

Supporting information

Ultra-high capacitance hematite thin films with controlled nanoscopic morphologies

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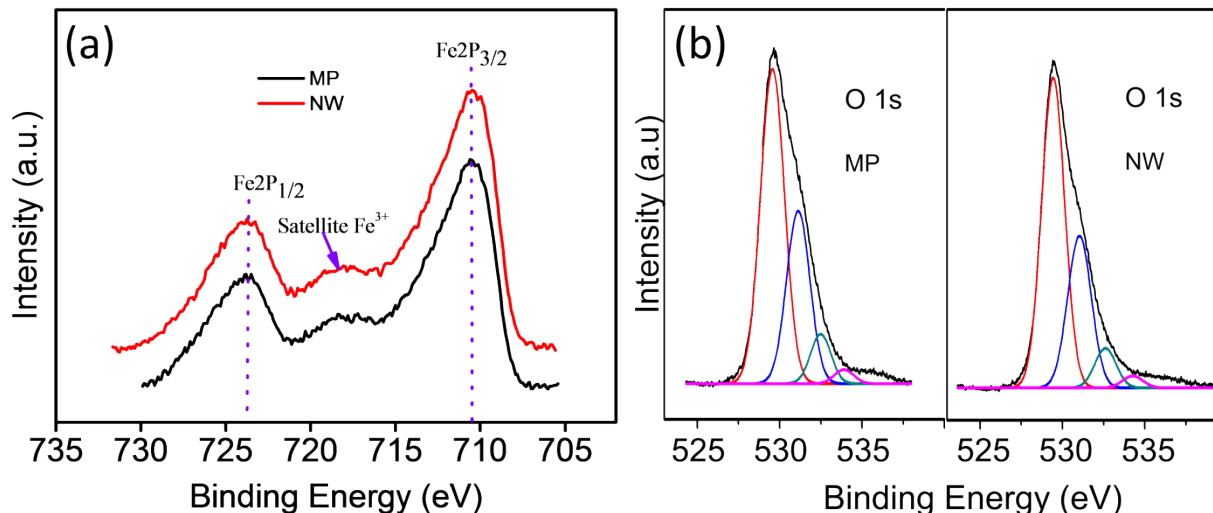


Fig. S1 XPS spectra of (a) Fe 2p, and (b) O 1s for MP and NW.

Both MP and NW samples were analyzed by XPS on the Fe 2p and O 1s regions. In both regions, the two samples show almost the same spectra. In the Fe 2p region (Fig. S1a), Fe 2p_{3/2} and Fe 2p_{1/2} peaks appear at 710.8 and 725.4 eV, respectively, which agree well with those of α -Fe₂O₃ (Hematite) in the literatures.^{1, 2} The satellite signature of Fe³⁺ ion is also observed at 718.8 eV, additional signature of α -Fe₂O₃. There is no peak at 708.3 eV that may be attributed to Fe²⁺, indicating that both MP and NW are free of any Fe²⁺ impurity. In the O 1s region, both MP and NW show a strong peak at 530.2 eV, which is assigned to O²⁻ in Fe-O bond of α -Fe₂O₃. The minority peaks with higher binding energies can be assigned to C-O bonds of surface carboxylic groups.^{1, 3} The resource of the carboxylic group can be justified as the residues from the removal of F127 surfactant.

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Estimation of the surface areas of MP and NW by adsorption of dye molecules

In order to estimate the surface areas of MP and NW, we performed adsorption measurement of N719 dye molecules. We choose N719 dye for these experiments for its strong absorption intensity for easy observation and its well-known binding behavior onto oxide surfaces. The Langmuir model of monolayer adsorption was used to analyze the adsorption data.

N719 solution in absolute alcohol with various concentrations ($C_{(sol)}$ =1.68, 2.48, 6.4, 10.2, 18.34, 29.78 μ M) were prepared. To each of the 5 mL solutions, a MP or NW sample (1×1 cm²) was immersed for 24h to ensure equilibration. The concentrations of film $C_{(film)}$ for the N719 solutions before and after the immersion were calculated by using the Beer-Lambert law:

$$\Delta A = \varepsilon \cdot l \cdot C_{(film)} \quad (1)$$

Where, ΔA is the absorbance change of the N719 solution before and after dyeing, ε is the extinction coefficient of N719 (1.41×10^4 L/mol), l is the light path length (1 cm). The absorbance change in the solution is attributed to the adsorption to MP and NW (considered to be $C_{(film)}$).

