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Supporting Information

Aggregative Growth of Quasi-Octahedral Iron Pyrite Mesocrystals in Polyol Solution through Oriented Attachment

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EXPERIMENTAL SECTION

Chemicals

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.0%) and elemental sulfur powder (S, 99.5%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.; triethylene glycol ($C_6H_{14}O_4$, TEG, 97.0%) was purchased from Tianjin DAMAO Chemical Reagent Co., Ltd.; absolute ethanol (CH_3CH_2OH, 99.7%) was purchased from Nanjing Chemical Reagent Co., Ltd. All chemicals were used as received.

Synthesis of Quasi-Octahedral Iron Pyrite Mesocrystals

In a typical procedure, 1.0 mmol $FeCl_3 \cdot 6H_2O$ was dissolved into 40 mL of TEG in a beaker with magnetic stirring at room temperature for 15 min to prepare Fe-TEG solution. To prepare S-TEG solution, 6.0 mmol elemental sulfur was added into 80 mL of TEG in a 250 mL three-necked round-bottom quartz flask, which was connected to a heating mantle and attached to a reflux condenser. When the S-TEG solution was heated up to a temperature of 230 ℃, the prepared Fe-TEG solution was quickly injected into the S-solution with continuous stirring. As long as the mixture was recovered to a temperature of 230 ℃, the reaction mixture was refluxed at this temperature for 10 min, and then cooled to room temperature by water-bath quenching. The precipitate was washed four times with dehydrated alcohol by redispersion and centrifugation (4000 rpm for 5 min).

Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with

Cu Kα radiation (40 kV and 40 mA) at a relative humidity of 60-70 % and 27 °C. Morphology and composition studies were performed on a Hitachi SU8010 cold field emission scanning electron microscope with Energy-dispersive X-ray (EDX) attachment. Raman spectra were recorded on a Renishaw RM2000 Raman Microprobe using a 532 nm Ar-ion laser. FTIR transmission spectra were recorded by a Bruker Vertex-70 Fourier transform infrared spectroscopy (FTIR) at ambient temperature. TEM and selected area electronic diffraction (SAED) were performed by an FEI Talos F200S field-emission transmission electron microscope with SAED attachment.

Reaction Mechanism

At high temperature, the hydroxyl groups in TEG could devote two hydrogen atoms and convert to aldehyde groups,[S1] which is confirmed by FTIR spectra of TEG solution before and after reaction in Figure S1 in the Supporting Information. A peak at ~1730 cm^{-1}, which is assigned to carbanyl groups (C=O), appears in the FTIR spectrum of TEG solution after reaction. Accordingly, the reaction mechanism of iron pyrite formation can be described as follows:

$$HO(CH_2)_2O(CH_2)_2O(CH_2)_2OH + 2S \rightarrow 2H_2S + CHOCH_2O(CH_2)OCH_2CHO$$

$$HO(CH_2)_2O(CH_2)_2O(CH_2)_2OH + Fe^{3+} \rightarrow Fe^{2+} + H^+ + CHOCH_2O(CH_2)OCH_2CHO$$

$$H_2S \leftrightarrow HS^- + H^+$$

$$HS^- \leftrightarrow S^{2-} + H^+$$

$$Fe^{2+} + S^{2-} \rightarrow FeS$$

$$FeS + S \rightarrow FeS_2$$

$$FeS + H_2S \rightarrow FeS_2 + H_2\uparrow$$

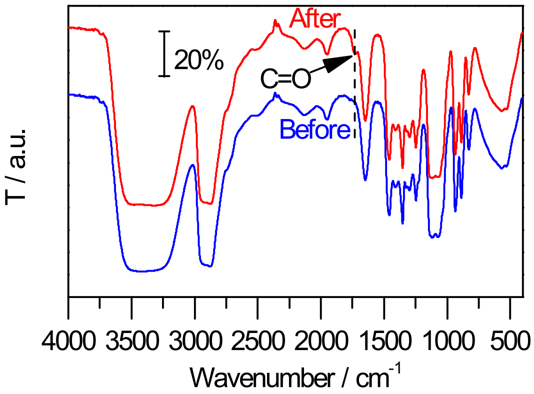

Figure S1. FT-IR spectra of TEG solution before and after reaction.

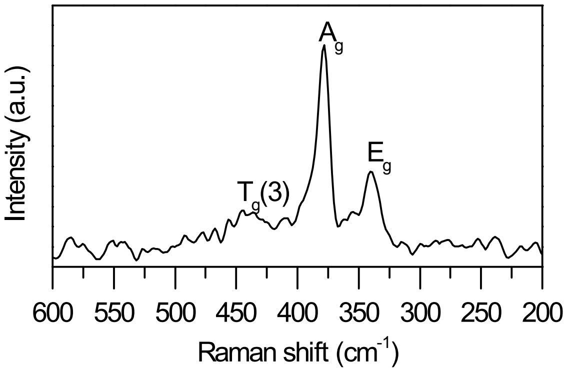

Figure S2. Raman spectrum of the synthesized iron pyrite mesocrystals in polyol solution at 10 min. The A_g, E_g, and $T_g(3)$ vibrational modes are consistent with phonon vibrations previously observed for iron pyrite[S2, 3].

