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Self-assembled one-dimensional MnO_2 @zeolitic imidazolate framework-8 nanostructures for highly efficient arsenite removal†

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Arsenite (As(III)) is more toxic and more difficult to remove from water than arsenate (As(V)). A pre-oxidation step is therefore necessary to achieve higher removal of As(III) . In this work, novel one-dimensional (1D) $\beta\text{-MnO}_2$ @ZIF-8 nanocomposites were successfully synthesized for the first time by a facile and rapid method to achieve concurrent oxidation and adsorptive removal of As(III) . In the synthesis step, the solution medium of methanol in the reaction plays a key role in reducing the interfacial energy and promotes the integration, leading to the deposition of ZIF-8 nanocrystals on $\beta\text{-MnO}_2$ nanowires. The synthesized $\beta\text{-MnO}_2$ @ZIF-8 exhibited a high surface area of $883 \text{ m}^2 \text{ g}^{-1}$. Batch experimental results showed that the as-obtained $\beta\text{-MnO}_2$ @ZIF-8 nanocomposites could oxidize As(III) to As(V) , exhibiting an improved adsorptive removal of arsenite compared to the ZIF-8 bulk. The kinetic and isotherm data of As(III) adsorption on $\beta\text{-MnO}_2$ @ZIF-8 nanocomposites were well fitted by pseudo-second-order and Langmuir models, respectively. The maximal adsorption capacity of As(III) was 140.27 mg g^{-1} at room temperature. Meanwhile, the unique 1D nanostructure of $\beta\text{-MnO}_2$ @ZIF-8 prevented ZIF-8 agglomeration in the aqueous solution. Moreover, the $\beta\text{-MnO}_2$ @ZIF-8 nanowires showed excellent settleability by gravity alone and strong mechanical stability.

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1. Introduction

Arsenic contamination has attracted growing concern globally because of its high toxicity and carcinogenicity, which shows a great threat to human health. Therefore, the maximum contaminant level of arsenic in drinking water is stringently limited at $10 \mu\text{g L}^{-1}$ by the World Health Organization.^{1–3} By comparing various technologies, adsorption is considered as a promising approach as a result of its easy maintenance, low cost and the availability of a wide range of adsorbents.^{4–8} Arsenic exists in two predominant species, namely, arsenite (As(III)) and arsenate (As(V)). Compared to As(V) , As(III) is more toxic, more mobile, and harder to remove due to its poor affinity for various adsorbents. With regard to this, the conversion of As(III) to As(V) by pre-oxidization is favoured to achieve effective As(III) removal.⁹ However, apparently, it is more desirable to develop an adsorbent with capabilities of both oxidation and adsorption for efficient removal of As(III) .^{10–12}

In recent years, metal–organic frameworks (MOFs) assembled by metal ions with organic ligands have attracted growing interest in many applications including water treatment due to their porous properties and tailorable chemistry.^{13–15} The highly uniform distribution of pores is ideal for trapping guest molecules and forcing them to participate in chemical coordination in some cases. Specifically, the target solvents generally have strong interactions with the organic ligands of MOFs for their diversified functional groups. In this respect, MOFs have been investigated in removing inorganic and organic pollutants in water with excellent capacity.^{16–18} However, in most cases, MOFs alone are unable to oxidize As(III) to As(V) and cannot achieve concurrent oxidation and adsorptive removal of As(III) .

On the other hand, despite of the merit of MOF materials, the removal of MOF nanoparticles from aqueous solution after adsorption has been a challenge due to their nanoscale size. Inadequate separation poses a risk of secondary contamination. Although magnetic separation, centrifugation and membrane filtration have been employed to separate nanomaterials, these methods are unfeasible for scalable production and are costly.¹⁹ Therefore, design and construction of advanced adsorption materials, which could not only achieve an outstanding As(III) removal but also overcome the separation difficulty by using an environmentally friendly method, is of great scientific and technical significance.

