Supporting Information

Facet-Induced Formation of Hematite Mesocrystals with Improved Lithium Storage Properties

Xiaochuan Duan,[a] Lin Mei,[b] Jianmin Ma,[a,b] Qiuhong Li,[b]* Taihong Wang,[b]* and Wenjun Zheng[a]*

Experimental

Synthesis: All reagents were analytical grade and used without any further purification. In the typical synthesis procedure of psudocubic hematite single-crystals, 1 mL methanol was put into 24 mL *N*,*N*-dimethyl formamide (DMF) under stirring to form a homogenous solution. Subsequently, 0.202 g of $Fe(NO_3)_3·9H_2O$ (0.5 mmol) was added into the above homogenous solution under continuous stirring. After stirring for 10 min, the total solution was transferred into a stainless-steel autoclave with a capacity of 33 mL, sealed and heated at 180 °C for 24 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water, and anhydrous ethanol for several times until the solution was neutral. The final product was dried in a vacuum at 80 °C for 3 h. For investigation of the effect of the composition of the mixed solvent, varying the amount of DMF and methanol could produce a series of hematite with different sizes and moephologies, while preserving all the other conditions described above.

Characterizations: The products were characterized by XRD, SEM, TEM, HR-TEM, and SAED measurements. XRD measurements were performed on a Rigaku D/max 2500 diffractometer with Cu Kα radiation (λ= 0.154056 nm) at V= 40 kV and I = 150 mA, and the scanning speed was 8°/min. Morphology observations were performed on a Hitachi S4800 field emission scanning electron microscope (FE-SEM). TEM, HR-TEM images and corresponding SAED patterns were recorded with a Tecnai G2 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 kV. N_2 adsorption/desorption isotherms were collected at liquid nitrogen temperature using a Quantachrome Nova 2000e sorption analyzer. The specific surface areas (SBET) of the samples were calculated following the multipoint Brunauer-Emmett-Teller (BET) procedure.

Electrochemical experiments: Electrochemical studies were characterized in CR2016-type coin cell with a multi-channel current static system Arbin (Arbin Instruments BT 2000, USA). The negative (anode) electrode consisted of 80 wt% active material, 10 wt% conductivity agents, and 10 wt% binder polymer binder on a copper foil. Test cells were assembled in an argon-filled glove box with water and oxygen contents less than 1 ppm. Li foil was used as counter electrode, polypropylene (PP) film (Celgard 2400) as separator. The electrolyte was 1m LiPF6 (EC/DC/DMC 1:1:1). The cells were discharge-charged between 0.05 and 3.0 V at room temperature.

Table S1. Summary of the Experimental Parameters and Their Corresponding Morphologies of Hematite Nanocrystals Obtained under Different Conditions.

No.	$n(Fe(NO_3)_3$ (mmol)	V(DMF) (mL)	$V(CH_3OH)$ (mL)	Morphology	Side Length (nm)
S-1	0.5	24	1	Psudocubic single-crystal	50
S-2	0.5	22	3	Psudocubic single-crystal	100
S-3	0.5	20	5	Rhombic mesocrystal	200
S-4	0.5	17	8	Ellipsoidal mesocrystal	400

All the reactions were conducted at 180 ºC for 24 h.

