Supplementary Materials for

Fabrication of MnO_x heterogeneous catalyst from wet sludge for degradation of azo dyes by activated peroxymonosulfate

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Text S1: Catalyst Characterization

The elemental compositions (C, H, and N) of selected samples were determined using a Flash EA 1112 elemental analyzer (CE Instruments).

X-ray diffraction (XRD) was performed with a XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Cu Kα radiation (λ = 1.5406 Å) from 10° to 60° 2θ at a scan rate of 6° min^{-1}. The degree of crystallinity was calculated from the XRD data using the Materials Data Incorporated software Jade 5.0.

Surface morphology was studied with an electron microscope. The scanning electron microscopy (SEM) micrographs were recorded using a field emission scanning electron microscope (FEI, SIRON) at a voltage of 25.0 kV. The sample surfaces were gold coated before the analysis.

X-ray absorption near-edge spectroscopy (XANES) studies were performed at BL14W1 of the Shanghai Synchrotron Irradiation Facility (SSRF) with stored electron energy of 3.5 GeV and ring currents of 200 mA. The station was operated with a Si (111) double crystal monochromator, and the measurements were performed using transmission mode. The XANES data were analyzed using the Athena program of IFEFFIT. The EXAFS function and $\chi(E)$ was obtained by subtracting the post-edge background from the overall absorption and then normalized with respect to the edge jump step.

Soft X-ray scanning transmission X-ray microscopy (STXM) was performed at beamline BL08U1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. This third-generation synchrotron storage ring was operated at 3.5 GeV, and the

STXM images have a high spatial resolution of <30 nm. The materials were ultrasonically dispersed in ethanol and dropped directly onto Si_3N_4windows. After evaporation of excess ethanol, the Si_3N_4windows were fixed to the sample holder of the STXM device and observed by a soft X-ray spectromicroscopy. Single-energy images at energies of L edge and pre-edge of metal elements were scanned and recorded as raw data. Then, image differences were calculated and analyzed for mapping chemical species over the scanned areas using the dual-energy ratio contrast analysis method. The 2D spatial distribution of metal elements can be mapped quantitatively from its absorption difference at two photon energies, peak and pre-peak of metal elements absorption edge, respectively. Reference standard spectra were collected for NEXAFS analysis using the total electron yield (TEY) model.

Supplementary Table

Table S1. The physicochemical characteristics of anaerobic sludge (wt %)

Water content	Proximate analysis		Heavy metals (mg/g)							
	Organic carbon	Ash	Zn	Cu	Pb	Cd	Cr	Co	Ni	Fe
80.01	11.98	59.09	0.050	0.144	0.064	0.002	0.128	0.003	0.023	12.92

Table S2 The preparation methods of catalysts and the removal of AR 73

Samples	Preparation methods	Removal rate (%)
MnO_x/HCAS-120	adding separate anaerobic sludge and $MnSO_4 \cdot H_2O$, then treating them for 12 h at 120 °C.	degradation: 98.3 adsorption: 2.85
MnO_x/HCAS-200	adding separate anaerobic sludge and $MnSO_4 \cdot H_2O$, then treating them for 12 h at 200 °C.	degradation: 10.2 adsorption: 2.61
MnO_x/HCAS-200-120	pretreating anaerobic sludge at 200 °C for 12 h, then preparing MnO_x at 120 °C for 12 h.	degradation: 98.7 adsorption: 2.76
HCAS-120	treating anaerobic sludge for 12 h at 120 °C	adsorption: 2.97
HCAS-200	treating anaerobic sludge for 12 h at 200 °C	adsorption: 2.66

The initial concentration 50 mg/L, 10 mL, T=25 ℃, pH 7.0, different MnO_x/HCAS catalyst dosage 0.01 g, Oxone dosage 1.0 g/L.

Supplementary Figure Captions

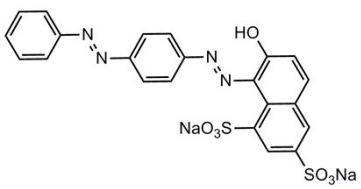
Figure S1. The chemical structures of anionic dyes.

