Supporting Information

PEDOT Coated Iron Phosphide Nanorod Arrays as High-Performance Supercapacitor Negative Electrodes

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Experimental Section

Synthesis of FeP nanorod arrays. The FeP nanorod arrays were synthesized on carbon cloth by a two-step method. First, FeOOH nanorod arrays were growth via a hydrothermal procedure.[1] The reaction solution was prepared by dissolving 0.182 g $FeCl_3 \cdot 6H_2O$, 0.107 g Na_2SO_4 into 15 mL DI water. The solution was then transferred to a 20 mL autoclave with a piece of carbon cloth immersed in. The autoclave was kept at 160 °C for 6 hours. The synthesized FeOOH nanorod arrays were converted to FeP nanorod arrays by a phosphidation process.[2,3] The FeOOH sample and 0.5 g NaH_2PO_2 were placed in a tube furnace and heated to 300 °C and kept for 2 h under static Ar atmosphere. The loading amount of FeP nanorod arrays was determined as 2.94 mg/cm^2 by a high-precision microbalance.

Synthesis of FeP/PEDOT nanorod arrays. The PEDOT were coated on FeP nanorod arrays using an in-situ polymerization method.[4] The coating process was performed in precursor solution containing 0.1 M $LiClO_4$, 0.03 M EDOT, and 0.07 M sodium dodecyl sulfate at 1 V for 1 min. The mass loading of PEDOT was 0.70 mg/cm^2. Pure PEDOT was coated on carbon cloth for comparison.

Preparation of MnO_2 electrode. The MnO_2 electrode was prepared by electrodeposition of MnO_2 on carbon cloth.[5] A three-electrode configuration was used with carbon cloth as the

working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode a 0.1 M manganese acetate and 0.1 M Na_2SO_4 aqueous solution as the electrolyte. The MnO_2 was obtained by applying a constant voltage of 1.0 V for 5 min. The mass loading of MnO_2 was 1.60 mg/cm^2.

Fabrication of the ASC. To fabricate the ASC, one FeP/PEDOT positive electrode and one MnO_2 electrode was sandwiched together with a separator (TF4030, NKK) in between. The device was then warped with duct tape and the electrolyte (1 M Na_2SO_4 aqueous solution) was injected. The device was then sealed with epoxy gel to avoid leaking. The thickness of the whole device including electrodes, electrolyte, and separator was measured to be 0.8 mm.

Material Characterizations. The FESEM images were taken from a Hitachi S-4800 FESEM. TEM/STEM characterizations were carried out using JEM-ARM200F (JEOL, Co. Ltd.). HRTEM images were obtained using aberration-corrected TEM with thermal field emission gun (FEG). The spherical aberration coefficient (C_S) was set to zero ($C_S = 0 \pm 2$ μm). HRTEM image simulations were obtained by the HREM software (HREM Research Inc.). EELS and STEM-EDS were acquired by using STEM mode with cold FEG gun equipped with Enfinium (Gatan, Ltd.) and dual silicon drift detectors (SDDs) of total detect solid angle of 1.7 sr. For HRTEM, EELS and EDS analysis, nanorods were dispersed on the holey carbon film/Cu grid by sonicated in ethanol. Acceleration voltage for all TEM/STEM observations were performed at 200 kV. The X-ray diffraction (XRD) was recorded on Rigaku MiniFlex II X-ray diffractometer. Raman spectra were collected by a Thermo-Fisher DXR dispersive Raman spectrometer with the excitation wavelengths of 532 nm.

Electrochemical measurements. For single electrode, the electrochemical measurements were performed in a 1 M Na_2SO_4 aqueous electrolyte at ambient temperature. The conventional three-electrode configuration was used with a Pt wire and Ag/AgCl as counter and reference electrodes, respectively. The electrochemical impedance spectroscopy (EIS) measurements were conducted with a potential amplitude of 5 mV in the frequency range of 0.01 Hz to 100 kHz. For the ASC device, a two-electrode configuration was used, in which the negative electrode serves as both counter and reference electrodes.