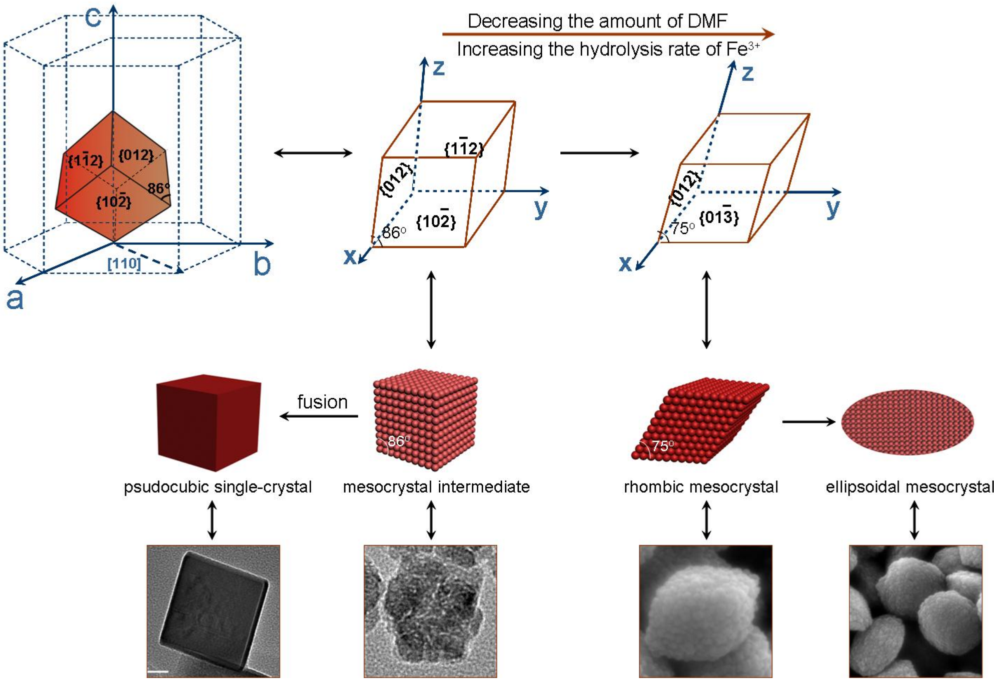
Proposed mechanism: Upon heating the reaction medium up to a sufficiently high temperature, the reactants chemically transform into active particles to form the hematite crystals, which can be formulated as:

$$HCON(CH_3)_2 + H_2O \longrightarrow NH(CH_3)_2 + HCOOH; \qquad (1)$$

$$HCOOH + CH_3OH \longrightarrow HCOOCH_3 + H_2O; \qquad (2)$$

$$2Fe^{3+} + 3H_2O + 6NH(CH_3)_2 \longrightarrow Fe_2O_3 + 6NH_2(CH_3)_2^{+}. \qquad (3)$$

Scheme S1. Schematic Illustration of the formation of hematite nanocrystals with different motphologies. It is clearly can be seen that the exposed planes can be tuned easily by adjusting the composition of the mixed solvent, which can further influence the crystallographic fusion during the crystal growth process to obtain the mesocrystals with high stability.



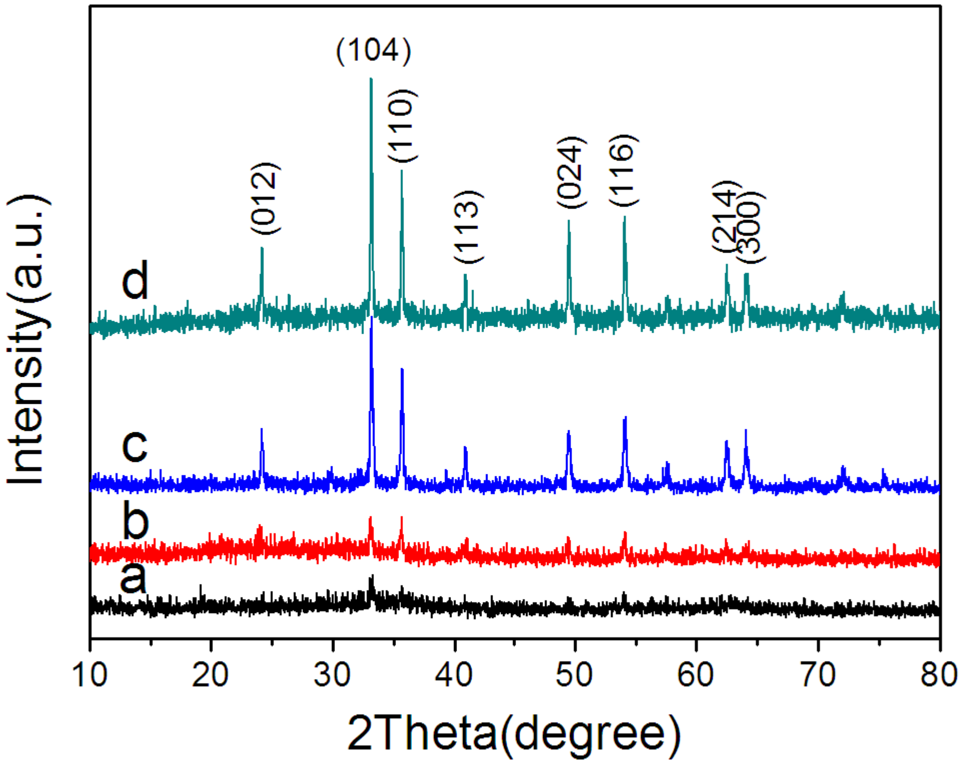


Figure S1. XRD patterns of hematite nano-pesudocubes (S-1) synthesized for (a) 2 h, (b) 6 h, (c) 12 h, and (d) 24 h when V(DMF):V(CH_3OH) = 24:1, respectively.