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In this work, we introduce a surfactant-free strategy to synthesize one-dimensional (1D) MnO_2 @MOFs nanowires (NWs) by assembling water-stable zeolitic imidazolate framework-8 (ZIF-8) nanoparticles (a subclass of MOFs) on the surface of β - MnO_2 NWs. A well-defined MnO_2 @ZIF-8 nanostructure was obtained for the first time by regulating the MnO_2 NW dosage into the precursor solutions of ZIF-8. Furthermore, we found that the solution medium plays a critical role in the formation of MnO_2 @ZIF-8 NWs. Such novel 1D composites were then applied in As(III) removal, exhibiting an enhanced adsorption capacity of As(III) compared to that on pristine ZIF-8 particles, as well as manifesting an excellent settleability under gravity alone in water.

2. Experimental section

2.1 Materials

$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-methylimidazole (2-MeIm) and polyvinylpyrrolidone (PVP K30, average Mw 40 000) were purchased from Sigma Aldrich. NaAsO_2 , NaOH, KOH, HCl, HNO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, NH_4Cl , KMnO_4 , sodium dodecylbenzenesulfonate (SDBS), *N,N*-dimethylformamide (DMF), methanol and ethanol were purchased from Beijing Chemical Works (China). Degussa P25 powder was kindly donated by Degussa Corp. All chemicals were of analytical grade and used as received without further purification.

2.2 Synthesis of 1D NWs

MnOOH NWs and β - MnO_2 NWs. Ultrathin MnOOH and β - MnO_2 NWs were synthesized as reported previously.²⁰ For MnOOH NW synthesis, 769 mg of SDBS and 444 mg of PVP K30 were dissolved in 70 mL of ultra-pure water under vigorous stirring until the solution was clarified. Subsequently, 203 mg of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 126.4 mg of KMnO_4 were added to the above mixture under continuous stirring until completely dissolved. The resulting dark solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 6 h and then naturally cooled down to room temperature. The obtained brown precipitates were collected by centrifugation at 8000 rpm for 10 min and washed several times with distilled water and methanol. Finally, the sample was obtained after a freeze-drying process for 2 days.

To obtain β - MnO_2 NWs, the dried MnOOH NWs were redispersed in 2 M NaOH and heated in a Teflon-lined stainless steel autoclave at 180 °C for 36 h and finally calcined at 300 °C for 2 h in a muffle furnace.

α - MnO_2 NWs. α - MnO_2 NWs were prepared according to Wang's method.²¹ 0.04 M KMnO_4 and 0.04 M NH_4Cl aqueous solutions were mixed in a 1:1 volume ratio with a total volume of 40 mL. The mixed solution was then magnetically stirred under ambient conditions for 30 min in a 50 mL Teflon-lined stainless-steel autoclave. The hydrothermal synthesis was conducted at 200 °C for 24 h. The resulting brown cotton-like product was collected by centrifugation at 8000 rpm for 10 min and washed several times with distilled

water. The sample was obtained eventually after being freeze-dried for 2 days.

TiO_2 NWs. TiO_2 NW synthesis is based on Zhang's approach.²² 0.2 g of commercial Degussa P25 powder was mixed with aqueous 10 M KOH. Then, 30 mL of the mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C under autogenous pressure for 48 h and then cooled to room temperature naturally. The obtained sample was collected by centrifugation at 8000 rpm for 10 min and washed several times with dilute HCl aqueous solution and deionized water until the pH value of the washing solution was about 7 before being calcined at 550 °C.

