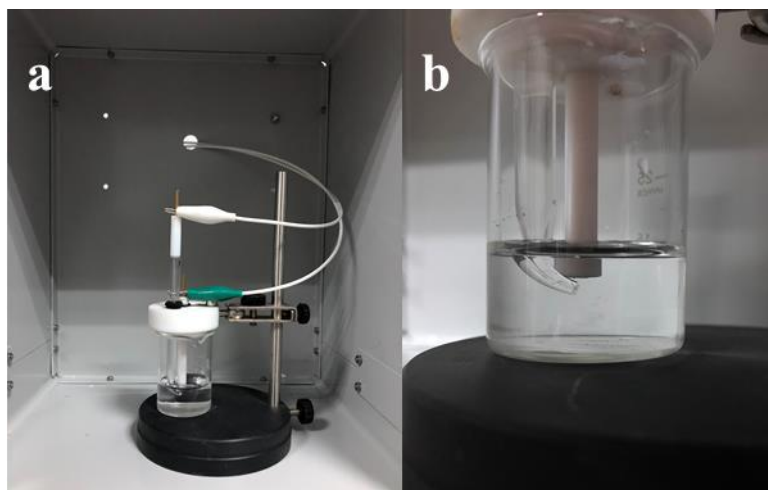
Figure S1. Side images of (a) the electrochemical measurements setup and (b) the local details at the electrodes.
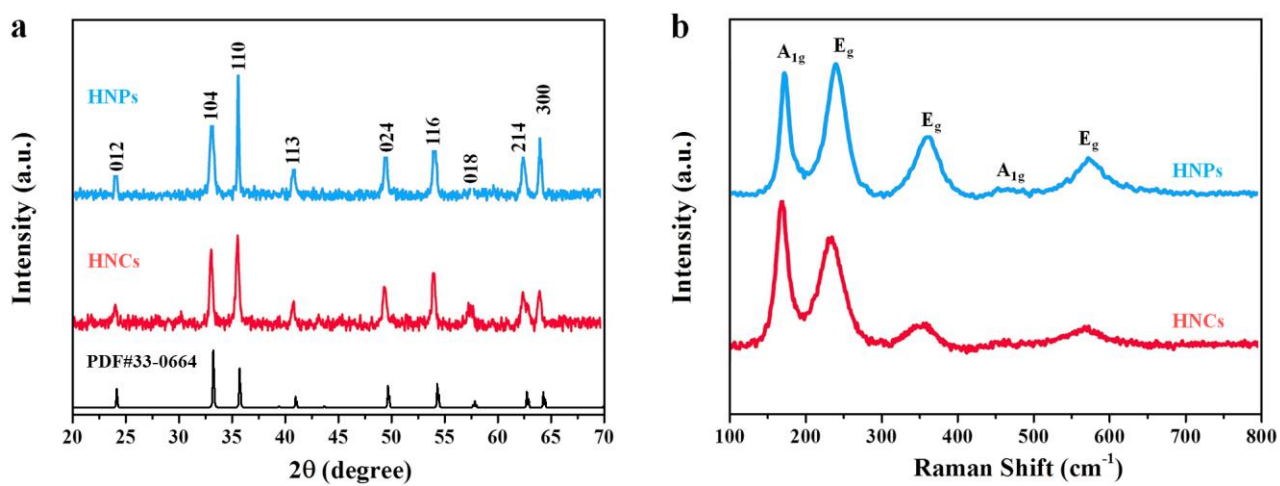

Figure S2. (a) Powder XRD patterns of different hematite nanoparticles. (b) Raman spectra of different hematite nanoparticles.