Figure S2. Experimental apparatus used for hydrothermal synthesis.

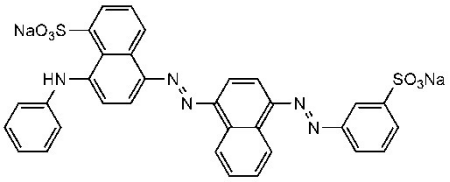
Figure S3. XRD patterns of (a) HCAS, (b) MnO_2 and (c) MnO_x/HCAS (∗, quartz; ○**,** graphite structure).

Figure S4. Degradation of AR 73 using MnO_x/HCAS /Oxone in the presence of MeOH and TBA (Initial concentration 50 mg/L, 100 mL, T=25 ºC, pH 7.0±0.2, samples dosage 0.1 g, Oxone dosage 1.0 g/L, MeOH=0.3 mol/L, TBA=0.3 mol/L).

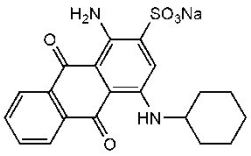
Figure S5. NEXAFS spectra of (a) Fe_2O_3, (b) Ni_2O_3, (c) ZnO, (d) CuO and (e) Cr_2O_3 reference at the L-edge.



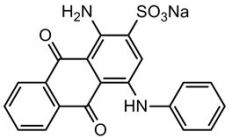
C. I. Acid Red 73



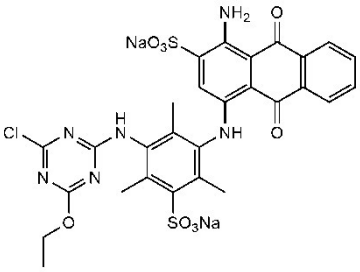
C. I. Acid Blue113



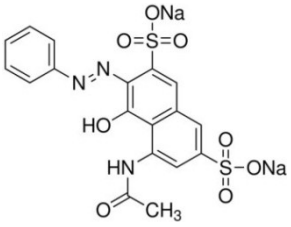
C. I. Acid Blue 62



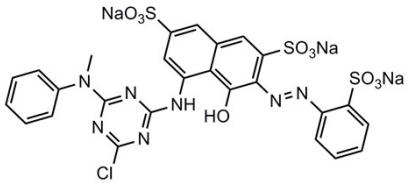
C. I. Acid Blue 25



C. I. Reactive Blue 74



C. I. Acid Red 1



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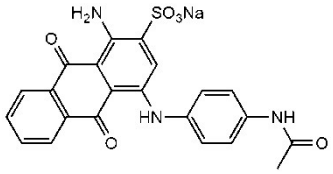
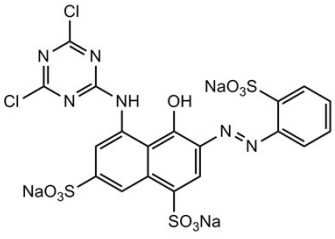


C. I. Acid Blue 40



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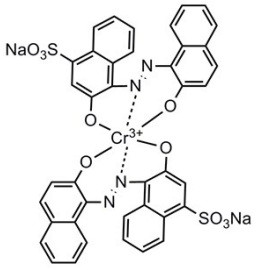