2.3 Synthesis of MnO_2 @ZIF-8 NWs

The assembling procedure for MnO_2 @ZIF-8 hybrids was carried out in methanol medium.²³ Firstly, 5 mL of 2-MeIm methanol solution (0.8 M) was transferred in a 20 mL capped scintillation vial. Then, 5 mL of β - MnO_2 NWs (2 mg mL^{-1} in absolute methanol solution) were added dropwise under continuous stirring at 800 rpm at room temperature. Afterwards, 5 mL of zinc methanol solution (0.1 M) was rapidly poured into the above mixture before sealing the vial tightly with a cap. Finally, the well-defined 1D MnO_2 @ZIF-8 NWs can be obtained after 2 h stirring. The resulting product was collected by centrifugation and then washed 3 times with methanol. Finally, the sample was dried by a freeze-drying process for 2 days. Other β - MnO_2 NW concentrations (1 and 3 mg mL^{-1}) were prepared to investigate the integrity effect of the products. The preparation procedures for MnOOH @ZIF-8, α - MnO_2 @ZIF-8 and TiO_2 @ZIF-8 NWs were the same as that for the MnO_2 @ZIF-8 NWs previously described, except that different nanowires were used. The synthetic strategies of MnO_2 @ZIF-8 NWs in DMF and ethanol solvents are the same as that in methanol. However, for that in aqueous solution, the 2-MeIm concentration was increased to 3.5 M to form ZIF-8 particles according to our previous investigation.²⁴

2.4 Characterization

Power X-ray diffraction (XRD) patterns were recorded on a diffractometer (AXS, Bruker, Germany) with a Cu target (40 kV, 40 mA, $\lambda = 1.54059 \text{ \AA}$) from 3° to 80° at a scan rate of 2° min^{-1} with a step size of 0.02° . The surface morphologies of the products were examined by scanning electron microscopy (SEM) (SU-8020, Hitachi, Japan) operated at an acceleration voltage of 1–15 kV in a high vacuum mode. Samples were mounted using conductive carbon double-sided sticky tape. A thin (*ca.* 10 nm) coating of gold was sputtered onto the samples to reduce the effects of charging. Transmission electron microscopy (TEM) (JEOL JEM-2010F; H-7500, Hitachi) was carried out at 120 kV and 200 kV modes, respectively. Thermogravimetric analysis (TGA) curves were recorded on a Netzsch instrument (STA 449 F3), running from room temperature to 1000 °C with a scan rate of $10^\circ \text{ C min}^{-1}$ under a steam of air. The nitrogen adsorption isotherms were measured at

liquid nitrogen temperature (77 K) using a gas adsorption analyzer (ASAP2020HD88; Micromeritics, USA); the sample was degassed at 150 °C for 3 h under vacuum prior to measurement. The surface area was then calculated using the Brunauer–Emmett–Teller (BET) method based on adsorption data. The functional groups of the products were identified by Fourier transform infrared spectroscopy (FT-IR) (Tenson 27; Bruker, Germany) in transmission mode. The zeta potentials were determined using a particle size and zeta-potential analyzer (DelsaNano C, Beckman Coulter Ltd., USA). X-ray photoelectron spectra (XPS) were determined by using an AXIS Ultra spectrometer (Kratos Analytical, Manchester, UK) with an Al K anode (1486.6 eV photon energy, 0.05 eV photon energy resolution, 300 W); it is worth noting that the 1D MnO_2 @ZIF-8 hybrids were sonicated for 30 min to peel off the attached ZIF-8 particles before MnO_2 species XPS measurement in order to meet the requirement of detecting depth. Inductively coupled plasma atomic emission spectroscopy (ICP) measurements (Optima 8300, Perkin Elmer Co., USA) were performed to determine the loadings of ZIF-8 in the samples based on zinc. Before measurements, dried samples were dissolved in a mixture of HCl and HNO_3 with a volume ratio of 3 : 1 overnight. A freeze-drying process was performed in a freeze dryer (Freezone 2.5 L, Labconco Corporation, USA) to avoid MnO_2 @ZIF-8 hybrids from aggregating by adding a small amount of de-ionized water prior to freezing.