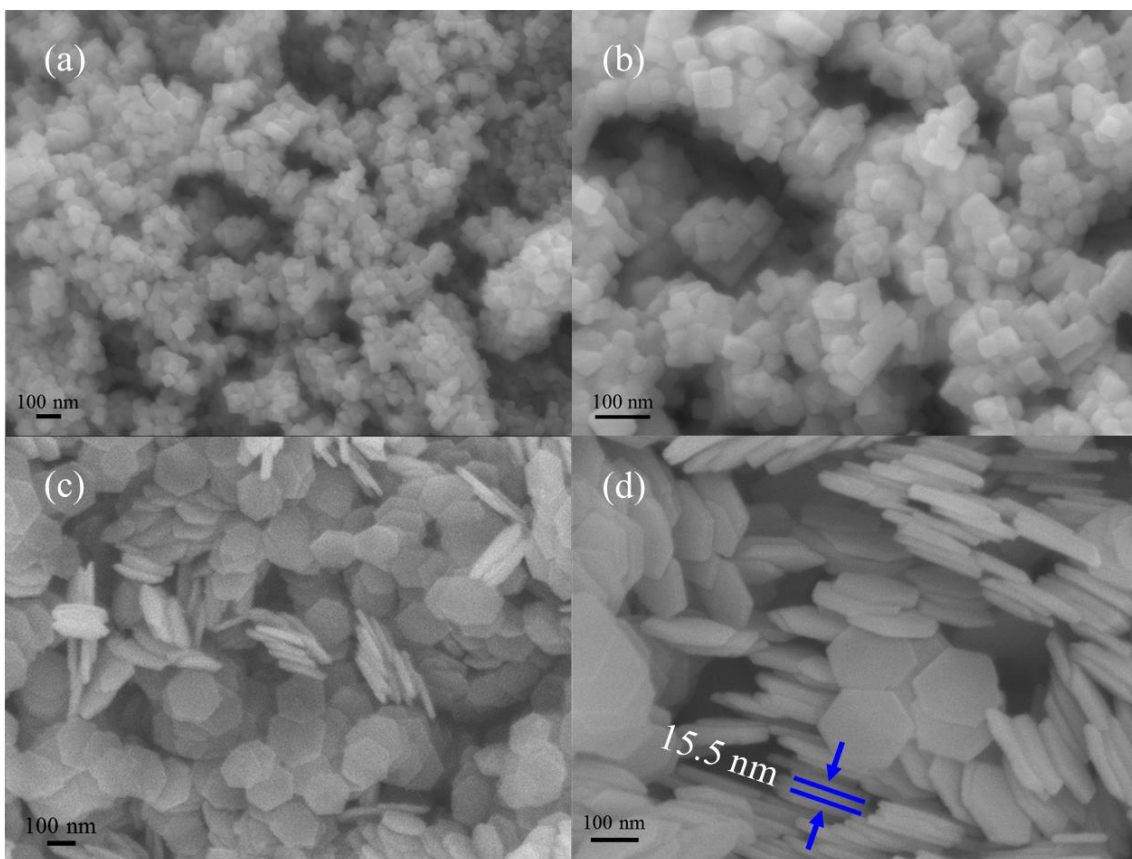
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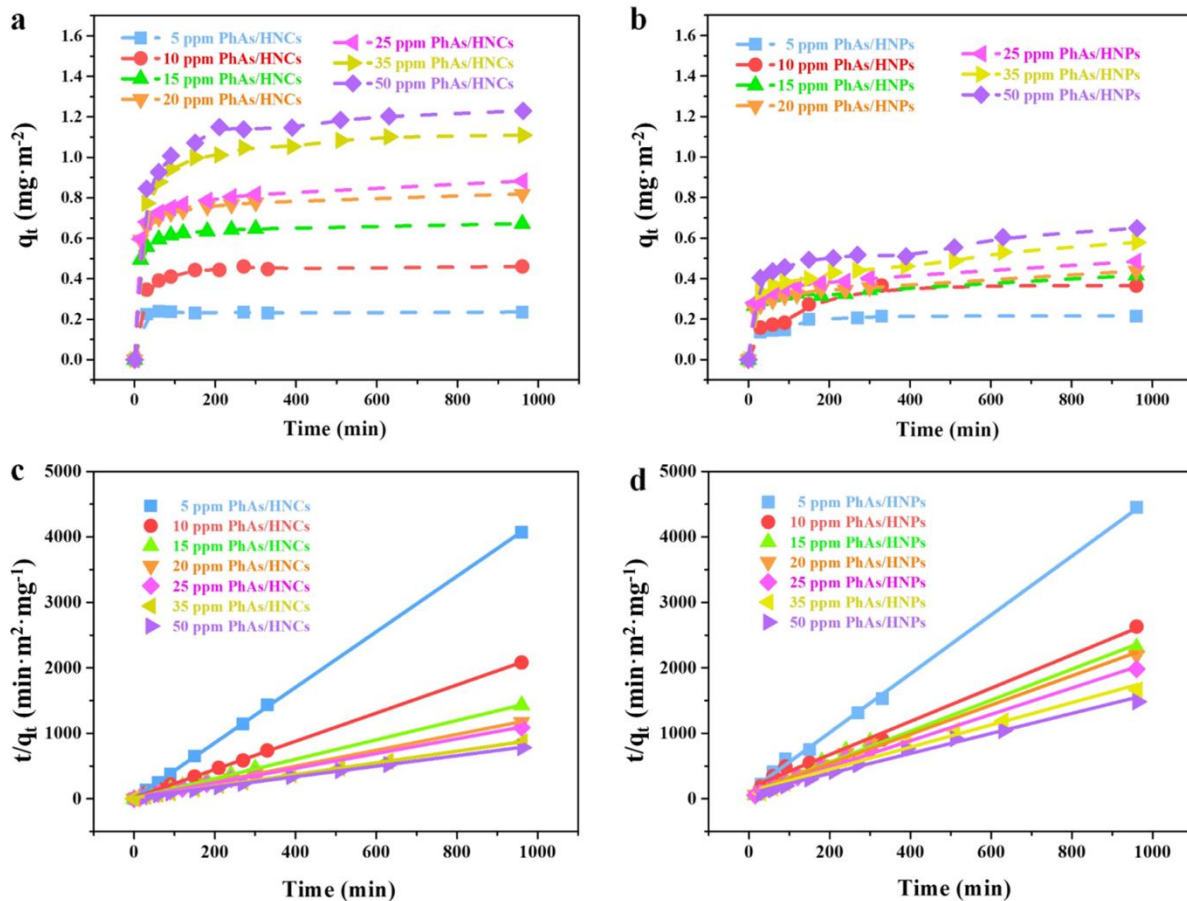
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