The theoretical concentration of film $C_{(theo)}$ at a saturated absorption can be obtained from the Langmuir model equation:

$$C_{(film)} = C_{(theo)} \cdot C_{(sol)} / (Kd + C_{(sol)}) \quad (2)$$

The Langmuir equation can be also described by the linear form:

$$1/C_{(film)} = Kd / C_{(theo)} \cdot 1/C_{(sol)} + 1/ C_{(theo)} \quad (3)$$

Where, $C_{(film)}$ is the concentration of film obtained from equation (1), $C_{(sol)}$ is the original concentration of N719 dye ($C_{(sol)}$ =1.68, 2.48, 6.4, 10.2, 18.34, 29.78 μ M), and Kd is a constant related to the affinity of the binding sites between N719 dye and hematite surface. The theoretical concentration of film ($C_{(theo)}$) at a saturated absorption can be obtained from the intercept of the linear pots as presented in Fig. S3, which derived from the equation (3).

The theoretical amount of dye $Q_{(\text{film})}$ absorbed on the surface, can be obtained according to the following equation:

$$Q_{(\text{film})} = C_{(\text{theo})} \cdot V \quad (4)$$

Where, $Q_{(\text{film})}$ is the theoretical total amount of dye absorbed on the surface at a saturated absorption, $C_{(\text{theo})}$ is the theoretical concentration of film at a saturated absorption obtained from the equation (3), V is the volume of dye solution (5 ml).

The theoretical specific surface areas (S) can be derived:

$$S = Q_{(\text{film})} \cdot N \cdot A_{cs} / w \quad (5)$$

here, $Q_{(\text{film})}$ is the theoretical total amount of dye absorbed on the surface at a saturated absorption obtained from equation (4), N is the Avogadro's number (6.023×10^{23}), A_{cs} is the adsorbate cross sectional area ($1.6 \times 10^{-18} \text{ m}^2$ for N719), and w is the sample weight ($40 \mu\text{g}$).

From the above Langmuir model, the surface areas were calculated to be $114 \text{ m}^2/\text{g}$ for MP and $368 \text{ m}^2/\text{g}$ for NW.

Calculations of the theoretical surface areas of MP and NW

For NW, the nanowires can be idealized into a long nanowire with diameter of $d = 6 \text{ nm}$. The circumference is $\pi \times d$. The surface area of the nanowire with a length l is $\pi \times d \times l$. From the mass of a NW sample ($40 \mu\text{g}$), and formula weight and density of hematite, l is calculated to be $2.7 \times 10^5 \text{ m}$. Therefore, the idealized surface area of a NW sample is $\pi \times 6 \times 10^{-9} \times 2.7 \times 10^5$ per $40 \mu\text{g}$ or $127 \text{ m}^2/\text{g}$.

For MP, the model is a thin film composed of 9 nm sized pore channels. The pore channels form a hexagonal array with the wall thickness of 5 nm . The overall morphology is the same as the perfect pore structure of an anodized aluminum oxide. For the film with 170 nm in thickness, 40

μg in mass, the number of pore channels can be calculated to be 6.54×10^{11} per 1cm^2 . Therefore, the surface area is calculated to be $\pi \times 9 \times 10^{-9} \times 170 \times 10^{-9} \times 6.54 \times 10^{11}$ per $40\ \mu\text{g}$ or $78\ \text{m}^2/\text{g}$.