2.5 Details of the adsorption experiment

As(III) stock solutions were prepared by dissolving NaAsO_2 in ultra-pure water and stored in the dark at 4 °C. Stock solutions were then diluted with ultra-pure water to predetermined concentrations for the following experiments. All volumetric flasks and vessels were cleaned by soaking in 10% HNO_3 for at least 24 h and rinsed several times with de-ionized water. Before adsorption experiments, $\beta\text{-MnO}_2$ NWs and ZIF-8 nanoparticle suspensions were treated in an ultrasonic bath for 10 min to avoid aggregation. MnO_2 @ZIF-8 NWs after freeze-drying are highly dispersed in water.

Adsorption isotherm experiments were conducted in 250 mL shaking flasks containing 100 mL of As(III) solution. The initial concentration of As(III) varied from 5 mg L^{-1} to 130 mg L^{-1} . The pH of the As(III) solution was adjusted to 7.0 ± 0.1 with diluted HCl and NaOH. After 20 mg of adsorbents was added to the As(III) solution, these flasks were shaken at 170 rpm for 24 h at 25.0 ± 1 °C. Each isotherm test was performed in triplicate, and the mean value was reported.

All adsorption isotherm data were fitted with Langmuir and Freundlich isotherm models.

The Langmuir isotherm:²⁵

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

The Freundlich isotherm:²⁶

$$Q_e = K_F C_e^{1/n}$$

where Q_e is the amount of adsorbed As(III) per gram of sorbent (mg g^{-1}); C_e is the equilibrium concentration of the adsorbate in the solution (mg L^{-1}); Q_m is the maximum amount of adsorbate uptake per unit mass of the sorbent (mg g^{-1}); K_L is the Langmuir equilibrium constant (L mg^{-1}); K_F is the relative adsorption capacity (mg g^{-1}) in Freundlich equilibrium and n is the intensity of adsorption.

The adsorption kinetic tests were performed in a glass beaker, which contained 500 mL of As(III) solution. The initial concentrations of As(III) in the solution were 8 and 40 mg L^{-1} . The pH of the As(III) solution was adjusted to 7.0 ± 0.1 using diluted HCl and NaOH solutions. After 0.1 g of sorbent was introduced into the glass beaker, the solution was mixed by using a magnetic stirrer at 170 rpm. The kinetic tests were run for 24 h, and approximately 4 mL of suspension was taken at specific time intervals to measure the As(III) concentration.

The kinetic data of adsorbents were fitted by a pseudo second-order kinetic model, which can be expressed as:²⁷

$$\frac{t}{Q_t} = \frac{1}{V_0 Q_e^2} + \frac{1}{Q_e} t$$

where V_0 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{h}^{-1}$), Q_e is the amount of As(III) ions adsorbed at equilibrium (mg g^{-1}), and Q_t is the amount of As(III) ions on the adsorbents at time t (h) (mg g^{-1}). Linear least-squares regression analysis was applied to acquire the best estimation of the constants for the model in arsenic adsorption kinetic tests.

3. Results and discussion

The synthesis process of MnO_2 @ZIF-8 NWs is illustrated in Scheme 1. Briefly, ultrathin tetragonal phase $\beta\text{-MnO}_2$ NWs (with an average diameter of 21 nm) were prepared *via* a hydrothermal reaction (Fig. S1, ESI†). The as-synthesized $\beta\text{-MnO}_2$ NWs were first dispersed in methanol solution by using a sonication process to obtain a certain concentration of $\beta\text{-MnO}_2$ -methanol solution with a brown color. Afterwards, a certain volume of $\beta\text{-MnO}_2$ solution was added dropwise under stirring into the 2-methylimidazole (2-MeIm) precursor solution. Subsequently, $\text{Zn(NO}_3)_2$ -methanol solution was

Scheme 1 Schematic illustration of the synthetic process of the MnO_2 @ZIF-8 NWs.

