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## **Supporting Information**

## **Reversible Perovskite-Fluorite Phase Transition** in Alumina-Supported CeFeO<sub>x</sub> Films

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This supporting information file provides the schematic diagram of the coulometric titration system, data for the mass increase of CeFeO<sub>3</sub> on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, X-ray diffraction (XRD) patterns of reduced CeFeO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after being calcined in air at different temperatures for 12 h, XRD patterns of the CeFeO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample reduced in 3% H<sub>2</sub>O, 10% H<sub>2</sub>, and 87% He at 1073 K for 12 h, the TEM image of bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> annealed at 1173 K for 24 h, and the TEM image of the CeFeO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample reduced in 10% dry H<sub>2</sub> for 12 h.



Fig. Sup1. Schematic diagram of the coulometric titration apparatus.



**Fig. Sup2** Plot of the mass increase normalized to the mass of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support as a function of the number of CeFeO<sub>3</sub> ALD super-cycles.



**Fig. Sup3** The XRD patterns of reduced  $CeFeO_x/\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined in air at different temperatures for 12 h. The sample was pretreated by 5 redox cycles followed by reduction in hydrogen at 1073K to obtain the reduced state.



Fig. Sup4 The XRD pattern of the CeFeO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample pretreated by 5 redox cycles followed by reduction in 3% H<sub>2</sub>O, 10% H<sub>2</sub>, and 87% He at 1073 K for 12 h.



Fig. Sup5 TEM images of (a) bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> annealed at 1173 K for 24 h, and (b) the CeFeO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample reduced in 10% dry H<sub>2</sub> for 12 h.