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Supplementary Information

Fe_3O_4@Coordination Polymer Microspheres with Self-Supported Polyoxometalates in Shells Exhibiting High-Performance Supercapacitive Energy Storage

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Section 1. Materials and methods

1.1 Materials.

Anderson-type POM, i.e. $[N(C_4H_9)_4]_4[Mo_8O_{26}]$, was synthesized as reported elsewhere.[1] Grafting two free amino groups onto a POM, i.e. $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$, also followed the literature method.[2] Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium acetate (NaOAc), ethylene glycol (EG), trisodium citrate (Na_3Cit), and sodium sulfite (Na_2SO_3) were purchased from Sinopharm Chemical Reagents Co. Ltd. Sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$), manganese acetate tetrahydrate ($MnC_4H_6O_4{\cdot}4H_2O$), tetrabutylammonium bromide, dimethylaminopropyl methacrylamide (DMAPMA), tris(hydroxymethyl) aminomethane (TRIS), poly(tetrafluoroethylene) (PTFE) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) were purchased from Shanghai Aladdin Reagent Company. *N,N'*-methylenebisacrylamide (MBA) was purchased from Fluka and recrystallized from acetone. 2,2-azobisisobutyronitrile (AIBN) was supported by Shanghai Shisihewei Reagent Company and recrystallized from methanol. 3-(trimethoxysilyl)propyl methacrylate (MPS) were purchased from Sigma Aldrich.

1.2 Synthesis of vinyl-modified Fe_3O_4 nanocrystal clusters.

Fe_3O_4 clusters were fabricated through a solvothermal process as previously reported in our group.[3] Typically, 2.2 g of $FeCl_3{\cdot}6H_2O$, 3.8 g of NaOAc, and 0.50 g of Na_3Cit were dissolved in 40 mL of EG to form a homogeneous yellow dispersion. Then, the mixture was transferred into a 100 mL three-necked flask and stirred vigorously at 160 °C for 1 h. The obtained dispersion was immediately transferred into a Teflon-lined stainless-steel autoclave (50 mL capacity) and placed in an oven. The reaction was allowed to proceed at 200 °C for 15 h. Afterwards, the dark precipitates were isolated by an applied magnet and rinsed several times with ethanol and deionized water to remove the residues from the products. The as-synthesized Fe_3O_4 clusters were dispersed in the mixture solution of ethanol (32 g) and water (9 g), with addition of 1 g MPS. Then the dispersion was transferred into a 100 mL three-necked flask. After injection of 2 mL of ammonia solution, the mixture was stirred at 70 °C for 24 h, to modify Fe_3O_4 clusters with MPS for immobilization of vinyl groups. After reaction, the products were washed with ethanol and deionized water for several times, and isolated by a magnet. The purified products were dried in vacuum for further use.

1.3 Synthesis of Fe_3O_4@PDMAPMA microspheres.

The Fe_3O_4@PDMAPMA microspheres were prepared via distillation-precipitation polymerization of DMAPMA in acetonitrile, with MPS-modified Fe_3O_4 clusters serving as seeds, MBA as crosslinking agent and AIBN as initiator.[4] Typically, 200 mg of Fe_3O_4 clusters were dispersed in 160 mL of acetonitrile in a 250 mL single-necked flask. Then, 800 mg of DMAPMA, 300 mg of MBA, and 37.5mg of AIBN were added to initiate the polymerization. The reaction mixture was heated from ambient temperature to 135^{o}C within 30 min, and the reaction was stopped until 60 mL of acetonitrile was distilled out in 1h. The obtained Fe_3O_4@PDMAPMA microspheres were collected by an applied magnet and washed with ethanol.

1.4 Synthesis of MP@POM-Zn(II) microspheres.

5 mg of POM (2.6 mmol) were dissolved in 3 mL of acetonitrile. To the above solution 10 mg Fe_3O_4@PDMAPMA microspheres were added and dispersed well with the aid of ultrasonication. Then the mixture was transferred to a 25 mL three-necked flask and stirred vigorously at ambient temperature for 30 min. Afterwards, 500 μL acetonitrile solution of $Zn(NO_3)_2 \cdot 6H_2O$ (10.6 mmol/mL) was injected dropwise into the above mixture solution within 5 min, and more acetonitrile was added to make up the solution volume to 5 mL. The reaction was allowed to proceed for another 30 min, during which the precipitates were formed gradually. Finally, the as-obtained products were isolated by a magnet and washed with acetonitrile and water repetitively for further use.