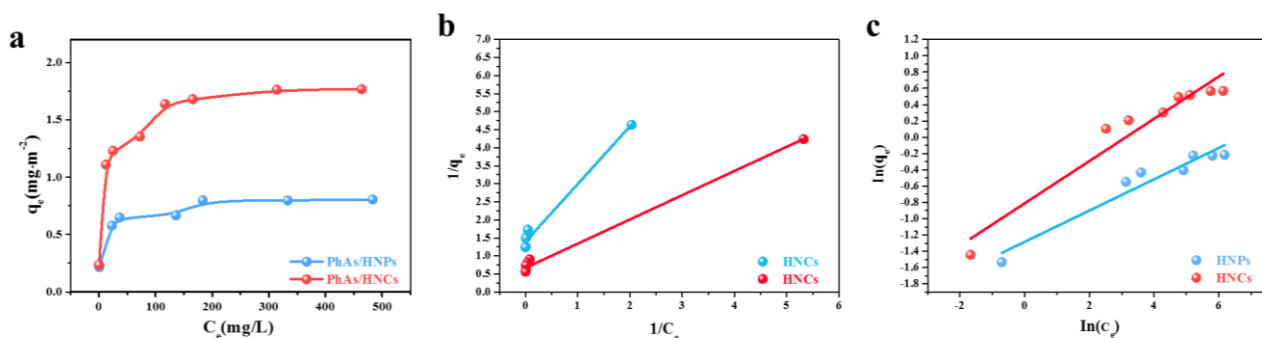
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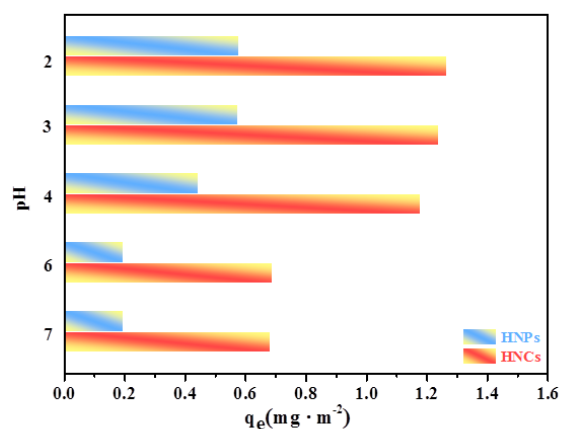
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