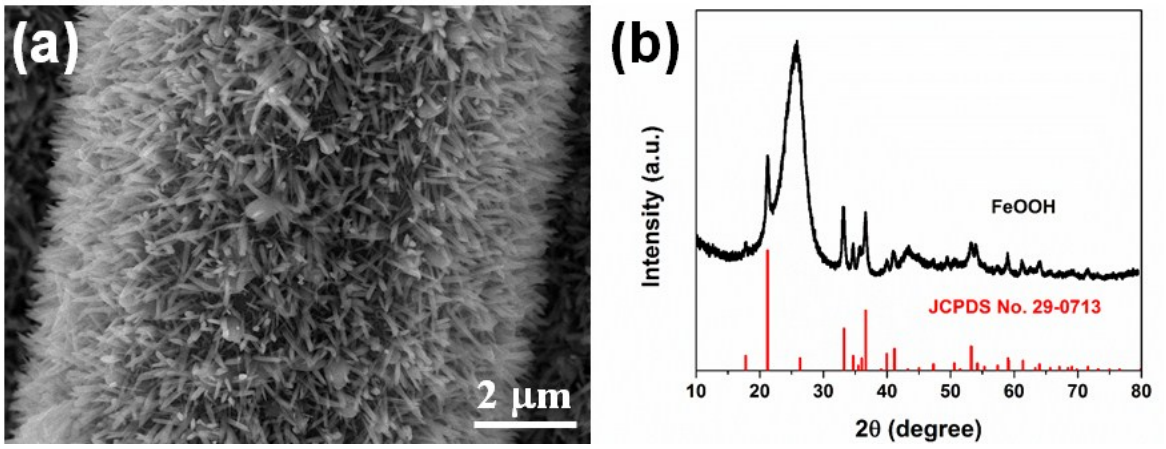

Figure S1. (a) FESEM image and (b) XRD patterns of FeOOH nanorod arrays.

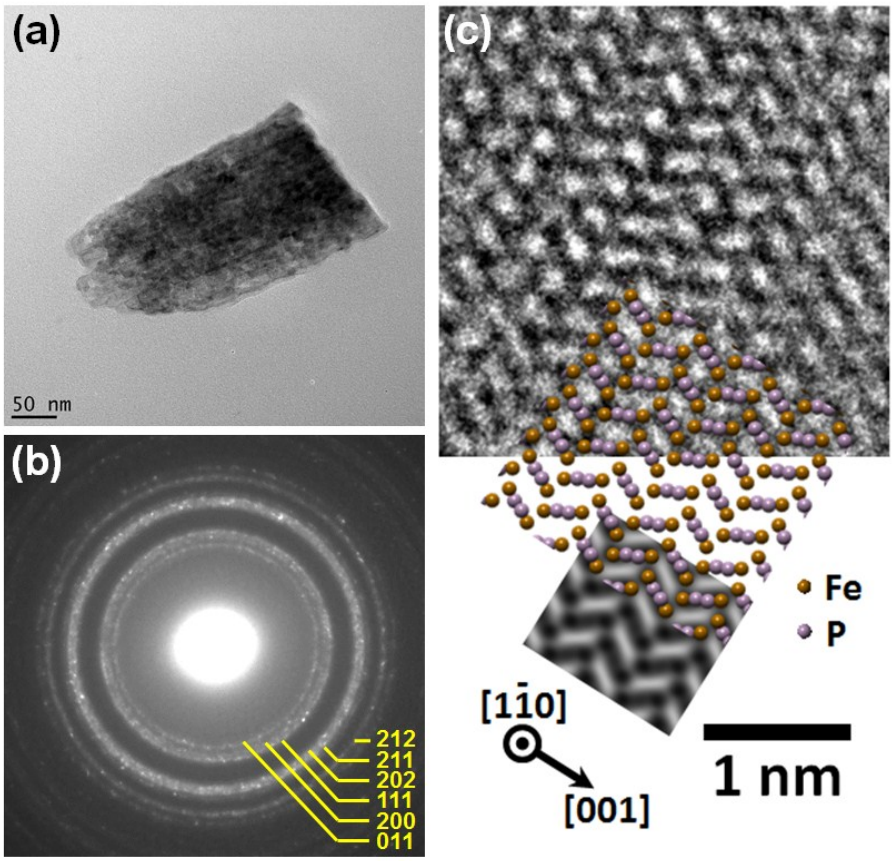

Figure S2. (a) TEM image, (b) SAED, and (c) HRTEM of FeP nanorod.