1.5 Characterization.

^{1}H NMR spectra was recorded on a Varian Mercury plus 400 MHz spectrophotometer using DMSO-d_6 as solvent at 298 K. High-resolution transmission electron microscopy (HR TEM) images were taken on a JEM-2010 (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV. Sample dispersion was cast onto a carbon-coated copper grid. Scanning electron microscopy (SEM) images were performed using a TS-5136MM (TESCAN, Czech) scanning electron microscope at an accelerating voltage of 20 kV. Sample dispersion was cast onto a glass sheet at room temperature and sputter-coated with gold. Powder X-ray diffraction (XRD) patterns were collected on a D8 advance (Bruker, Germany) diffraction meter with Cu KR radiation at $\lambda = 0.154$ nm operating at 40 kV and 40 mA. Magnetic characterization was carried out with a vibrating sample magnetometer on a Model 6000 physical property measurement system (Quantum Design, USA) at 300 K. Hydrodynamic diameter (D_h) and ζ-potential measurements were conducted with a Nano ZS Zetasizer (model ZEN3600, Malvern Instruments) using a He-Ne laser at a wavelength of 632.8 nm. Fourier transform infrared (FT-IR) spectra were recorder on a Magna-550 (Nicolet) spectrometer. The samples were dried and mixed with KBr to be compressed to a plate for measurement. Inductively Coupled Plasma-atomic emission spectrometry (ICP-AES) was performed by a P-4010 (Hitachi, Japan) spectrometer.

1.6 Electrochemical test.

Electrochemical measurements were performed in a three-electrode system on CHI 660a electrochemical workstation (CH Instruments Inc., Shanghai) in 1 M Na_2SO_3 aqueous solution at ambient temperature. The MP@POM-Zn(II) films were prepared by roller using 15 mg of MP@POM-Zn(II) powder, 1.5 mg of acetylene black powder, and 1.5 mg of PTFE, and were cut to a circular shape with diameter of 1 cm and mass of about 10 mg. The as-made film on Ti mesh was directly used as working electrode with graphite and Ag/AgCl as counter and reference electrodes, respectively. Cyclic voltammetry (CV) was performed within the potential window of -0.8 to 0.2 V. Constant current charge-discharge behaviors were performed within the potential window of -0.7 to -0.1 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range from 10 kHz to 10 mHz. Besides, a areal capacitance (C_a) was calculated using Equation (1), where I is the constant discharge current, t is the discharging time, V is the voltage drop upon discharging (excluding the IR drop), and S is the geometrical area of the electrode.