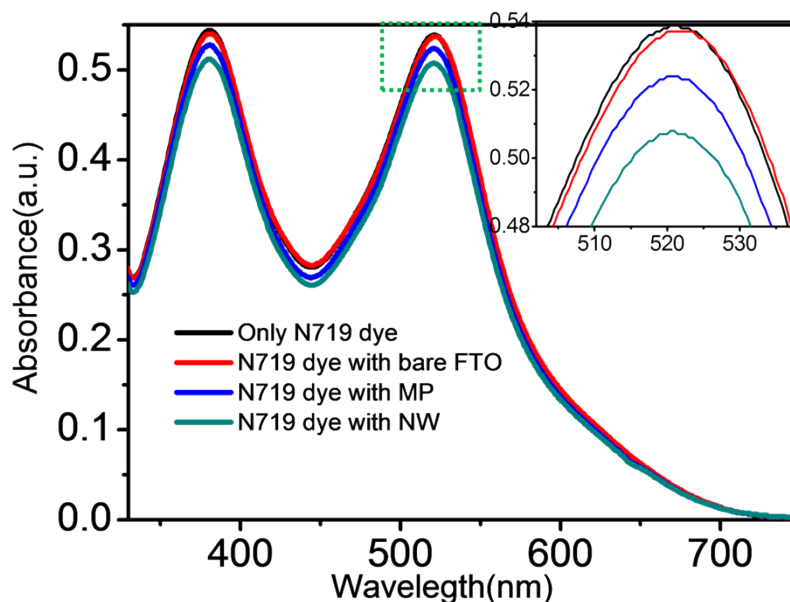


Fig. S2 UV-Vis absorption spectra of N719 dye solution ($[\text{N719}] = 29.78\ \mu\text{M}$) after immersing hematite thin films for 24 h. The inset is the enlarged spectra of the marked area with a green box.

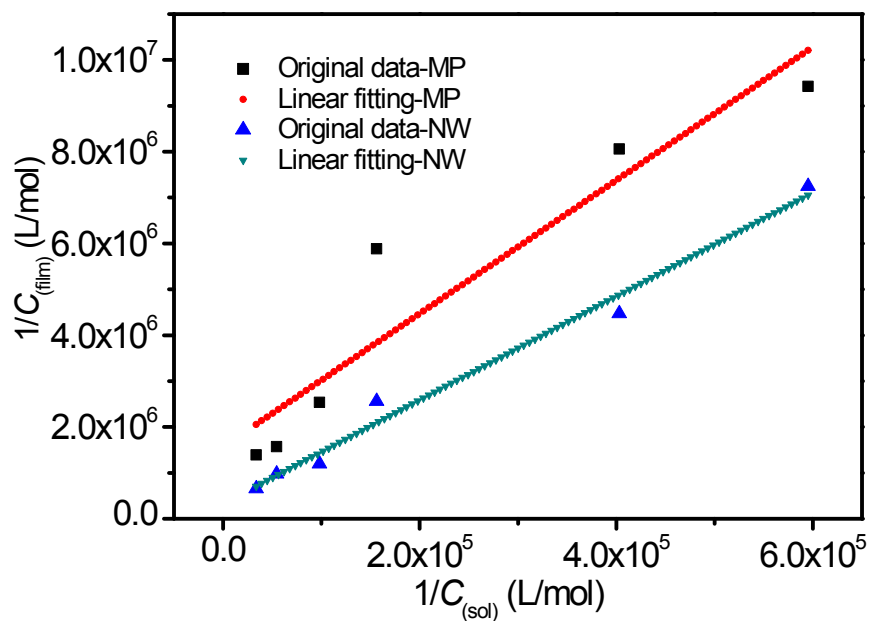


Fig. S3 Plots of the equation (3) derived from Langmuir model on the adsorption data of N719 onto MP and NW.

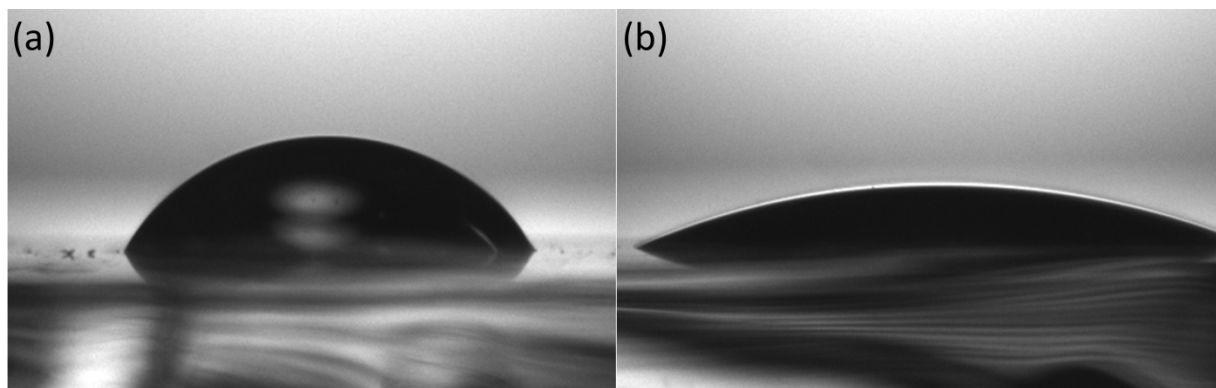


Fig. S4 Optical images of (a) MP and (b) NW with 5 μL water drops onto the surface.