Fig. 1 (a) SEM image of the as-synthesized MnO_2 @ZIF-8 NWs; (b and c) TEM and HRTEM images; inset in (c) shows the corresponding SAED image. (d) XRD patterns of the products by controlling different MnO_2 NW additions.

poured into the above mixture rapidly. Finally, well-defined MnO_2 @ZIF-8 NWs were obtained with continuous stirring for 2 h at room temperature.

The scanning electron microscopy (SEM) image in Fig. 1a shows that ZIF-8 particles densely and homogeneously attached on the surface of MnO_2 NWs. In other words, MnO_2 NWs can act as templates that induce ZIF-8 particles approaching. Moreover, the MnO_2 NWs maintained their quite long length after ZIF-8 nanoparticles were attached, indicating the high mechanical strength of the MnO_2 NWs. The transmission electron microscopy (TEM) image of the MnO_2 @ZIF-8 NWs reveals that the thickness of the ZIF-8 shell is 30 ± 5 nm (Fig. 1b). Further, the high-resolution TEM (HRTEM) image in Fig. 1c also demonstrates that the crystal structure of β - MnO_2 NWs remained after the assembling process, evidenced by the consistent lattice spacing of 0.32 nm. Meanwhile, the selected-area electron diffraction (SAED) patterns yielded $\{110\}$, $\{101\}$ and $\{200\}$ zone axes which match those of the pristine β - MnO_2 NWs (inset) (Fig. S1, ESI†). The powder X-ray diffraction (XRD) patterns confirm that such 1D nanostructures are composed of MnO_2 (JCPDS number: 24-0735) and ZIF-8 (Fig. 1d). The prominent peaks of MnO_2 in MnO_2 @ZIF-8 composites start to be remarkable with increasing content. Different concentrations of MnO_2 NWs in the synthesis step significantly affect the morphology of the resultant MnO_2 @ZIF-8 composites (Fig. S2, ESI†). Part of the ZIF-8 particles self-aggregated in the solution when insufficient MnO_2 NWs (1 g L^{-1}) were added, while MnO_2 NWs were

not fully covered by ZIF-8 nanoparticles when excess MnO_2 NWs (3 g L^{-1}) were used. Therefore, the MnO_2 @ZIF-8 composites synthesized at the optimal MnO_2 concentration of 2 g L^{-1} were used in the following experiments.

N_2 sorption isotherms of the MnO_2 NWs before and after ZIF-8 attachment are compared (Fig. 2a). The N_2 sorption curve for MnO_2 @ZIF-8 NWs exhibits a type-I isotherm, which is the same as that of ZIF-8. However, the BET surface area of MnO_2 @ZIF-8 NWs is calculated to be $883 \text{ m}^2 \text{ g}^{-1}$, which is lower than that of the ZIF-8 particles (Table 1). This is because of the less porous MnO_2 NW cores whose surface area is only $37 \text{ m}^2 \text{ g}^{-1}$. Furthermore, the thermal stability of MnO_2 @ZIF-8 NWs was tested by thermogravimetric analysis (TGA). MnO_2 @ZIF-8 NWs show a very similar tendency to ZIF-8 particles (Fig. 2b). For ZIF-8, a sharp weight loss from 250 to 600 °C was observed, which is mainly because of the decomposition of 2-MeIm and its structural collapse. Therefore, the sacrificial weight of MnO_2 @ZIF-8 NWs is reasonable considering that derived from the ZIF-8 shell between 250 and 600 °C. In contrast, MnO_2 NWs are relatively stable in the high temperature. In addition, the ZIF-8 loading rate (wt%) for MnO_2 @ZIF-8 NWs with moderate MnO_2 NWs was analyzed at 64% by ICP analysis (Table S1, ESI†). This value lies very close to the weight loss result of MnO_2 @ZIF-8 NWs from TGA data.