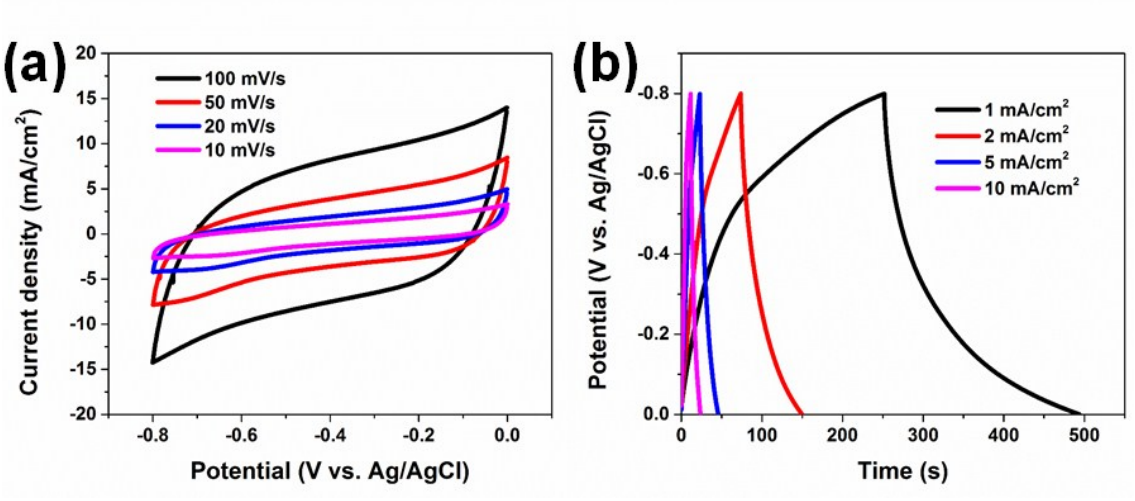

Figure S3. (a) CV curves of FeP electrode collected at scan rates from 10 to 100 mV/s. (b) Galvanostatic charge/discharge curves of FeP electrode at current densities from 1 to 10 mA/cm^2.

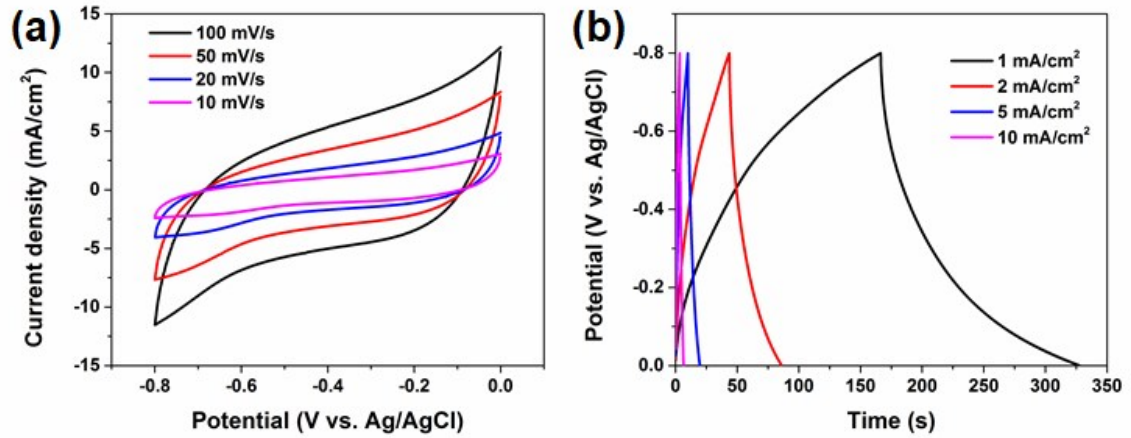

Figure S4. (a) CV curves of pure PEDOT collected at scan rates from 10 to 100 mV/s. (b) Galvanostatic charge/discharge curves of pure PEDOT at current densities from 1 to 10 mA/cm^2.