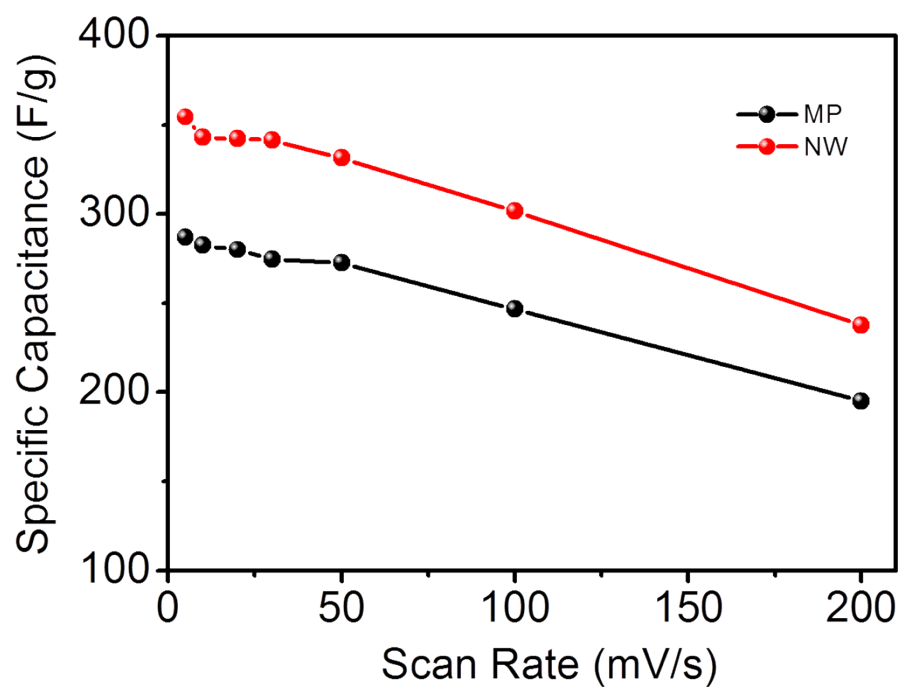


Fig. S5 Variations of specific capacitance of MP and NW electrodes as a function of scan rate in a 0.5 M Na_2SO_3 electrolyte solution.

Table.S1 Comparison of recent reports on supercapacitors based on hematite

Morphologies	Technique	Modification	Potential range (V)	Electrolyte	Csp (F/g)	Ref
Nanotube arrays	Anodization of iron foil	N/A	-0.8-0	1.0 M Li ₂ SO ₄	138	1
Nanograins	Electrospinning technique	N/A	-0.1-0.9 vs.Ag/AgCl	1 M LiOH	102	2
Porous fibers					256	
Nanorods	Hydrothermal method	N/A	-1(-0.2) vs. SCE	6 M KOH	36	3
		Reduced graphene sheets/Fe ₂ O ₃			320	
Nanospheres	Spray deposition	Incorporation with MWNT	0-2.8V	1 M LiClO ₄	33	4
Thin film	Successive ionic layer adsorption and reaction (SILAR) method	N/A	-0.6-0.1 vs. SCE	1 M NaOH	178	5
Mesoporous multi-layered nanosheets	Solution-based precipitation process	N/A	-0.6-0 vs. SCE	1 M Li ₂ SO ₄	116.25	6
Nanostructures	Chemical precipitation method	Ti-doped	-0.6-0.6 vs.Ag/AgCl	1 M LiClO ₄	147	7
		Polypyrrole-Ti doped			176	
MP	Sol-gel	N/A	-0.8-0 vs.Ag/AgCl	0.5 M Na ₂ SO ₃	283.2	This work
NW					365.7	

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