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Electronic Supplementary Information (ESI) for

Controllable One-pot Synthesis of $FeSe_2$ Nanooctahedra Embedded Microtubes by Sacrificial Self-Template Method

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This file contains:

S1: The possible chemical equation

$SeO_2 + CH_2OHCH_2OH + OH^- = Se + CH_2OHCOO^- + 2H_2O$ (1)

$4Fe^{3+} + CH_2OHCH_2OH + 5OH^- = 4Fe^{2+} + CH_2OHCOO^- + 4H_2O$ (2)

$6Se + 2Fe^{2+} + 6OH^- = 2FeSe_2 + Se_2O_3^{2-} + 3H_2O$ (3)

$Se_2O_3^{2-} + CH_2OHCH_2OH = 2Se + CH_2OHCOO^- + 3H_2O$ (4)

Comprehensive consideration of all the results and reference, the formation of SeO_2 microtubes and nanosheets may possibly conduct according to pervious chemical equations. For existence of reaction (4), the Se is residual unavoidably.

S2: Detailed explanation about morphology evolution of the $FeSe_2$

Here, we proposed a "dual-template" mechanism to explain the morphology evolution process of the $FeSe_2$. In the early stages of the reaction, SeO_2 was reduced into Se particle with assistance of ethylene glycol (EG). Gradually, these nuclei became crystal seeds through crystallization. Meanwhile, EG was attached to the active surface of particles. Polyvinylpyrrolidone (PVP) was prone to cover the surface of particle, moulding the shape of particles into rod and making crystallization along a specific orientation. Absence of PVP or break of the PVP chain takes responsible for the formation of the final nanooctahedra $FeSe_2$ alloy. The EG reduced the Fe^{3+} into Fe^{2+} at the same time, which then reacted with Se with the assistance of EG and sodium hydroxide (NaOH). The NaOH absorbed H^+ ions to make water alkaline and ensure the normal conduction of reduction reaction. The reaction rate along the [001] direction (c axis) was much faster than that at the normal plane due to the "restriction protection" of PVP on specific crystal facets. Therefore, the primary Se nuclei grew

up to a one-dimensional rod-like structure and finally evolve into nanooctahedras $FeSe_2$ embedded microtube via Ostwald ripening.

S3: Detailed discussion about formation of $FeSe_2$ microtubes

From the S1 we can know that EG is the reduction, so the production will remain as Se if the EG is deficient and can't transform into $FeSe_2$ (Fig. S1a-b). However, the final tube structure will collapse (Fig. S1c-d) if EG usage go overboard, which is similar to the situations of reaction for a long period of time (Fig. 1c) and replacement Fe^{3+} with Fe^{2+} (Fig. S2g-h). The main reason is that remnant Se is media for $FeSe_2$ embedded in it. In addition, the NaOH is an additive to adjust the pH value which is important to keep the further reaction of $FeSe_2$ formation going. An alkaline environment may protect the product of Se and $FeSe_2$ from being destroyed by acid at the same time. The absence of NaOH will cause reaction (2-4) unable to continue and none $FeSe_2$ can be obtained. However, if the dosage of NaOH is excess, the morphologies of mid Se rods and final $FeSe_2$ tubes can't be promised (Fig. S2c-d), too. For the reason that the OH^- can turn Fe^{3+} into $Fe(OH)_3$, the reduction of Fe^{3+} and formation of $FeSe_2$ will becomes more difficultly. The final phase of product will transform into Fe_2O_3 (Fig. S3). Besides, if the reaction temperature is not high enough, the reaction equation may not conduct successfully and the $FeSe_2$ microtubes can't form, too (Fig. S2a-b). As for PVP, we have known, as surface active agent, it is important to form Se rod. So the usage of it should be controlled at a suitable level to avoid its side effect (Fig. S2e-f).

Sample	PVP	Reaction time	NaOH	Holding Temperature	Rate of A:B
Fig. 1a	0.5 g	24 h	0.14 g	190 °C	30:10
Fig. 1b	0.5 g	42 h	0.14 g	190 °C	30:10
Fig. 1c	0.5 g	60 h	0.14 g	190 °C	30:10
Fig. 1d	none	42 h	0.14 g	190 °C	30:10
Fig. S1a	0.5 g	42 h	0.14 g	190 °C	25:15
Fig. S1c	0.5 g	42 h	0.14 g	190 °C	35:5
Fig. S2a	0.5 g	42 h	0.14 g	170 °C	30:10
Fig. S2c	0.5 g	42 h	0.28 g	190 °C	30:10
Fig. S2e	1.0g	42 h	0.14 g	190 °C	30:10
Fig. S2g	0.5 g	42 h	0.14 g	190 °C	30:10

Note: Other conditions are same to preparation of $FeSe_2$ microtubes in experimental section, except $FeSO_4$ is used in sample Fig. S2g

Table S1 The reaction time and dosage of PVP of sample a-d in Fig. 1.