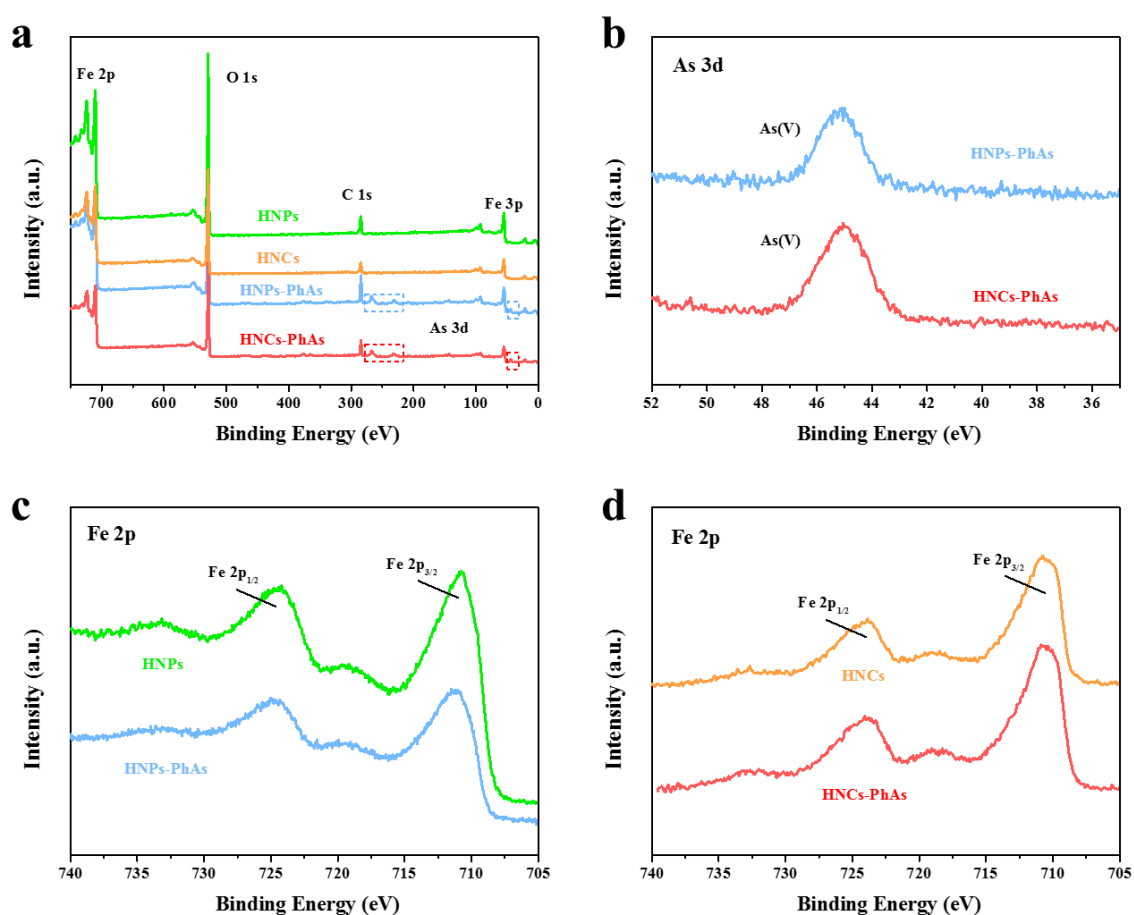
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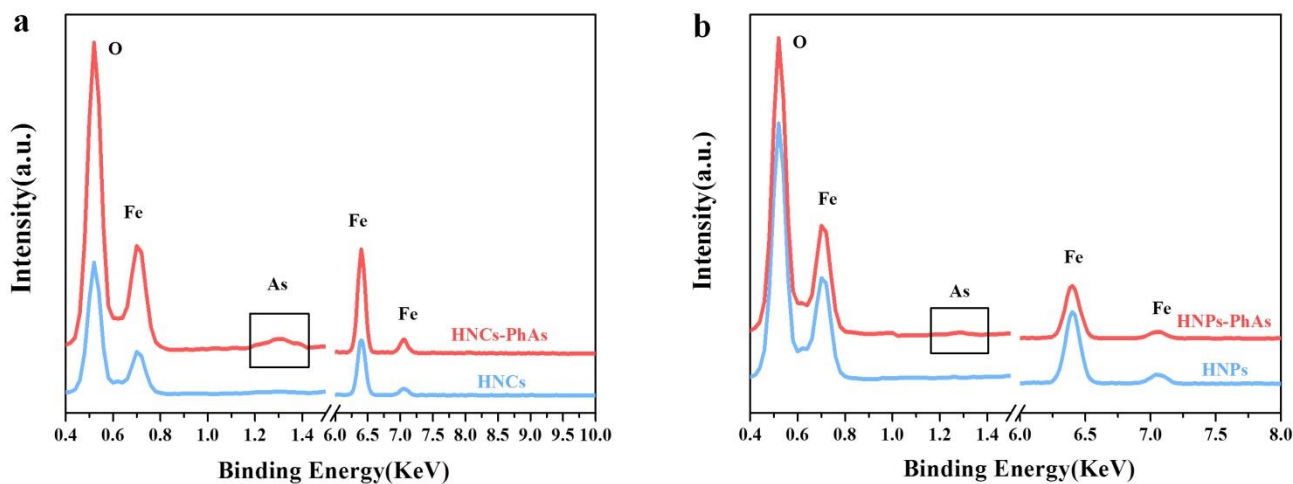
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