To gain knowledge of the growth process, we carried out a growth kinetic study (Fig. 3). The assembling reaction is very rapid. At the very initial period of 20 s, homogeneous

Fig. 2 (a) Nitrogen adsorption-desorption isotherms and (b) TGA curves of ZIF-8 nanoparticles, β -MnO₂ NWs and MnO₂@ZIF-8 NWs.

Table 1 N₂ gas adsorption-desorption analyses of the ZIF-8 nanoparticles, β -MnO₂ NWs and MnO₂@ZIF-8 NWs

	Samples		
	ZIF-8	β -MnO ₂ NWs	MnO ₂ @ZIF-8 NWs
Surface area (m ² g ⁻¹)	1310	37	883
Pore volume (cc g ⁻¹)	1.17	0.16	0.98

nucleation did not occur in the solution. Instead, ZIF-8 nuclei were formed on the top surface of MnO₂ NWs. Then, crystal growth was observed within 1 min. In addition, well-defined MnO₂@ZIF-8 NWs can be obtained within 5 min. The whole procedure evidences a highly efficient protocol. On the other hand, the thickness of the ZIF-8 shell can be tuned by regulating the concentration of the ZIF-8 precursor (Fig. S3, ESI†). However, we notice that the solvent category exerted a strong

influence on the ZIF-8 assembling (Fig. S4, ESI†). Like methanol, ethanol elicits a positive role in forming uniform MnO₂@ZIF-8 NWs. On the contrary, homogeneous nucleation for ZIF-8 nanoparticles occurred in water and DMF solvent, which means the newly ZIF-8 seeds tend to approach their own parent phase to self-aggregate together in the both solvents.

In the liquid phase, heterogeneous nucleation should occur easily, since a stable nucleating surface is already present. Nevertheless, the lattice mismatch between ZIF-8 and β -MnO₂ is calculated to be 36.28%, which is too high for the growth of a core-shell structure because of a large interfacial energy (Table 2 and Fig. S5, ESI†).²⁸ In this case, ZIF-8 nuclei prefer to self-aggregate together to minimize surface energy for subsequent growth.²⁹ While methanol as protic solvent provides opportunities for forming hydrogen bonds with MnO₂ NWs, this results in lowering the surface energy of

Fig. 3 Growth kinetics of the MnO₂@ZIF-8 NWs in methanol solution. Scale bars: 500 nm.

Table 2 Summary of lattice mismatches of different hybrid 1D core-shell nanostructures reported here

Core	β -MnO ₂ (110)	MnOOH (111)	α -MnO ₂ (211)	TiO ₂ (101)
Shell	ZIF-8 (110)	ZIF-8 (110)	ZIF-8 (110)	ZIF-8 (110)
Mismatch (%)	36.28	12.62	38.97	31.77

Fig. 4 Proposed mechanism for the formation of MnO₂@ZIF-8 NWs in methanol solution.

MnO₂ NWs and facilitating the subsequent hetero-growth of ZIF-8 nanoshells (Fig. 4).^{30–32} Consequently, the newly formed ZIF-8 nuclei on the surface of β -MnO₂ NWs grow until completely covered. According to this viewpoint, we also successfully prepared well-assembled MnOOH@ZIF-8, α -MnO₂@ZIF-8 and TiO₂@ZIF-8 NWs in methanol solution despite of the large lattice mismatches between them (Fig. S6, ESI†). Meanwhile, we reasonably exclude the polyvinylpyrrolidone (PVP) effect and the probable contributions of chemical coordination between MnO₂ and 2-MeIm or zinc

on the formation of MnO₂@ZIF-8 NWs. In the FTIR spectra of the β -MnO₂ NWs, no PVP characteristic peaks could be observed. Moreover, the surface properties of MnO₂ NWs after immersion in the individual precursors of ZIF-8 are similar to their pristine conditions (Fig. S7, ESI†).