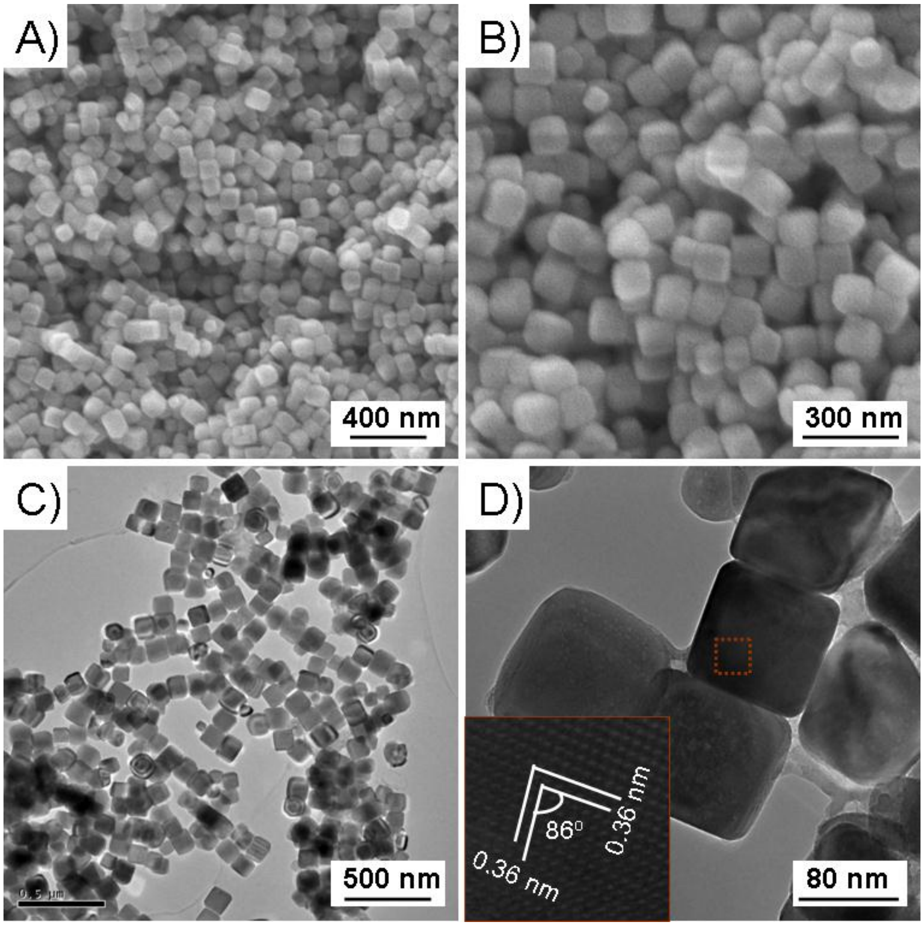


Figure S2. (A) Low- and (B) high-magnification SEM images of as-synthesized hematite nano-pesudocubes (S-2) when V(DMF):V(CH_3OH) = 22:3; (C) Typical low- and (D) high-magnification TEM images of S-2, the inset of panel D is the corresponding HRTEM image.

When decreasing the amount of DMF to change the volume ratio of DMF:CH_3OH to 22:3, the hematite nano-pesudocubes with an average edge length of 100 nm are obtained (Figure S2). The HRTEM image incident that those pesudocubic nanocrystals are also bound by {012} planes. The increase of the edge length (from 50 to 100 nm) can be attributed to the accelerated rate of Fe^{3+} hydrolysis with increasing the amount of CH_3OH.