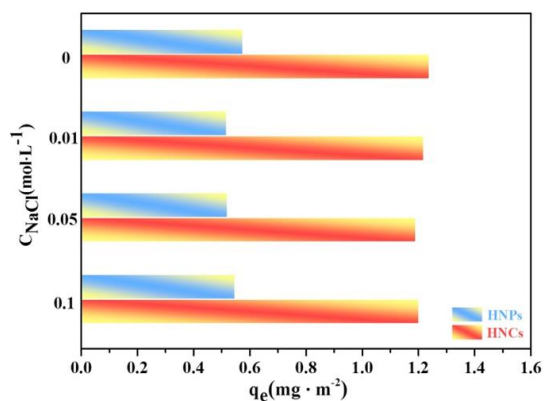
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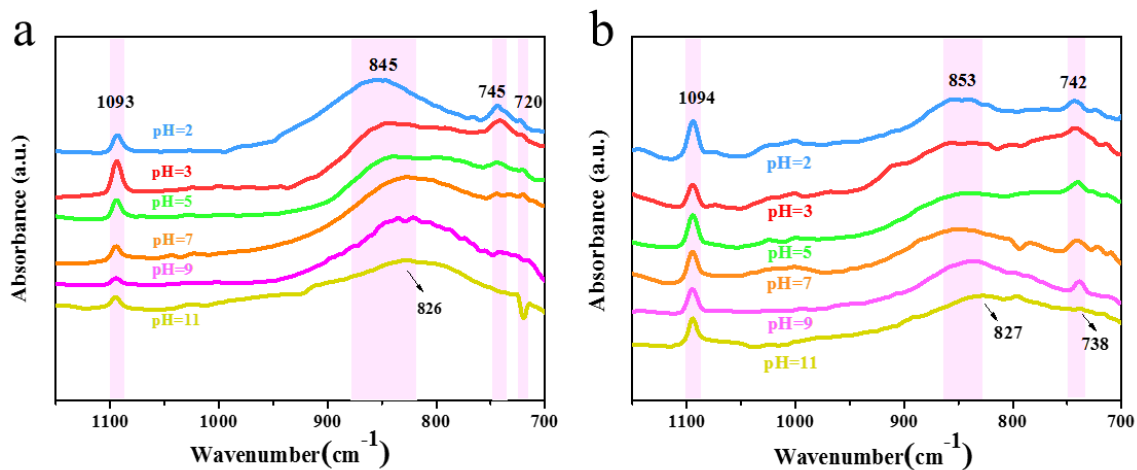
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