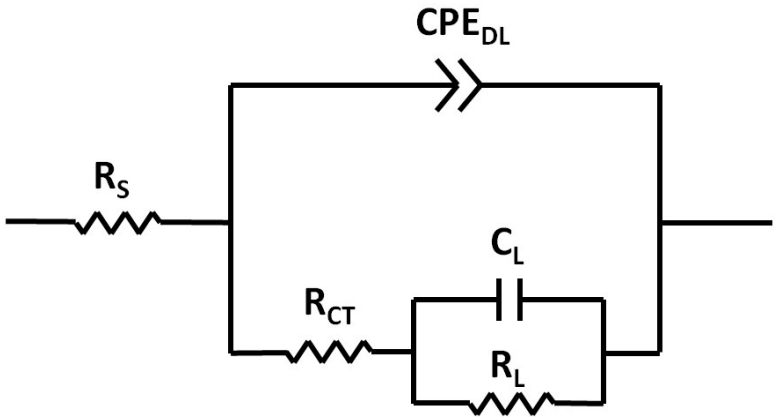

Figure S5. The equivalent circuit for the electrochemical impedance spectra.

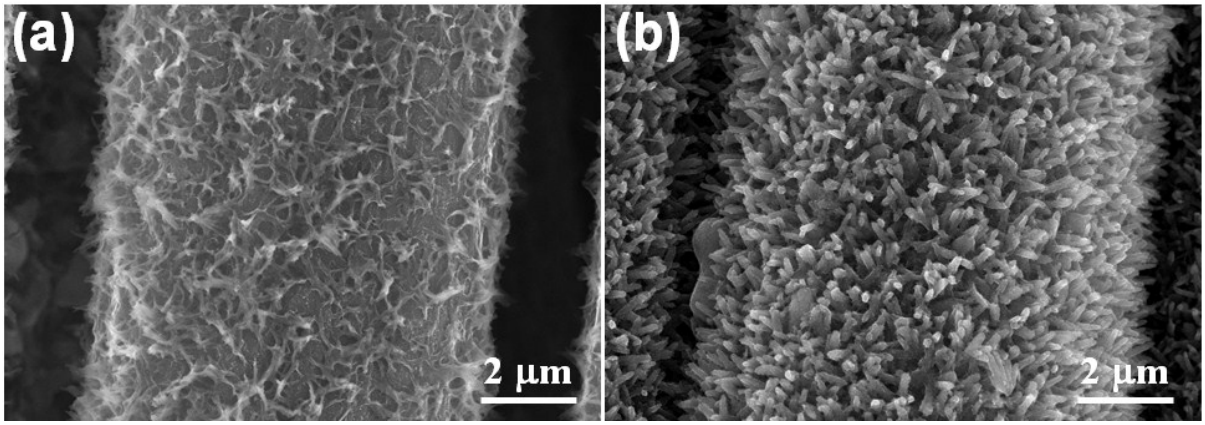

Figure S6. FESEM images of (a) FeP and (b) FeP/PEDOT nanorod arrays after cycling test.

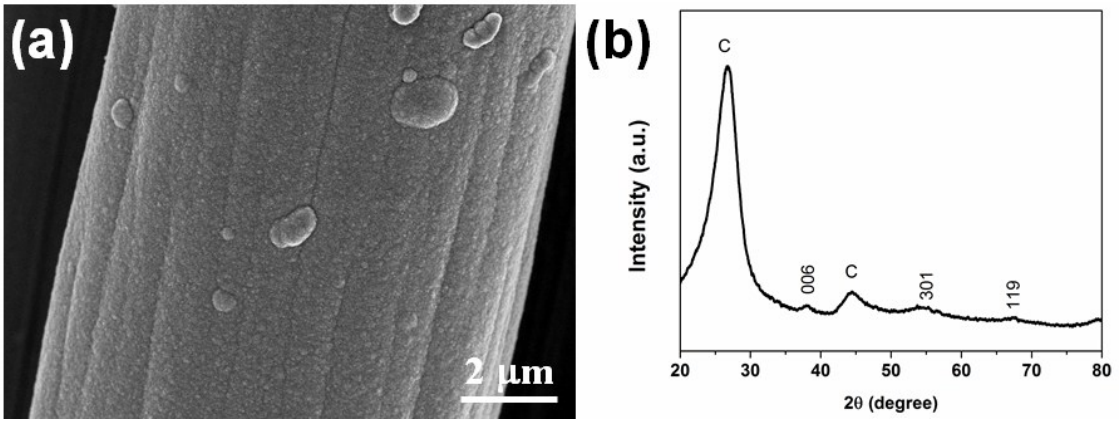

Figure S7. (a) FESEM image and (b) XRD patterns of MnO_2 electrode.