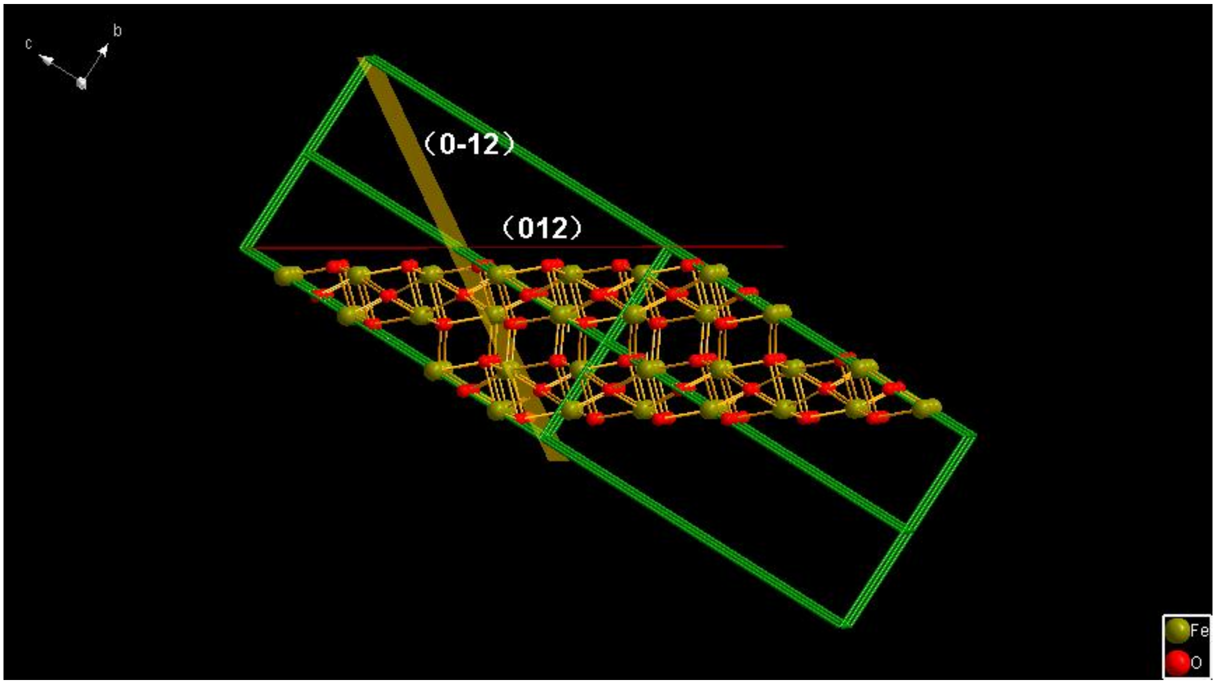


Figure S3. Side view of (012) plane terminations of hematite, which can be clearly seen the O-terminated layer and Fe-terminated layer arranged alternately on (012) surface.

Table S2. Pore Structure Parameters of Samples Obtained under Different Conditions.

Sample	Time (h)	Surface Area (m^2•g^{-1})	Total Pore Volume (cm^3•g^{-1})
S-1, amorphous particles	2	77.43	0.338
S-1, mesocrystal intermediate	6	35.76	0.181
S-1, single-crystal	24	12.56	0.078
S-3, rhombic mesocrystal	24	33.98	0.256