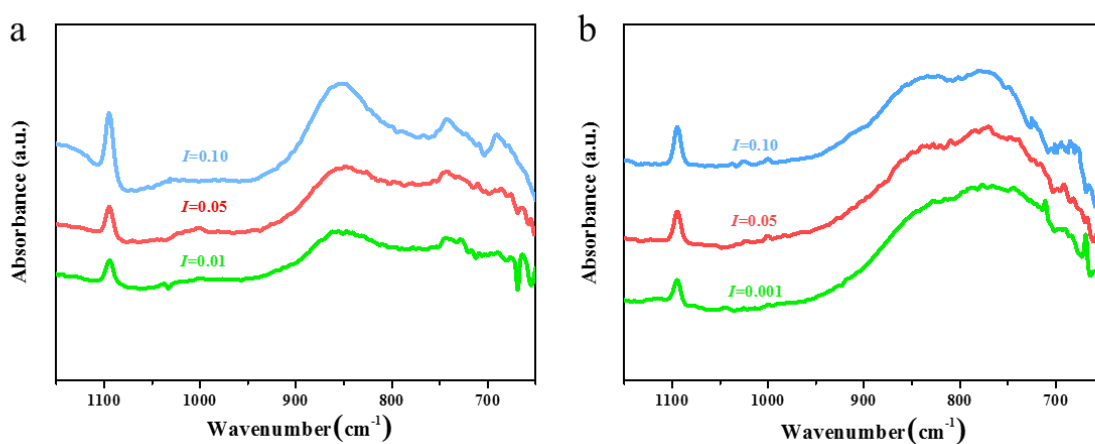
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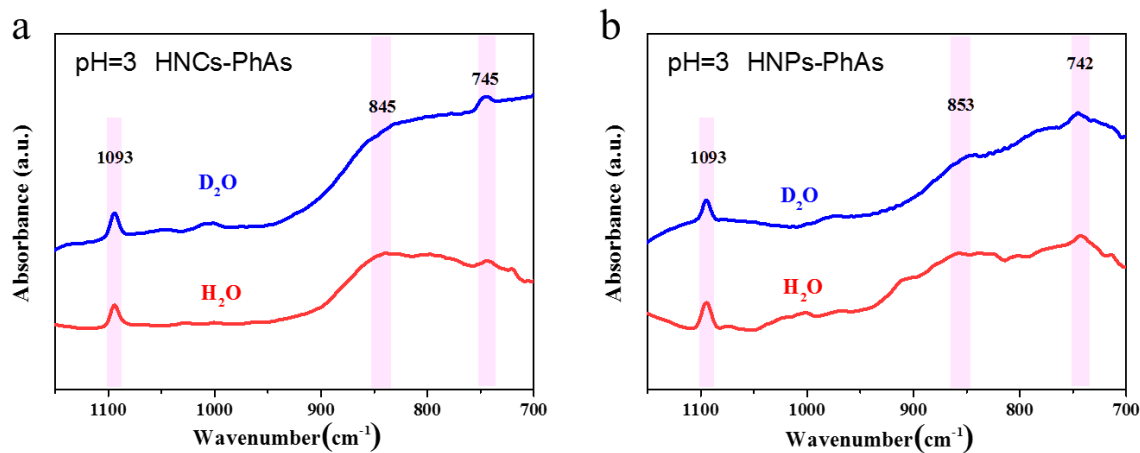
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