$$C_a = I \times t / (\Delta V \times S) \qquad (1)$$

References

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Section 2. SEM images

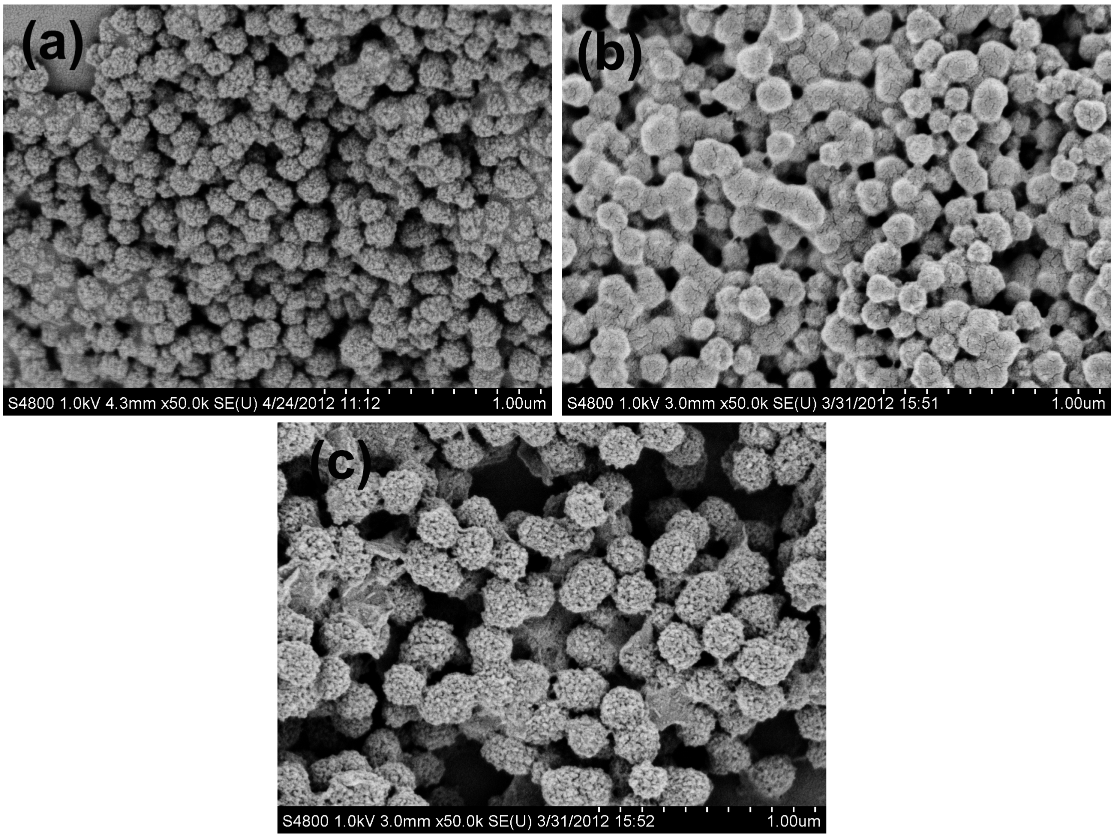

Fig. S1 SEM images of Fe_3O_4 (a), Fe_3O_4@PDMAPMA (b), MP@POM-Zn(II) (c).

Section 3. FTIR spectra

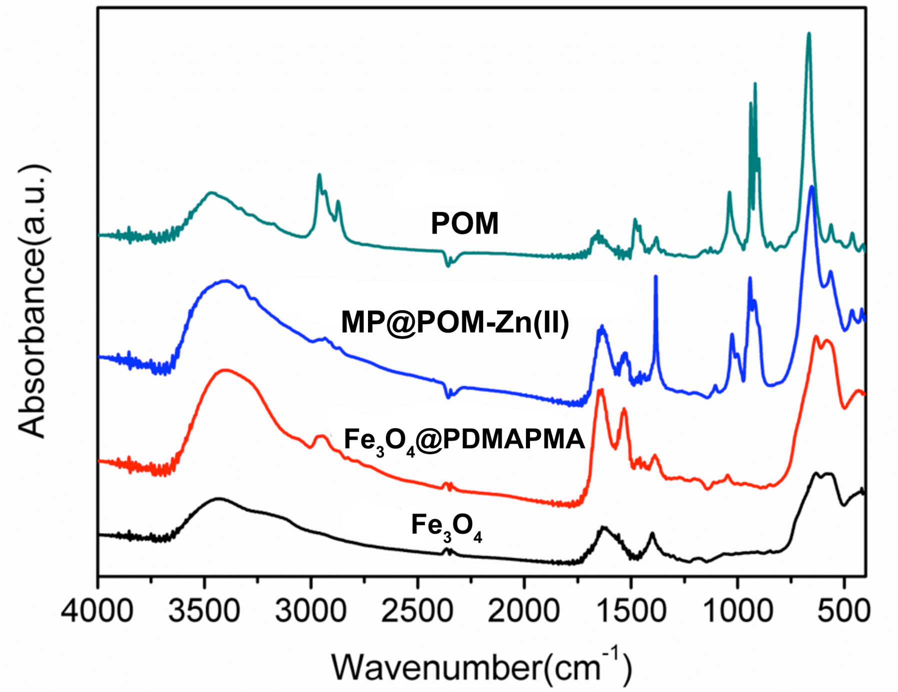

Fig. S2 FTIR spectra of POM, Fe_3O_4, Fe_3O_4@PDMAPMA, and MP@POM-Zn(II). It can be seen that the spectrum of MP@POM-Zn(II) both displayed the characteristic peaks of 1638 and 1529 cm^{-1} due to the amide I and II bands, and of 1026, 943-900 and 664 cm^{-1} due to the C-O, Mo=O and Mo-O-Mo bands, respectively, implying that the resultant particle was a composite containing POM and PDMAPMA simultaneously.