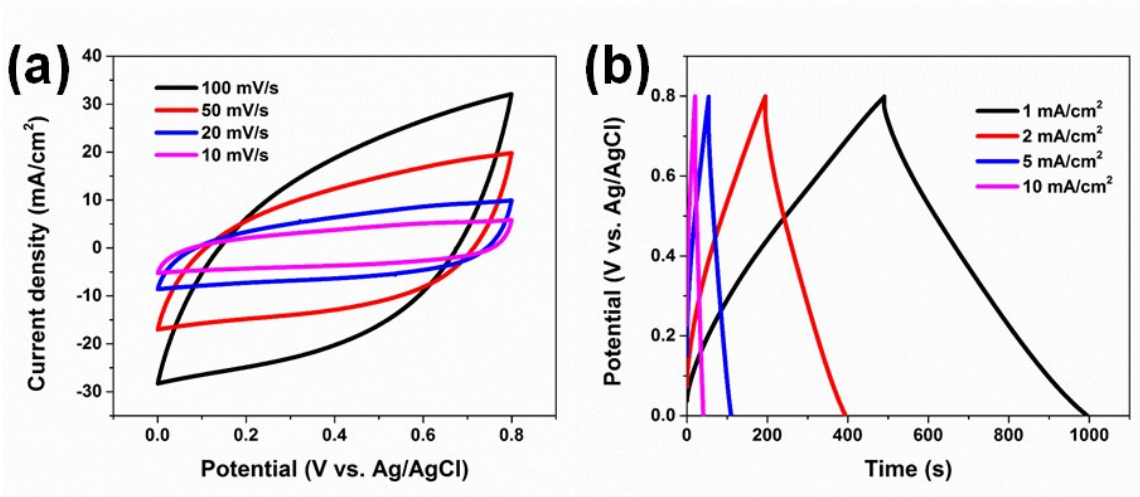

Figure S8. (a) CV curves of the MnO_2 electrode collected at scan rates from 10 to 100 mV/s. (b) Galvanostatic charge/discharge curves of the MnO_2 electrode at current densities from 1 to 10 mA/cm^2.

Table S1. Comparison of capacitive performances of reported negative electrode materials and their corresponding ASCs

Negative electrode material	Areal capacitance	ASC device	Volumetric capacitance (mF/cm^3)	Energy density (mWh/cm^3)	Cycling performance	Ref.
FeP/PEDOT	790.59 mF/cm^2 at 1 mA/cm^2	MnO_2//FeP/ PEDOT	4.53 F/cm^3 at 1 mA/cm^2	1.61	81.17% after 5000 cycles	Present work
Fe_2O_3	180.4 mF/cm^2 at 1 mA/cm^2	MnO_2//Fe_2O_3	1.5 F/cm^3 at 2 mA/cm^2	0.55	84% after 5000 cycles	6
Oxygen-deficient Fe_2O_3	382.7 mF/cm^2 at 0.5 mA/cm^2	MnO_2//Fe_2O_3	1.21 F/cm^3 at 0.5 mA/cm^2	0.41	81.6% after 6000 cycles	7
α-Fe_2O_3@PANI	103 mF/cm^2 at 0.86 mA/cm^2	PANI//α-Fe_2O_3@PANI	2.02 F/cm^3 at 5 mV/s	0.35	95.77% after 10000 cycles	8
Fe_2O_3/PPy	382.4 mF/cm^2 at 0.5 mA/cm^2	MnO_2//Fe_2O_3/ PPy	0.8355 F/cm^3 at 10 mV/s	0.22		9
$CoSe_2$	332 mF/cm^2 at 1 mA/cm^2	MnO_2//$CoSe_2$	1.77 F/cm^3 at 1 mA/cm^2	0.588	94.8% after 2000 cycles	10
Mn_3O_4	372.5 mF/cm^2 at 1 mA/cm^2	$Ni(OH)_2$// Mn_3O_4	2.07 F/cm^3 at 1 mA/cm^2	0.35	83.3% after 12000 cycles	11
RGO		H-MnO_2 //RGO	0.72 F/cm^3 at 10 mV/s	0.25	95.5% after 5000 cycles	12
RGO	250 mF/cm^2 at 10 mV/s	MnO_2/ZnO// RGO	0.52 F/cm^3 at 10 mV/s	0.234	98.4% after 5000 cycles	13
H-TiO_2@C		H-TiO_2@ MnO_2 //H-TiO_2@C	0.71 F/cm^3 at 10 mV/s	0.3	91.2% after 5000 cycles	14

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