C. I. Acid Blue 193

Figure S1

Figure S2

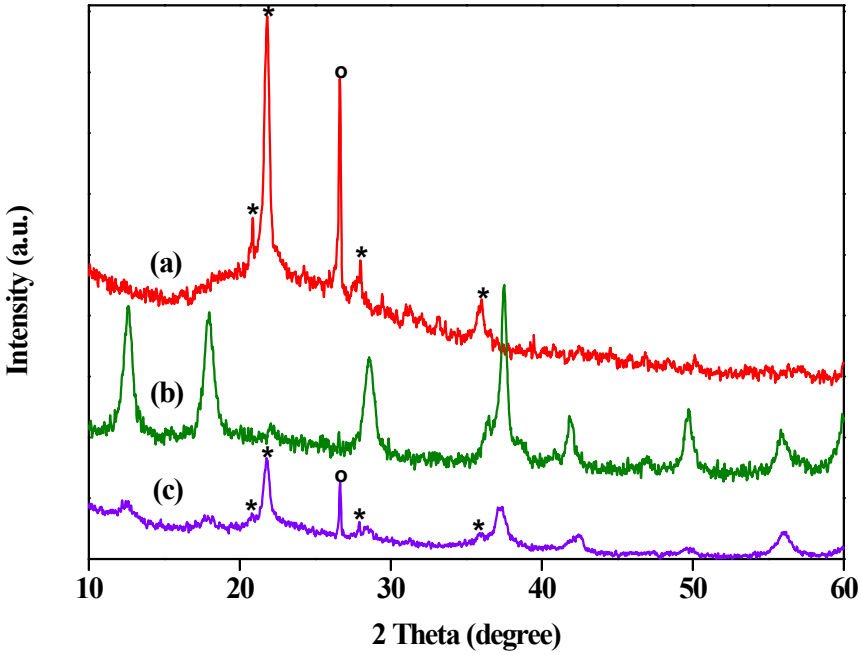

Figure S3

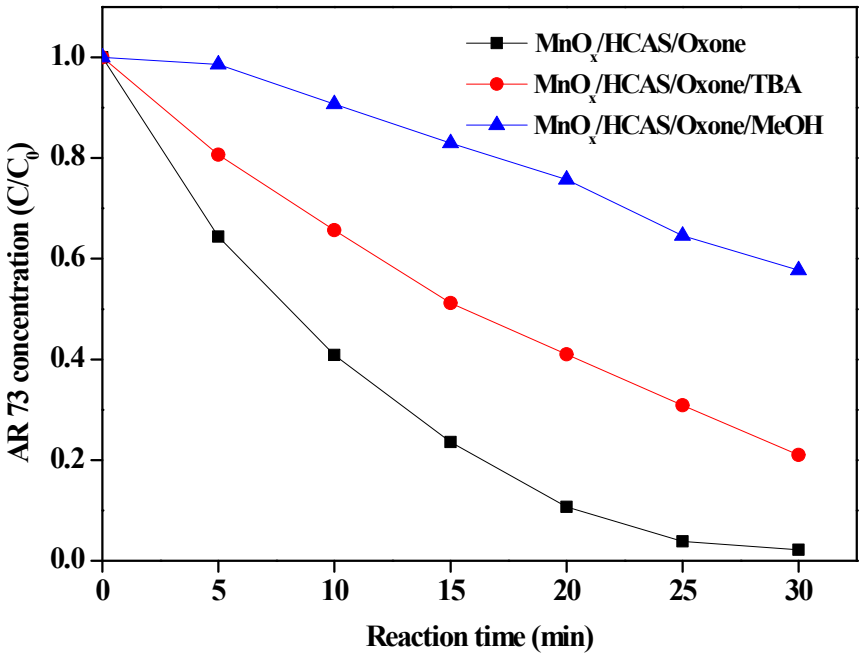
MnO$_x$/HCAS/Oxone
MnO$_x$/HCAS/Oxone/TBA
MnO$_x$/HCAS/Oxone/MeOH
AR 73 concentration (C/C$_0$)
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
Reaction time (min)