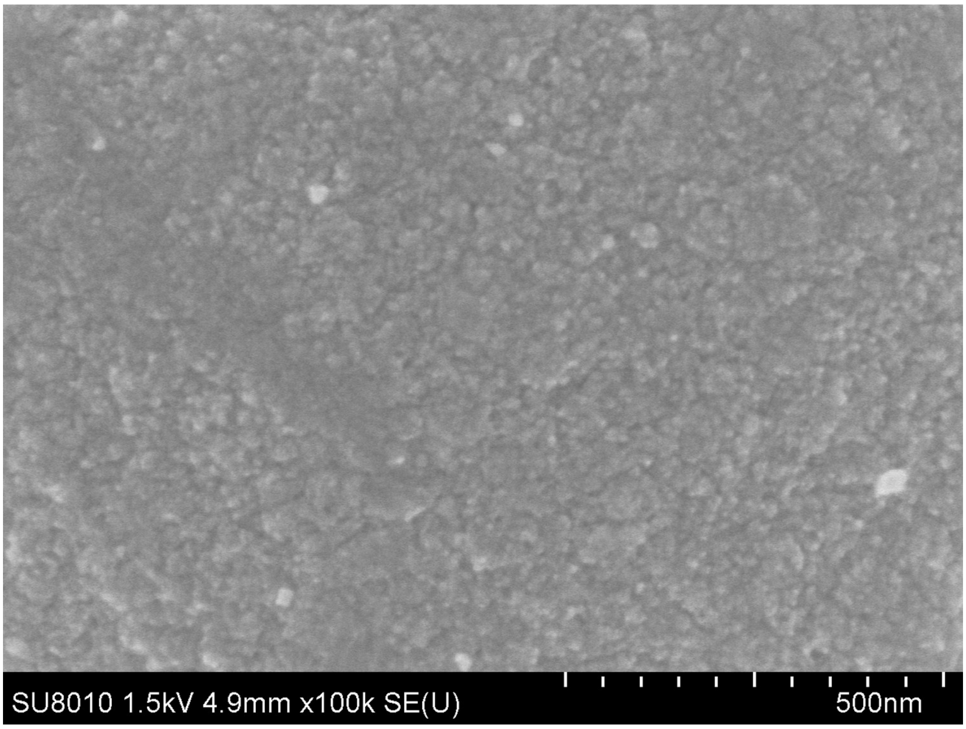

Figure S3. Feature SEM micrograph of the rough surface of the prepared iron pyrite mesocrystals. It can be seen that the rough surface consists of nano particles (<50 nm).

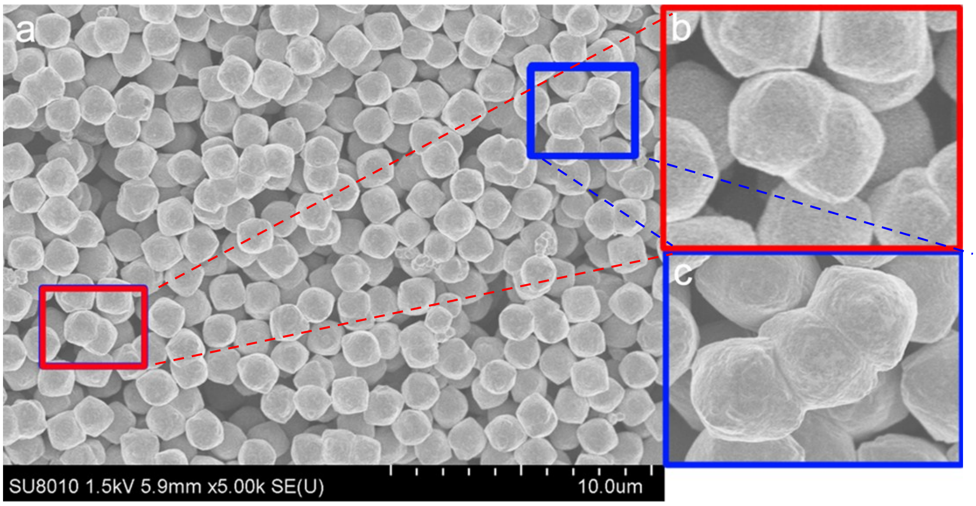

Figure S4. SEM micrographs of twin (in red box) and triplet (in blue box) crystals through aggregation growth

References

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(S2) Bhandari, K. P.; Roland, P. J.; Kinner, T.; Cao, Y.; Choi, H.; Jeong, S.; Ellingson, R. J., Analysis and characterization of iron pyrite nanocrystals and nanocrystalline thin films derived from bromide anion synthesis. *Journal of Materials Chemistry A* **2015,** 3, (13), 6853-6861.

(S3) Bi, Y.; Yuan, Y.; Exstrom, C. L.; Darveau, S. A.; Huang, J., Air Stable, Photosensitive, Phase Pure Iron Pyrite Nanocrystal Thin Films for Photovoltaic Application. *Nano Letters* **2011,** 11, (11), 4953-4957.