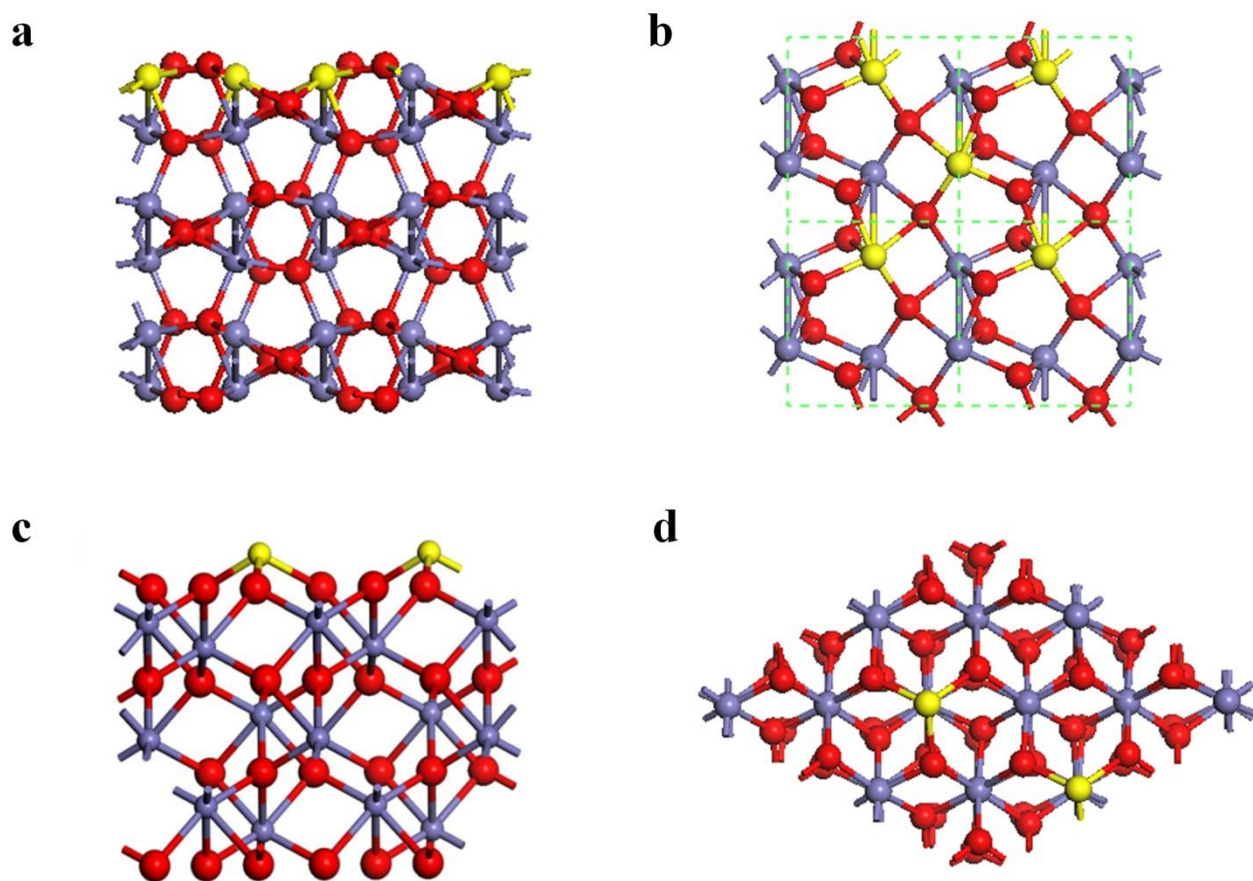
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Table S1. Comparison of morphological parameters of HNPs and HNCs.

