Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Construction of a novel cuboid-shape Mn-Urea nanozyme with arsenic(V)-enhanced oxidase-like activity as a colorimetric probe for the selective detection of inorganic arsenic

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Table of contents

Experimental Section

Reagents and Chemicals

Manganese chloride ($MnCl_2·4H_2O$, >99.0%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) (https://www.aladdin-e.com/). Urea (H_2NCONH_2, ⩾ 99.5%) and copper (II) sulfate pentahydrate ($CuSO_4·5H_2O$, >99.0%) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. (Chongqing, China) (https://www.cd1958.com/). Cobalt (II) chloride hexahydrate ($CoCl_2·6H_2O$, AR) and sodium carbonate (Na_2CO_3, >98%) were obtained from Shanghai Titan Scientific Co., Ltd. (Shanghai, China) (https://www.titansci.com/us.jsp). Arsenic (V) standard solution (As(V), 1001 μg/mL) and Arsenic (III) standard solution (As(III), 1000 μg/mL) were purchased from Beijing North Weiye Metrology Research Institute. N-ethylmaleimide (NEM, >98.0%), ferric chloride hexahydrate ($FeCl_3·6H_2O$, >99.0%) and cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, >99.0%) were purchased from Macklin (Shanghai, China) (http://www.macklin.cn/). Acetic acid (HAc, >99.0%), sodium acetate (NaAc, >99.0%), isopropanol (IPA, ≥99.7%), sodium chloride (NaCl, ≥99.5%), potassium chloride (KCl, ≥99.5%), sodium bicarbonate ($NaHCO_3$, ≥99.5%), ethanol (≥99.7%), lead nitrate ($Pb(NO_3)_2$, >98%), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$, >98.0%), and magnesium sulfate heptahydrate ($MgSO_4·7H_2O$, >98.0%) were purchased from Chengdu Chron Chemicals Co., Ltd. (Sichuan, China) (http://www.chronchem.com/en/). The 3,3′,5,5′-tetramethylbenzidine (TMB, >98.0%) was purchased from Adamas-beta (Shanghai, China) (http://www.adamas-beta.com). *P*-benzoquinone (PBQ, >99.0%) and potassium phosphate (K_3PO_4, AR) were purchased from Meryer Biochemical Technology Co., Ltd. (Shanghai, China) (https://www.meryer.com). Water used for all the experiments was purified by a water purification system (ATSelem 1820A, Antesheng Environmental Protection Equipment Co., Ltd., Chongqing, China) (http://www.atshb.com/). All chemicals were of analytical grade, and used as received without further purification.

Apparatus and Measurements

Transmission electron microscopy (TEM) images and element distribution analysis were recorded using a JEM 2100 (JEOL Ltd. Tokyo, Japan, https://www.jeol.co.jp/en/) electron microscope working at 200 kV, which is equipped with an energy dispersive X-ray spectrometer (EDX). Thermogravimetric analysis (TGA) was carried out on the Mettler TGA/DSC1/1600LF (Mettler-Toledo AG, Analytical, Switzerland, https://www.mt.com/cn/zh/home.html) from 30 °C to 800 °C at a heating rate of 10 $K \cdot min^{-1}$ under N_2 gas flow. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Tensor 27 spectrometer (Bruker, USA, https://www.bruker.com/) between 4000 cm^{-1} and 400 cm^{-1} in KBr media. X-ray diffraction (XRD) patterns were obtained using a X'pert Powder diffractometer (Malvern Panalytical Ltd., Netherlands, https://www.malvernpanalytical.com/en/) with secondary beam graphite monochromated Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Kalpha system using monochromatic Al Ka radiation (1486.6 eV), and the obtained binding energies were referenced to the C 1s line set at 284.8 eV. UV-Vis absorption spectra were recorded using a UV-8000 spectrophotometer (Shanghai Yuanshan Instrument Co., Ltd, Shanghai, China, https://www.metash.com).

Table S1 Comparisons on the kinetic constants of different nanozymes with oxidase-like activity.

Nanozyme	Substrate	K_m (mM)	V_{max} (10^{-8} Ms^{-1})	Ref.
OV-Mn_3O_4 NFs	TMB	1.6	3.97	[1]
Pd cubes		0.43	1.8	[2]
Cu-Pt		0.29	0.75	[3]
Fe-Co-LDH		0.34	5.4	[4]
AP-Cu nanozyme		2.49	3.73	[5]
UMnzyme		0.18	5.89	This work

K_m and V_{max} are the Michaelis constant and the maximum reaction velocity, respectively.