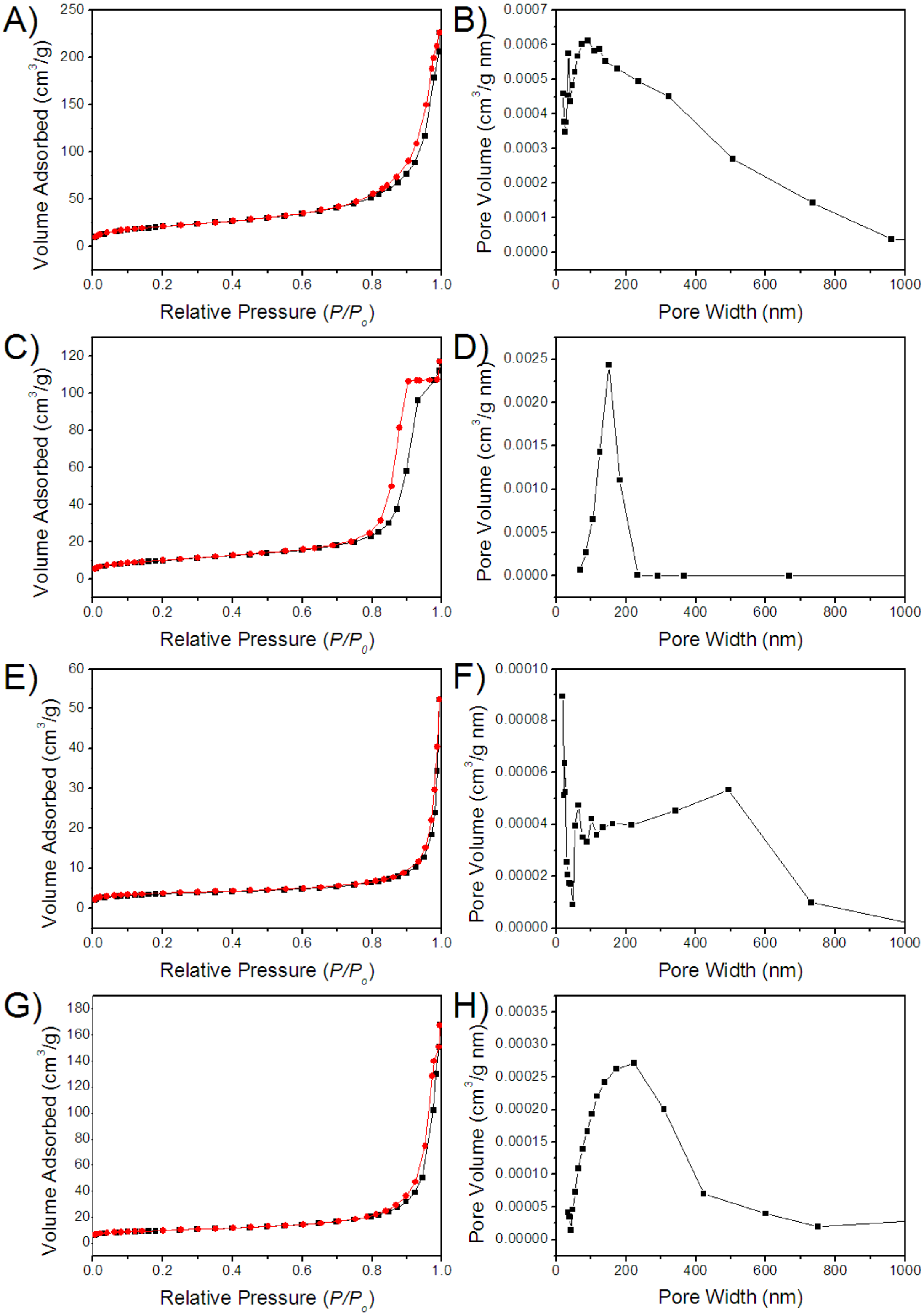


Figure S4. Nitrogen adsorption-desorption isotherms (A, C, E, and G) and the corresponding pore size distribution curves (B, D, F, and H) for the as-prepared samples under different conditions: S-1, 2 h; S-1, 6 h; S-1, 24 h and S-3, 24 h, respectively.