Section 4. DLS measurement

Table S1. DLS and ζ-Potential results of Fe_3O_4 cluster, Fe_3O_4@PDMAPMA and MP@POM-Zn(II)

Sample	Hydrodynamic Diameter (nm)[a]	PDI	ζ-Potential (mV)
Fe_3O_4 cluster	130	0.076	-10.9
Fe_3O_4@PDMAPMA	295	0.039	+42.6
MP@POM-Zn(II)	394	0.159	+22.2

[a] The hydrodynamic diameters of Fe_3O_4@PDMAPMA and MP@POM-Zn(II) were relatively larger than those of particles observed in TEM images (Fig. 1) due to the swelling behaviors of the hydrophilic shells in water.

Section 5. Quantitative analysis of POM contents

Table S2. Effect of feeding amounts of POM and Zn(II) on the encapsulation of Fe_3O_4@PDMAPMA with POM-based coordination polymers.

Sample	Feeding Amounts		POM content (wt%)[a]
	POM (mmol)	Zn(II):POM (molar ratios)	
MP@POM-Zn(II)-1	2.6	2:1	24.4
MP@POM-Zn(II)-2	5.2	2:1	31.4
MP@POM-Zn(II)-3	5.2	4:1	32.6
MP@POM-Zn(II)-4	5.2	8:1	40.1

[a] The particles were digested by dilute nitric acid solution completely, and the concentrations of Mo and Mn elements were determined by ICP-AES analysis for evaluating the contents of POM within the composite particles.