Table S2 Comparisons on the colorimetric detection of As(V) with previously reported methods.

Material	Target	Linear range (μg/L)	LOD (μg/L)	Ref.
CoOOH nanoflakes	As(V)	4−500	3.72	[6]
AgNPrs	As(III)	5−1000	5	[7]
Fe-Co-LDH	As(III)	7.5−625	2.63	[4]
–	As(V)	8−100	8	[8]
UMnzyme	As(V)	12.5–75 and 75–250	2.4	This work

Table S3 Detection of As(V) in environmental water samples.

Samples	Added (μg/L)	Found (μg/L)	Recovery (%) [a]	RSD (%) (*n*=3)
Yun Lake	0	0[b]	–	–
	25.0	23.6	94.1	8.2
	62.5	64.7	103.5	0.4
	125.0	129.5	103.6	4.2
Jin Lake	0	0	–	–
	25.0	22.4	89.5	4.4
	62.5	59.3	94.9	1.6
	125.0	128.0	102.4	3.6

[a] Recovery = (found concentration-original concentration) ×100%/added concentration

[b] The detection value is lower than the quantification limit of this method

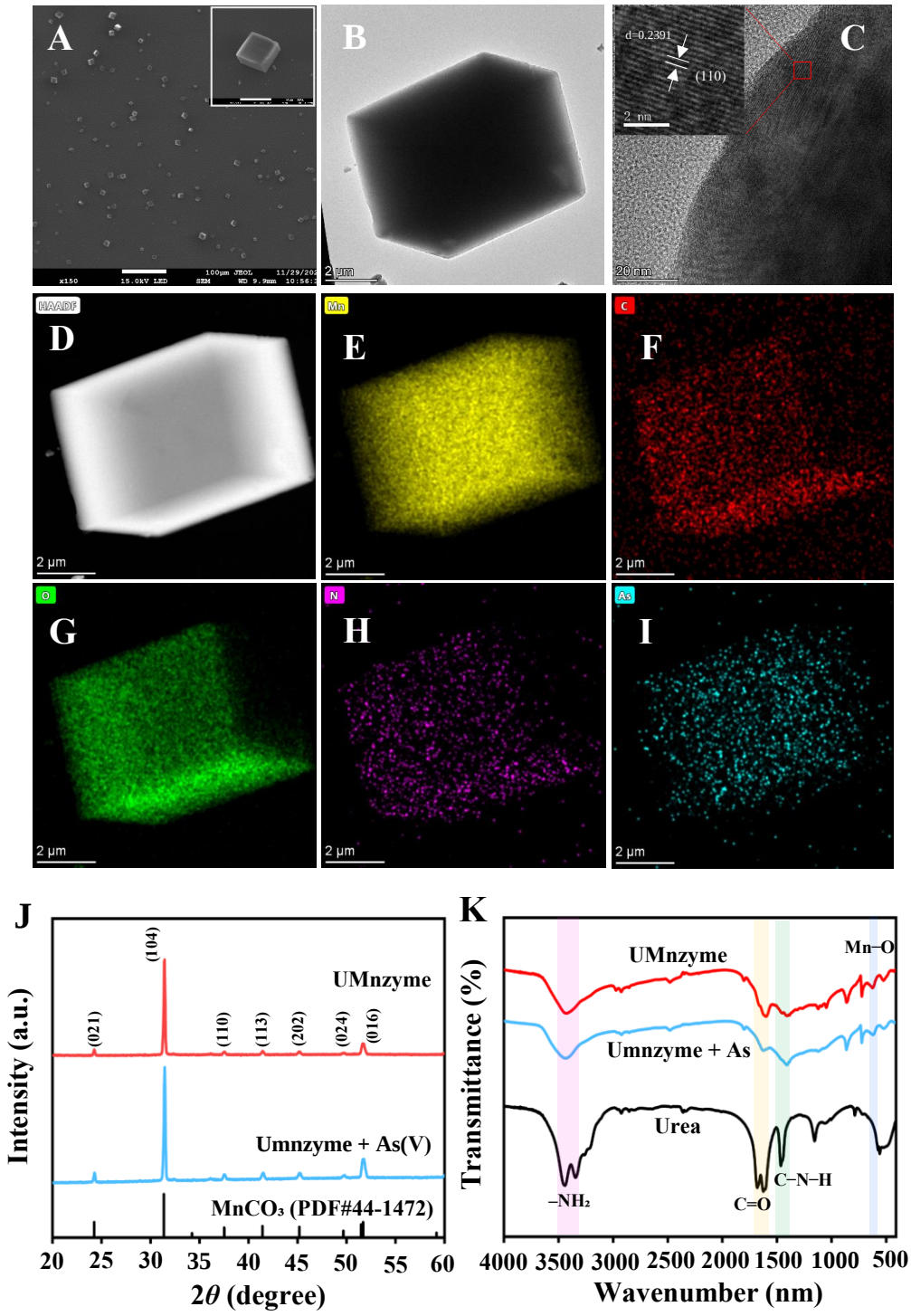

Fig. S1 (A) SEM images of UMnzyme after incubation with As(V); (B) TEM and (C) HRTEM images of UMnzyme after incubation with As(V); (D–I) EDS mapping images: elemental mapping of corresponding (E) Mn, (F) C, (G) O, (H) N, and (I) As; (J) XRD patterns of UMnzyme before and after incubation with As(V); and (K) FT-IR spectra of urea, and UMnzyme before and after incubation with As(V).

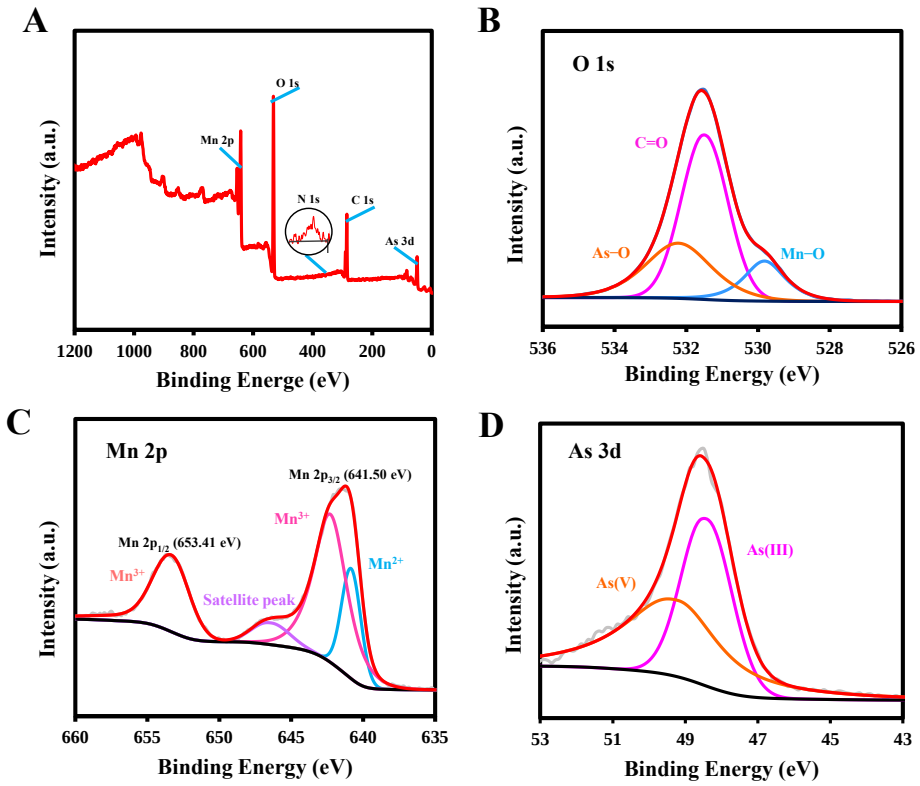

Fig. S2 The XPS spectra of UMnzyme after incubation with As(V). (A) the full-scan survey spectrum, (B) O 1s spectrum, (C) Mn 2p spectrum, (D) As 3d spectrum.