Sample	Dominantly exposed facet	SSA (m²/g)	Length (nm)	Width (nm)	Height (nm)
HNPs	{001}	20.9	−	~79.3	~15.5
HNCs	{012}	20.4	~30.3	~30.3	~30.3

Table S2. The macroscopic adsorption kinetics parameters of PhAs onto the two types of hematite nanocrystals with different exposed facets.

| C (mg/L)	HNCs (SSA: 20.4 m²/g)			C (mg/L)	HNPs (SSA: 20.9 m²/g)		
	q_e (mg/m²)	k_2	R^2		q_e (mg/m²)	k_2	R^2
5	0.23	0.37	0.9995	5	0.22	0.0095	0.9831
10	0.46	0.015	0.9983	10	0.18	0.0089	0.9947
15	0.68	0.009	0.9998	15	0.33	0.0067	0.9864
20	0.82	0.006	0.9995	20	0.42	0.0038	0.991
25	0.89	0.004	0.9989	25	0.44	0.0031	0.9917
35	1.12	0.003	0.9994	35	0.49	0.0029	0.9928
50	1.24	0.002	0.9991	50	0.58	0.0016	0.9846

Table S3. Equilibrium adsorption isotherm fitting parameters.

entry	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	q_m (mg/m²)	R^2	K_F	n	R^2
HNPs	0.87	0.72	0.98	0.28	5.21	0.94
HNCs	0.10	1.49	0.99	0.44	3.86	0.94

Table S4. Best-fitted EXAFS parameters for As.

entry	shell	CN	R(Å)	σ^2 (Å^2)
HNCs	As-Fe	2	3.07	0.0059
	As-O	3	1.71	0.0010
	As-C	1	2.53	0.0019
HNPs	As-Fe	1	3.44	0.0031
	As-O	3	1.65	0.0054
	As-C	1	1.87	0.0010

Table S5. The IR frequencies and corresponding models from the FTIR spectra of different samples.

Samples	Models and IR frequencies (cm^{-1})			
PhAs (Solution)	Models	υ(aromatic C-H)	υ(As-O)	υ(As-C)
	IR frequencies	1098	985, 911, 877	770
PhAs-HNCs	Models	υ(aromatic C-H)	υ(As-O)	υ(As-OFe) or υ(As-OH)
	IR frequencies	1093	957, 905, 845, 827	776, 745, 720
PhAs-HNPs	Models	υ(aromatic C-H)	υ(As-O)	υ(As-OFe) or υ(As-OH)
	IR frequencies	1093	999, 905, 853, 826	763, 742

Table S6. Comparison of calculated inter-atomic distances and literature datas of bidentate binuclear (BB) and monodentate mononuclear (MM) complexes.

Bond	Theoretical data		Literature data	
	MM	BB	MM	BB
As-Fe1	4.68 Å	3.07 Å	4.66 Å	3.29 Å
As-Fe2	3.44 Å	3.07 Å	3.36 Å	3.29 Å
As-O1	1.52 Å	1.67 Å	1.62 Å	1.70 Å
As-O2	1.65 Å	1.67 Å	1.77 Å	1.71 Å
As-C	1.87 Å	1.90 Å	1.91 Å	1.91 Å
As-OH	1.79 Å	1.78 Å	1.82 Å	1.73 Å

Table S7. Calculated frequencies of organoarsenic-iron oxide clusters.

Complex structure	Frequencies (cm^{-1})	
	υ(As-O)	υ(As-OFe) or υ(As-OH)
BB	966, 906, 841	740, 710
MM	1005, 856, 826	763, 741