Section 6. Characterizations of magnetic properties

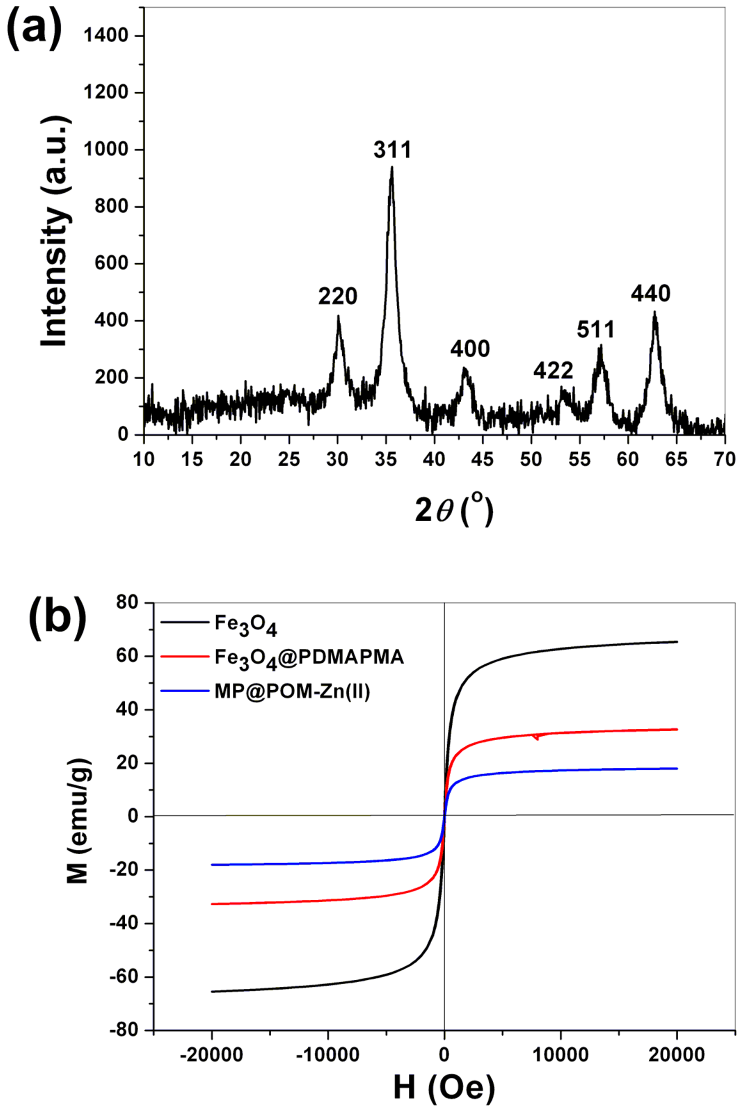

Fig. S3 (a) Powder XRD spectrum of MP@POM-Zn(II) particles; (b) Magnetic hysteresis curves of Fe_3O_4 clusters, Fe_3O_4@PDMAPMA and MP@POM-Zn(II) particles. The PXRD patterns showed the typical diffraction peaks, which can be well indexed to the cubic structure of Fe_3O_4 crystal (JCPDS 75-1610). Meanwhile, the saturation magnetization of MP@POM-Zn(II) could be estimated to 18.1 emu/g from the blue curve in Fig. S3b.

Section 7. Charge-discharge curves

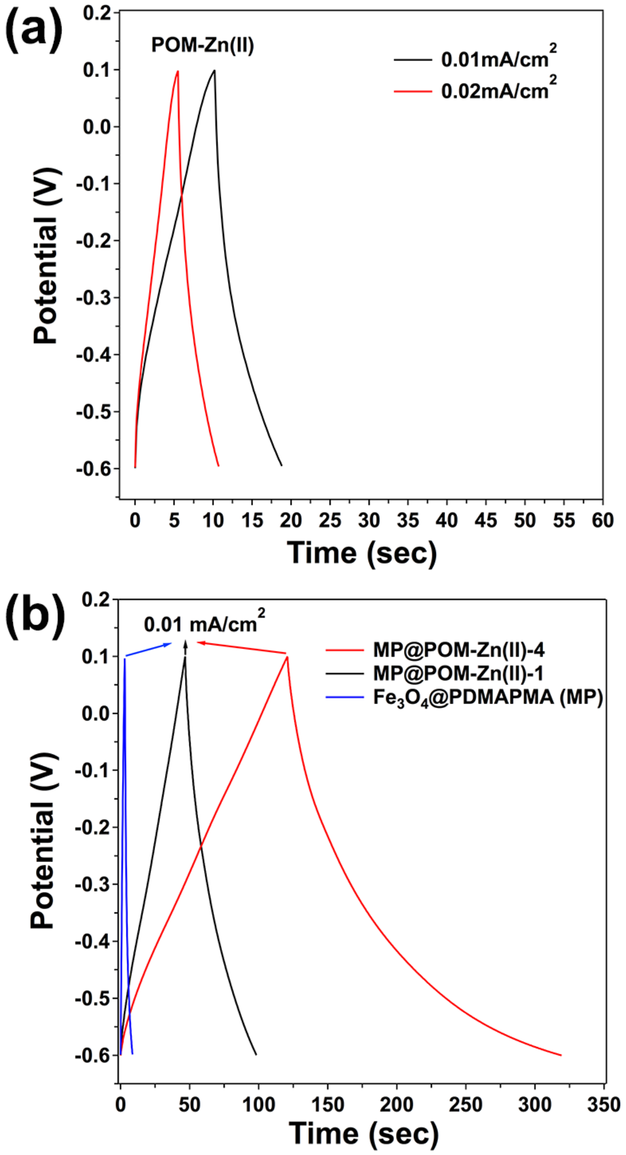

Fig. S4. (a) Charge-discharge curves of the film electrode prepared by the POM-Zn(II) coordination polymers at 0.01 and 0.02 mA/cm^2, respectively. The areal capacitance of POM-Zn(II) was calculated to be 0.15 mF/cm^2 at 0.01 mA/cm^2. (b) Charge-discharge curves of the Fe_3O_4@PDMAPMA (MP) film, the MP@POM-Zn(II)-1 film and the MP@POM-Zn(II)-4 film at 0.01 mA/cm^2, respectively. The POM contents are 24.4 wt. % for the MP@POM-Zn(II)-1 (entry 1 in Table S2) and 40.1 wt. % for the MP@POM-Zn(II)-4 (entry 4 in Table S2). The areal capacitances estimated from the discharging segments were approximately 0.08 mF/cm^2 for the Fe_3O_4@PDMAPMA film, 1.54 mF/cm^2 for the MP@POM-Zn(II)-1 film, and 2.85 mF/cm^2 for the MP@POM-Zn(II)-4 film.