The adsorption experiments were carried out to evaluate the As(III) removal capacity of MnO₂@ZIF-8 NWs in aqueous solution. It is noted that there is no significant difference between ZIF-8 particles and MnO₂@ZIF-8 NWs in As(III) removal when the initial As(III) concentration is lower than 20 mg L⁻¹. However, MnO₂@ZIF-8 NWs start to show a better adsorption ability of As(III) than that of ZIF-8 at a relatively high As(III) level. The As(III) adsorption behaviour on MnO₂@ZIF-8 NWs can be well fitted by the Langmuir model (Fig. 5a). The As(III) adsorption capacity of MnO₂@ZIF-8 NWs is calculated to be 140.27 mg g⁻¹, which is about 1.6 times higher than that of pristine ZIF-8 nanoparticles (90.8 mg g⁻¹) (Fig. 5a and Table S2, ESI†). The adsorption capacity of As(III) for MnO₂@ZIF-8 NWs is competitively larger than those of reported arsenic adsorbents (Table 3).

The higher As(III) uptake on MnO₂@ZIF-8 NWs should be attributed to the oxidation ability of MnO₂ NWs in the core. Our previous study has revealed that ZIF-8 has a high pH_{IEP}

Fig. 5 (a) Fitted adsorption isotherms of As(III) on (1) MnO₂@ZIF-8 NWs, (2) ZIF-8, and (3) β -MnO₂ NWs (the solid curve represents the Langmuir model, while the dashed curve indicates the Freundlich model). (b) Photographs of two vials containing MnO₂@ZIF-8 NWs and ZIF-8 nanoparticles after gravity settling for 0.5 h in aqueous solution, respectively. (c) Schematic illustration of the As(III) removal process on MnO₂@ZIF-8 NWs. The blue part represents ZIF-8 particles, and the red particles stand for As(III) ions.

Table 3 Comparison of As(III) adsorption capacity with various adsorbents in the references

Adsorbents	pH	Concentration range (mg L ⁻¹)	As(III) $Q_{\max}$ (mg g ⁻¹)	Reference
GN- α -FeOOH aerogel	8.0	1–16	13.42	3
Fe–Mn binary oxide	6.9	0–40	100.4	11
MnO ₂ /activated alumina	7.0	0–250	19.63	33
SnO ₂ nanospheres	7.0	0.5–100	112.7	34
CuO nanoparticles	8.0	0.1–100	26.9	35
ZrO ₂ ·xH ₂ O	7.0	0.3–100	47.1	36
γ -Fe ₂ O ₃ nanoparticles	6.0	0.1–600	320.0	37
Fe–Cu binary oxide	7.0	5–60	122.3	38
Magnetic Fe–Mn binary oxide	6.5	0.5–40	56.1	39
MnO ₂ @ZIF-8 NWs	7.0	5–130	140.27	This study

of 9.6, and As(v) can be easier adsorbed *via* electrostatic attraction than As(III) on ZIF-8.⁴⁰ To confirm the oxidation of As(III) on MnO₂@ZIF-8 NWs, XPS was conducted to measure the elemental species. As shown in Fig. 6, the Mn 2p spectra had no obvious change after reaction with As(III). Nevertheless, we can clearly see that the intensity of the Mn 2p peaks decreased after As(III) adsorption. In terms of O 1s spectrum, a significant decrease in the Mn–O–Mn bond at 529.9 eV after As(III) adsorption was also observed, and a Mn–O–H peak at 531 eV became notable. This indicates that As(III) has stronger interactions with O than that with the Mn atom. Similar results were also reported by Zhang *et al.*'s study on the removal of As(III).⁴¹ Noticeably, an As 3d line after adsorption was detected and was fitted well with two components having binding energies at 44.2 and 45.2 eV which are assigned to As(III) and As(v) in arsenic oxides, respectively.^{42,43} This result confirms that the oxidation of As(III) to As(v) oc-

curred on MnO₂ NWs. The redox reaction pathway can be briefly represented as follows:

