Supporting Information for

Nanoparticles of Lanthanide oxysulfate/oxysulfide for improved oxygen storage/release

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EXPERIMENTAL

Materials
All chemicals were used as purchased without further purification: analytical grade solvents (Sigma-Aldrich), sodium dodecyl sulfate (99%, Sigma-Aldrich), octadecane (99%, Sigma-Aldrich), nickel(II) chloride hexahydrate (99.9%, Sigma-Aldrich), acetylaceton (acac, 98%, Fluka) and lanthanide chlorides (LnCl₃·6H₂O, Stem Chemicals).

Preparation and characterization of nanosized Pr₂O₂SO₄
The NPs of Pr₂O₂SO₄ were prepared by a previously reported miniemulsion method starting from Pr(acac)₃. To prepare nanodroplets in a miniemulsion containing Pr³⁺, the dispersed hydrophobic phase was obtained by dissolving 100 mg of Pr(acac)₃ and 20 mg of octadecane in 5 mL of dichloromethane. The dispersed phase was then added dropwise to a continuous phase consisting of 50 mg of SDS in 16 mL of water. The mixture was vigorously stirred at room temperature for 1h (pre-emulsion) and then ultrasonicated for 5 min under ice cooling at 62% amplitude with time interval 1 s (Qsonica Sonicator, 500W, 1/2 inch tip) yielding a greenish milky miniemulsion. The hydrophobic phase was then removed by careful evaporation at slightly reduced pressure and room temperature (to avoid aggregation), until an opaque dispersion appeared. The obtained dispersion was freeze-dried, yielding Pr-containing fluffy powders. To obtain solid Pr₂O₂SO₄, thermal decomposition was performed by calcination at 850 °C in an air atmosphere for 1 h with a heating rate of 10 °C min⁻¹. TGA was used to evaluate conversion of the freeze-dried Ln-containing nanodroplets into the solid particles. The structure of the Pr₂O₂SO₄ was identified by a Bruker D8 Advance X-ray diffractometer using Co Kα radiation (1.789 Å) at 35 kV and 40 mA. The data were collected from 5.0° to 80°2θ with a step size of 0.020°2θ and a counting time of 0.5 s per step. Lattice constants of Ln-oxysulfates and Ln-oxides were calculated and corrected using MDI JADE software. The particle size and morphology were analyzed by TEM (JOEL JEM-2100) with 200 kV acceleration voltages. High Resolution TEM images were acquired on a FEI Titan TEM, equipped with Cs image corrector at 300 kV, using a low beam current density of 0.08 A/cm². Energy Dispersive X-Ray (EDX) mapping was performed in STEM mode, using an Oxford Instruments X-MaxN 100TLE detector. The chemical composition of NPs was
analyzed by energy dispersive X-ray spectroscopy (EDS) on a JEOL-JMS 6010 scanning electron microscope with an acceleration voltage of 20 kV.

For the preparation of Ni-doped Pr$_2$O$_2$SO$_4$ nanoparticles, 25 mg of as-synthesized Pr$_2$O$_2$SO$_4$ was added into 200 µL of NiCl$_2$ solution (containing 1.5 wt% Ni corresponding to Pr$_2$O$_2$SO$_4$). The mixture was firstly dried at 50 °C, and then calcined at 450 °C in an air atmosphere for 1.5 h with a heating rate of 10 °C min$^{-1}$.

The reduction/re-oxidation profiles of Pr$_2$O$_2$SO$_4$ NPs were measured by temperature-programmed reduction and re-oxidation (TPR/TPRO) in a conventional homemade flow-reactor, as shown in Figure S5. A tubular quartz reactor with 6 mm inner diameter was firstly filled with a layer of quartz wool, followed by a layer of 200 mg of SiC and 15-20 mg of Pr$_2$O$_2$SO$_4$ sample, followed by another 200 mg of SiC. The reactor was connected to an inert system and to a differential evacuation system. After a careful flushing by He, the reactor was heated in a flowing gas mixture of 10% H$_2$ in Ar (20 mL min$^{-1}$) with a constant rate 10 °C min$^{-1}$ until 900 °C. The H$_2$ consumption was monitored by a TCD (thermal conductivity detector). After the completion of the TPR measurement, the sample was cooled down in a N$_2$ flow. This was followed by evacuation and a second heating in a flow of 20% O$_2$ in He (20 mL min$^{-1}$) at a heating rate 10 °C min$^{-1}$ up to 900 °C to measure the TPRO profile. The effluent gas was analyzed by a homemade mass spectrometer equipped with Hartmann & Braun URAS 10E RGA (residual gas analyzer). The overall H$_2$ and O$_2$ consumptions in TPR and TPRO are calibrated by the redox of a known amount of CuO. To calculate the redox rate of the Ni-doped Pr$_2$O$_2$SO$_4$ sample, 15-20 mg of Pr$_2$O$_2$SO$_4$ was kept at 600/700 °C, 10 % H$_2$ in Ar and 5% O$_2$ in He were applied in the reduction and oxidation, respectively.
Figure S1. TGA profile of Pr-containing nanodroplets prepared by miniemulsion method. The continuous weight loss between 30 and 200 °C is due to the dehydration from structurally bound water. While the significant weight loss above 200 °C is due to the combustion of organic moieties in the composite along with the formation of Pr$_2$O$_2$SO$_4$ [W. Zhang et al. RSC Adv. 2015, 5, 69861-69869].

Figure S2. TEM images of the solid Pr$_2$O$_2$SO$_4$ NPs.
Figure S3. EDS spectrum of (a) Pr$_2$O$_2$SO$_4$ and (b) Ni-doped Pr$_2$O$_2$SO$_4$ NPs. The amount of Ni is 1.89 wt%. 


Figure S4. Powder XRD patterns of Pr$_2$O$_2$SO$_4$ and Ni-doped Pr$_2$O$_2$SO$_4$.

Figure S5. HRTEM images of Ni-doped Pr$_2$O$_2$SO$_4$ nanoparticles confirming their crystalline nature. (a) Inset is the corresponding SAED pattern. (b) The corresponding HRTEM image of the red circle portion of Pr$_2$O$_2$SO$_4$ nanoparticles. The calculations on the selected lattice space result in 1.57, 0.72, 0.55, 0.45 and 0.36 nm, corresponding to the interplanar space of (001), (002), (100), (100), (310) and (202) crystallographic plane, respectively. The results are in fair agreement with the interplanar space of the standard (PDF#41-0679).
Figure S6. Image of TPR/TPRO setup used in the experiment.