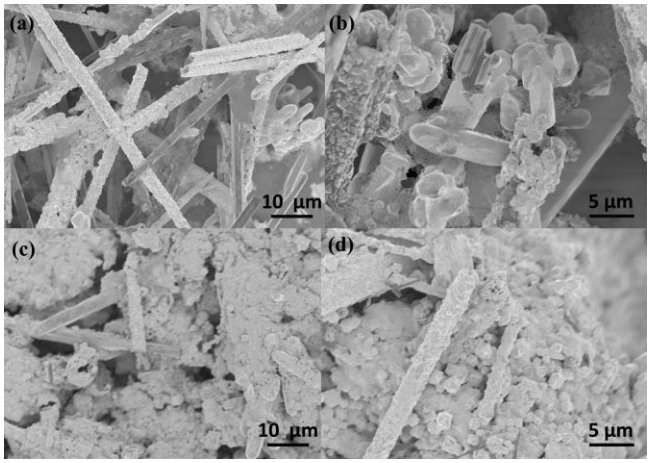

Fig. S1 SEM images of condition: (a, b) deficient EG and (c, d) too much dosage of EG.

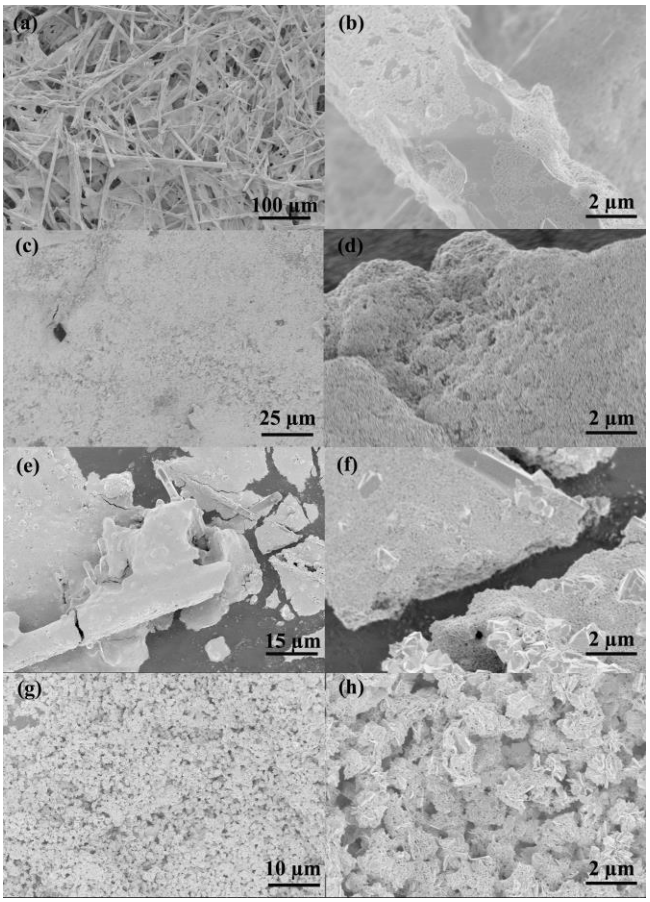

Fig. S2 SEM images of condition: (a, b) holding temperature 170 °C, (c, d) too much dosage of NaOH, (e, f) superfluous PVP and (g, h) replacement $Fe^{3+}$with $FeSO_4$.

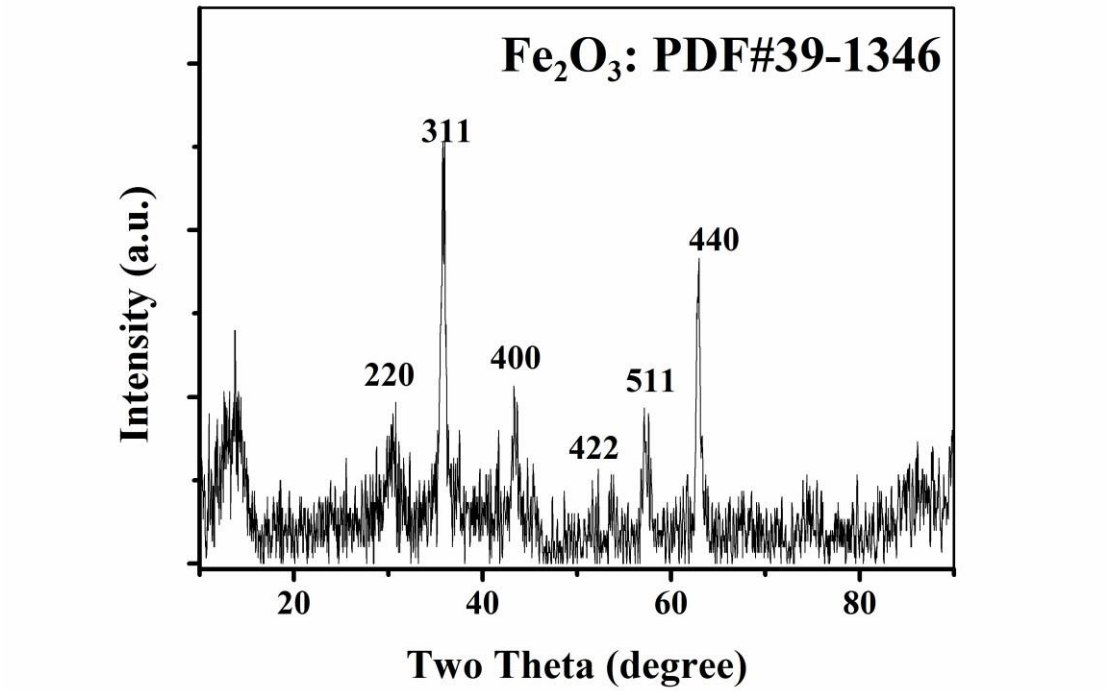

Fig. S3 XRD pattern of final products in condition: too much dosage of NaOH.