Owing to the As(v) species that are more active and negatively charged at pH = 7, they can be more readily removed from water by adsorbents (Fig. 5a).³ On the other hand, the aperture pore of ZIF-8 is 3.4 Å; however, the hydrated diameter of As(III) is too large to fit through the ZIF-8 shell (7.70 Å).^{44,45} We therefore speculate that gap defects between the ZIF-8 crystals may exist, leading to As(III) diffusion into the interior (Fig. 5c). In fact, the defect problem has been recognised in the MOF-based membrane field.^{46–49} To better understand the As(III) diffusion process, the adsorption kinetics were conducted on ZIF-8 and MnO₂@ZIF-8 NWs at two different As(III) concentrations, respectively (Fig. 7). An

Fig. 6 High-resolution XPS spectra of (a) Mn 2p, (b) As 3d, and (c and d) O 1s before and after As(III) adsorption.

Fig. 7 Adsorption kinetics of ZIF-8 and MnO₂@ZIF-8 NWs in the low concentration range of 8 mg L⁻¹ and in the high concentration range of 40 mg L⁻¹.

interesting phenomenon was found in which the kinetic curves of both adsorbents almost overlap at a low initial As(III) concentration of 8 mg L⁻¹. This means that the adsorption rates of As(III) on both adsorbents at low As(III) concentrations are similar, indicating that sufficient adsorption sites are available on both adsorbents for As(III) adsorption. Nevertheless, the adsorption rate of MnO₂@ZIF-8 NWs became slower than that of the ZIF-8 adsorbent when the As(III) concentration is 40 mg L⁻¹, according to the value of the adsorption rate constant k (Fig. 7 and Table S3, ESI†). This can be explained as follows: when the external binding sites were occupied gradually until saturation on both adsorbents at a high As(III) concentration, the internal diffusion becomes the dominant rate limiting step during the adsorption process. Compared with MnO₂@ZIF-8 composites where ZIF-8 compacted along 1D MnO₂ NWs, ZIF-8 particles tend to self-agglomerate as a porous bulk in water (Fig. S8 and S9, ESI†), in which the higher As(III) gradient driving the As(III) ions more readily adsorbed the internal binding sites of the ZIF-8 bulk (Fig. 5c and S9, ESI†). As a result, MnO₂@ZIF-8 NWs had a higher adsorption capacity than ZIF-8 particles due to the adsorption-oxidation process, while their adsorption rate is slightly slower than the latter.

Apart from the enhanced removal performance of As(III), MnO₂@ZIF-8 NWs also exhibit an excellent settling velocity under gravity after adsorption. It was observed that after 30 min of settling, the MnO₂@ZIF-8 NWs were well settled, leaving a clear supernatant in the vial. By comparison, ZIF-8 nanoparticles suspended stably in the aqueous solution (Fig. 5b). In addition, MnO₂@ZIF-8 NWs still maintained their morphology after As(III) adsorption, which indicates that they have stability and good mechanical strength (Fig. S10, ESI†).

4. Conclusions

In summary, we have synthesized high quality 1D MnO₂@ZIF-8 nanostructures by a simple and rapid method. The formation mechanism of the as-synthesized hybrid has been investigated, where the solvent medium plays a key role in the assembling. Methanol is beneficial to decrease the interfacial energy during the integration reaction. The

as-obtained MnO₂@ZIF-8 NWs exhibited a superior removal capacity of As(III) with the maximal adsorption capacity of As(III) of 140.27 mg g⁻¹ at room temperature. Compared with the pristine ZIF-8 adsorbent, the oxidation of As(III) by MnO₂ NWs in the core results in the improved As(III) removal performance on MnO₂@ZIF-8 NWs. Furthermore, the efficient adsorbent can be easily separated from water owing to its excellent settlement rate. We therefore believe that the 1D novel hybrids will make it possible for their potential application in arsenic removal.

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