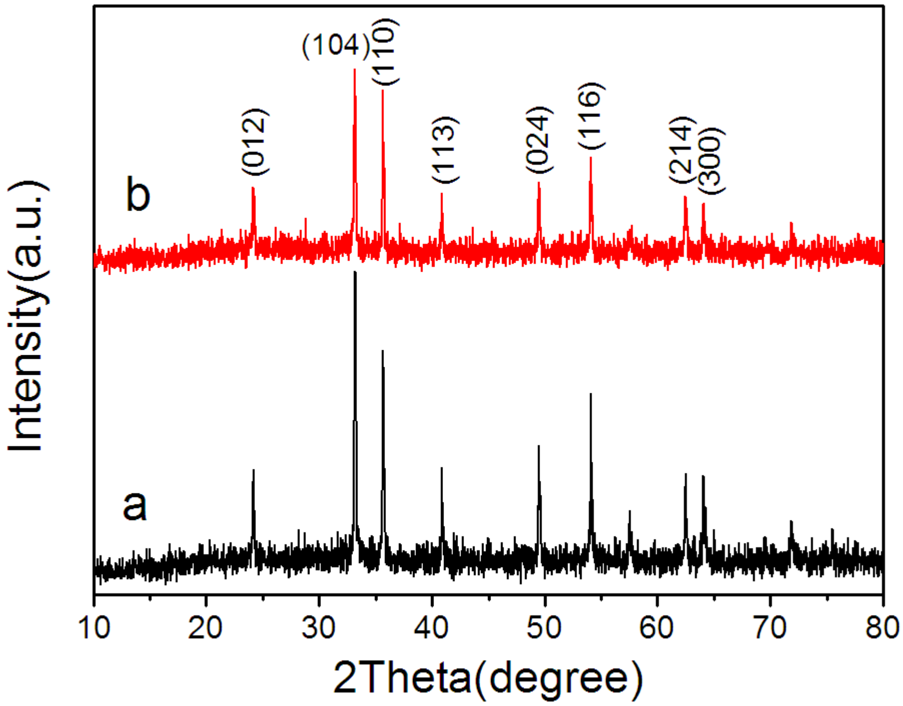


Figure S5. XRD patterns of as-synthesized hematite nanocrystals with different morphologies from different solvent mixtures (volume ratios, total volume of 25 mL): (a) S-3, rhombic mesocrystal, V(DMF):V(CH_3OH) = 20:5; (b) S-4, ellipsoidal mesocrystal, V(DMF):V(CH_3OH) = 17:8. In all patterns, it is evident that all the diffraction peaks can be perfectly indexed to the rhombohedral α-Fe_2O_3 (JCPDS Card 33-0664).

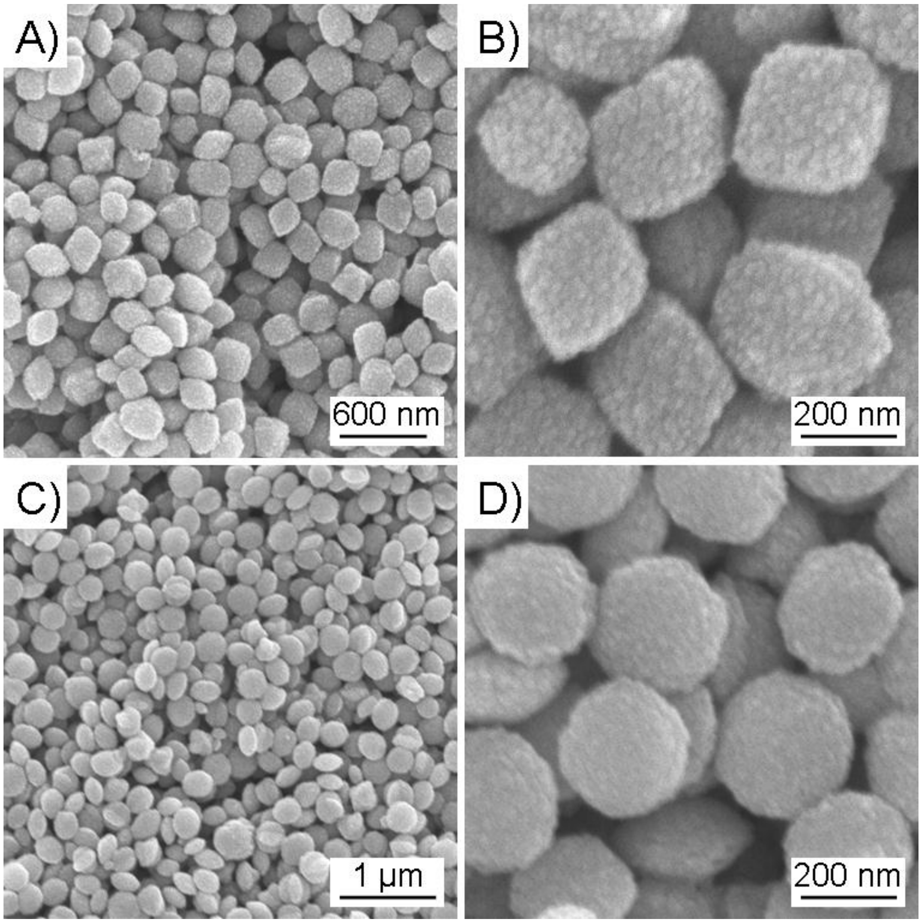


Figure S6. (A, C) Low- and (B, D) high-magnification SEM images of S-3 and S-4, respectively, indicating that high stability of as-prepared hematite mesocrystals with prolonging the reaction time to 72 h.

