Electronic Supplementary Information

Nonclassical crystallization controlled by centrifugation

Ming Hu and Ji-Sen Jiang*

Department of Physics, Center of Functional Nanomaterials and Devices, East China Normal University. Shanghai 200241, China. Tel and Fax: +86-21-54342940.

E-mail: jsjiang@phy.ecnu.edu.cn

Experimental Details.

Materials: All Chemicals including $K_4[Fe(CN)_6] \cdot 3H_2O$, $FeCl_3 \cdot 6H_2O$, cetyltrimethylammonium bromide (CTAB), absolute ethanol and n-hexane were analytically pure and used without further purification.

Method: 168.9 mg K₄[Fe(CN)₆]•3H₂O was added into 40 mL de-ionized water to form clear solution A, subsequently transferred into a centrifugal tube with a volume of 100 mL . 290 mg CTAB and 108.1 mg FeCl₃•6H₂O were added into 10 mL absolute ethanol to form a clear solution and then mixed with 30 mL n-hexane to form clear solution B. After carefully transferred solution B into the centrifugal tube with solution A to form a two phase system, the centrifugal tube was placed into the centrifugal machine quickly and centrifugated at a required speed. Solution B was on the top and solution A was below it. Prussian blue was slowly formed at the interface of two phases through the diffusion of $[Fe(CN)_6]^{4-}$ and Fe^{3+} . As the start process of a centrifugal machine was time-consuming, we had to choose a slow reaction system. After the centrifugal time continued to 7 h, we stopped the machine. The

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blue precipitate collected from theolemanantaro Mathiel (EShteriforgatEngliber) was Prussian blue separated by This journal is © The Royal Society of Chemistry 2010 centrifugation.

As the acceleration of centrifugal machine is time consuming, there will be almost several minutes until the rotation speed could reach the set value. The CTAB added during the experiment is aim to inhibit the diffusion of Fe^{3+} from oil phase into water phase, thus the precipitation rate of Prussian blue could be very slow. Such a role could also be played by TBAB also. If there is not any surfactant, the Fe^{3+} ions will diffuse from oil phase into water phase very soon, and will result in precipitation very quick. Thus the centrifugation will not be able to control the crystallization process.

Characterization: The phase composition of sample was monitored by X-ray diffraction (XRD) using an X'Pert-Pro MPD diffractometer with Cu K α radiation and conventional θ -2 θ geometry. A JEOL JEM-2100F transmission electron microscope operating at 200 kV accelerating voltage was used for transmission electron microscopy (TEM) analysis and selected area electron diffraction (SAED).



Fig. S1. XRD pattern of sample obtained when the centrifugation speed was 3600 r/min.



Fig. S2. HRTEM image of Prussian blue crystal obtained when the centrifugation speed was 3600 r/min. The crystal shows core–shell structure composed of crystalline core and amorphous shell.



Fig. S3. HRTEM image of Prussian blue crystal obtained when the centrifugation speed was 3600 r/min. The crystal shows core–shell structure composed of crystalline core and amorphous shell. Moreover, an amorphous particle attaches to crystal which is highlighted by the white noose.

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Fig. S4 Crystallization occurs in the amorphous precursors.