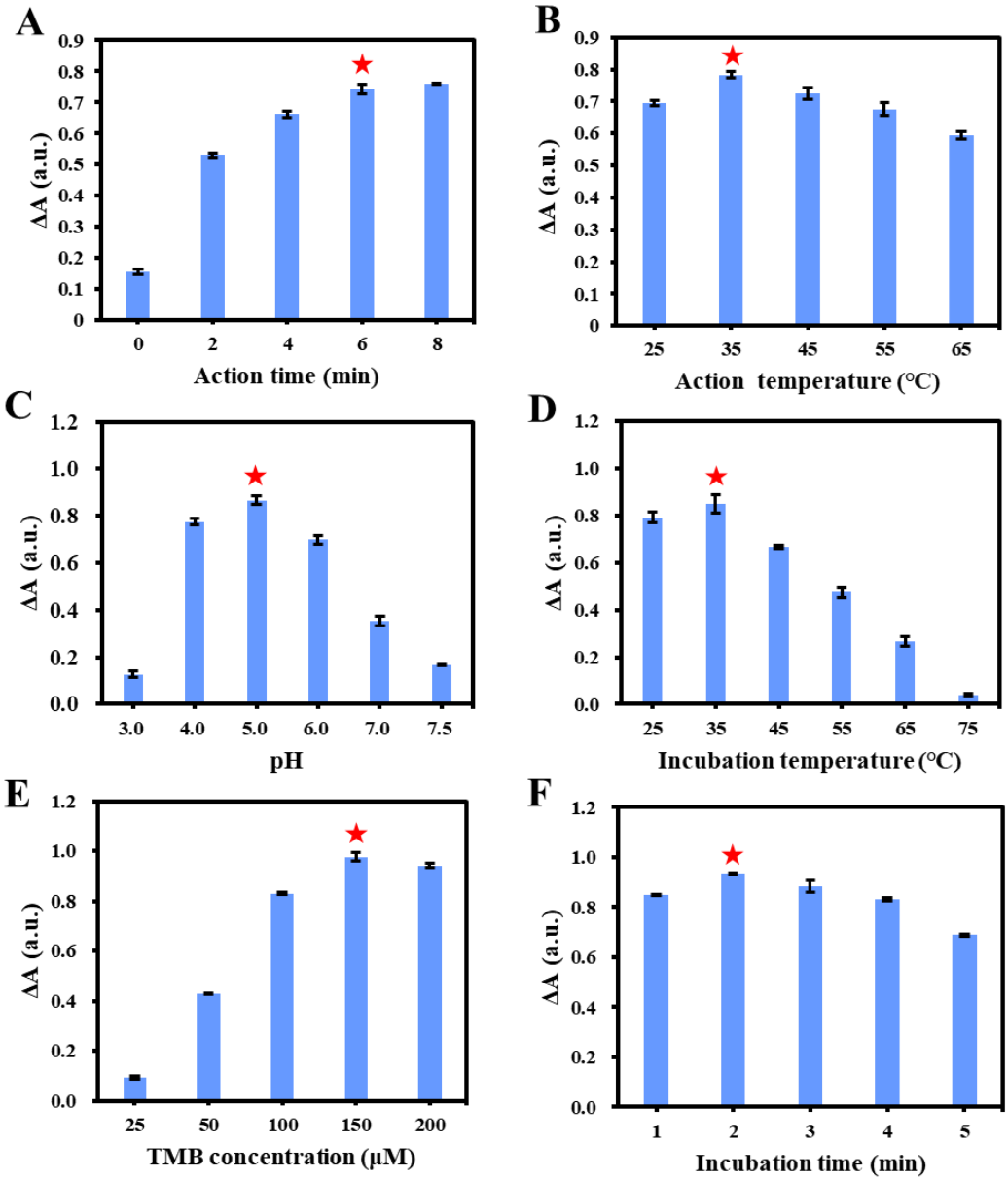

Fig. S3 Effects of the (A) action time and (B) temperature between As(V) and UMnzyme, (C) pH of acetate buffer, (D) incubation temperature of reaction solution, (E) TMB concentration, (F) incubation time of reaction solution on the oxidase-like activity of UMnzyme.

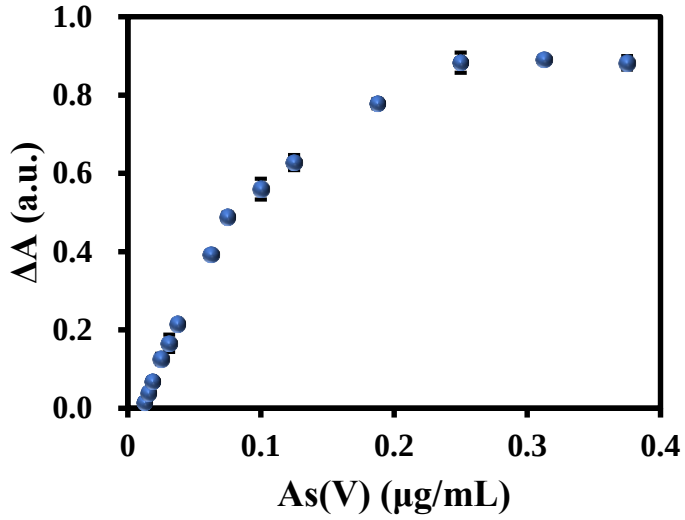

Fig. S4 The plot of the change in absorbance at 652 nm of the reaction system with different added As(V) concentration.

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