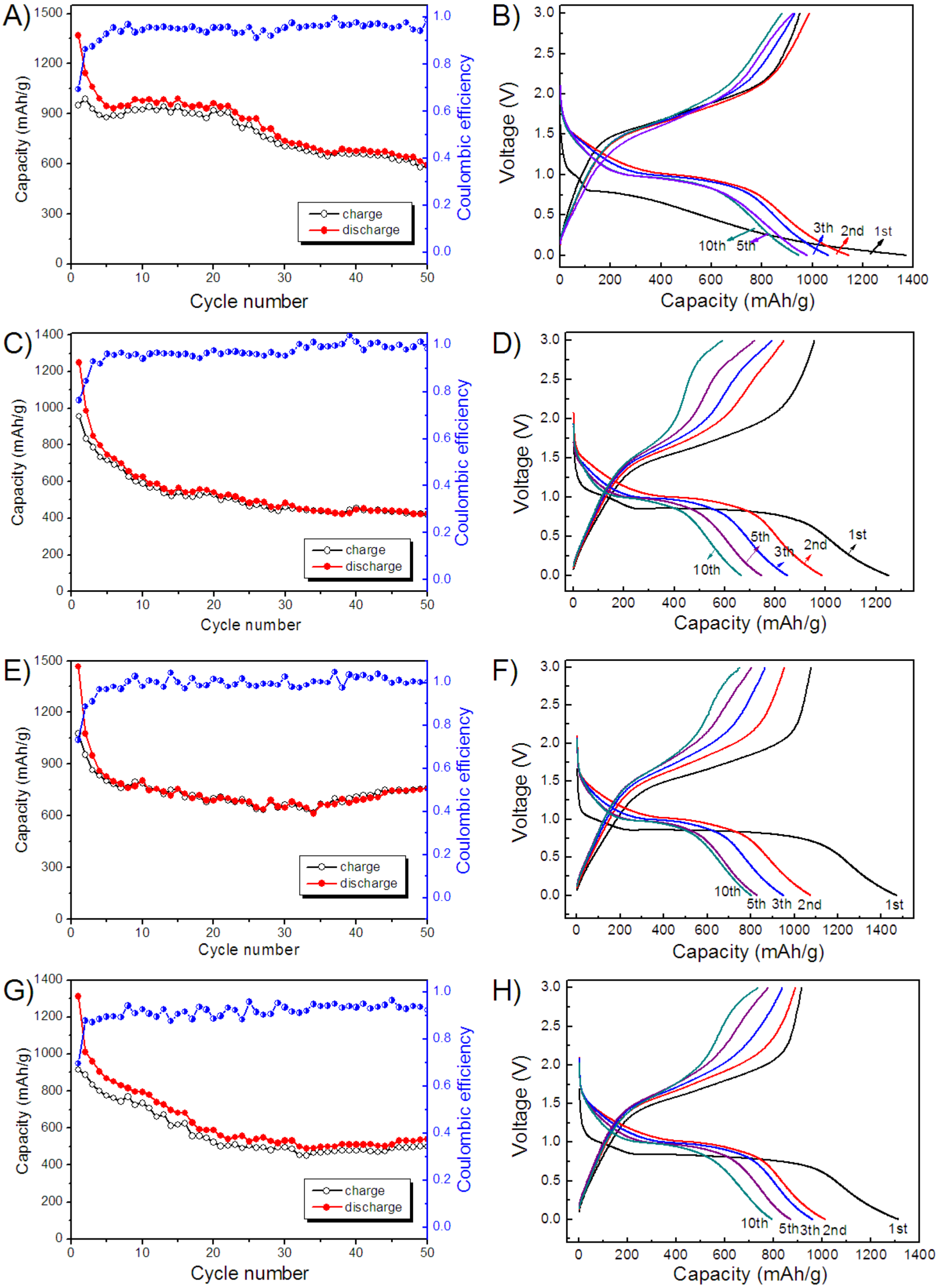


Figure S7. The detailed cycling performance and voltage profiles of the electrode made from the as-prepared α-Fe_2O_3 nanostructures with different morphologies: (A, B) S-1; (C, D) S-2; (E, F) S-3; (G, H) S-4.