Figure S4

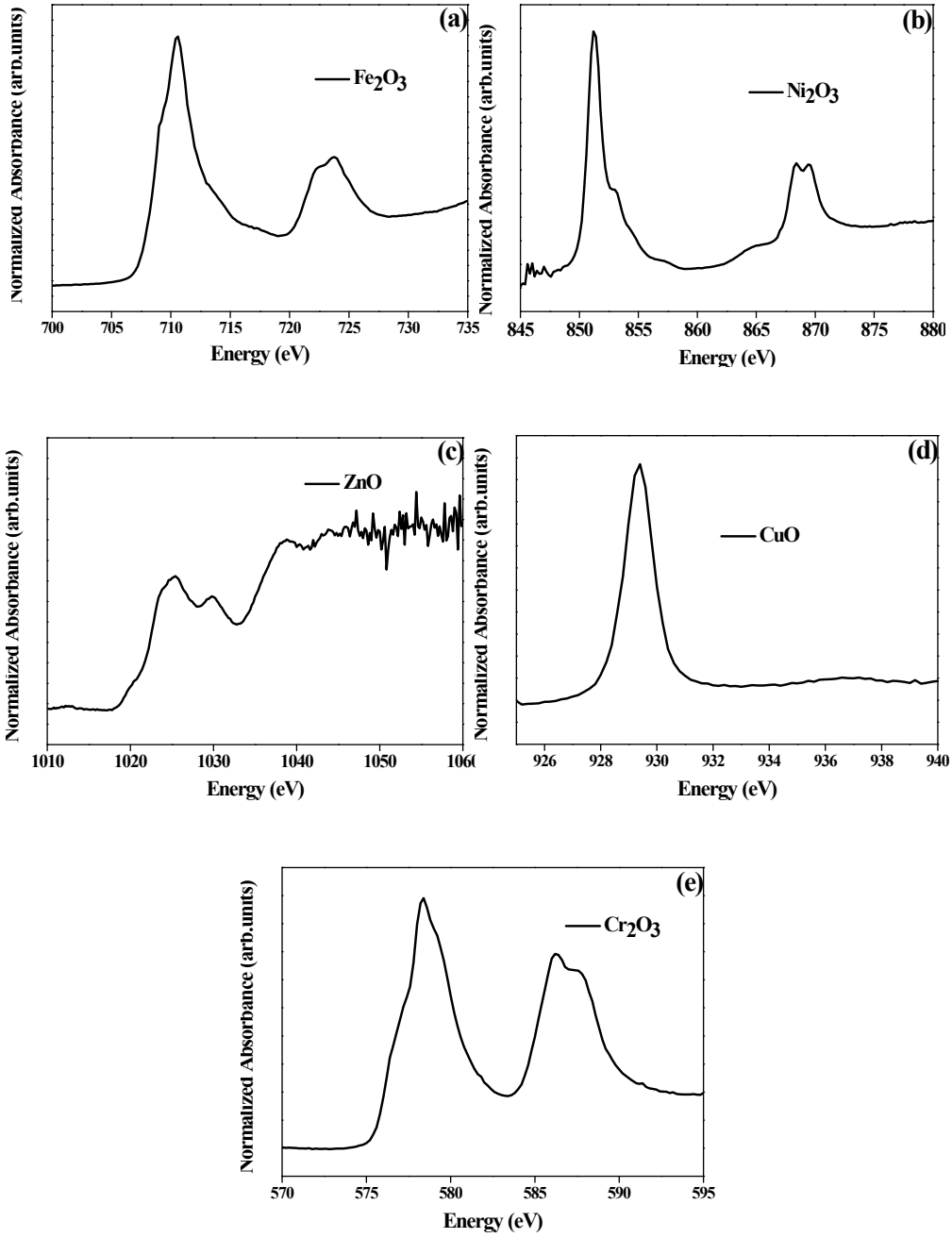
(a)
Fe2O3
Normalized Absorbance (arb.units)
700 705 710 715 720 725 730 735
Energy (eV)
(b)
Ni2O3
Normalized Absorbance (arb.units)
845 850 855 860 865 870 875 880
Energy (eV)
(c)
ZnO
Normalized Absorbance (arb.units)
1010 1020 1030 1040 1050 1060
Energy (eV)
(d)
CuO
Normalized Absorbance (arb.units)
926 928 930 932 934 936 938 940
Energy (eV)
(e)
Cr2O3
Normalized Absorbance (arb.units)
570 575 580 585 590 595
Energy (eV)

Figure S5