Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Mechanistic aspects of photo-induced formation of peroxide ions on the surface of cubic Ln_2O_3 (Ln = Nd, Sm, Gd) under oxygen

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Electronic supplementary information (ESI)

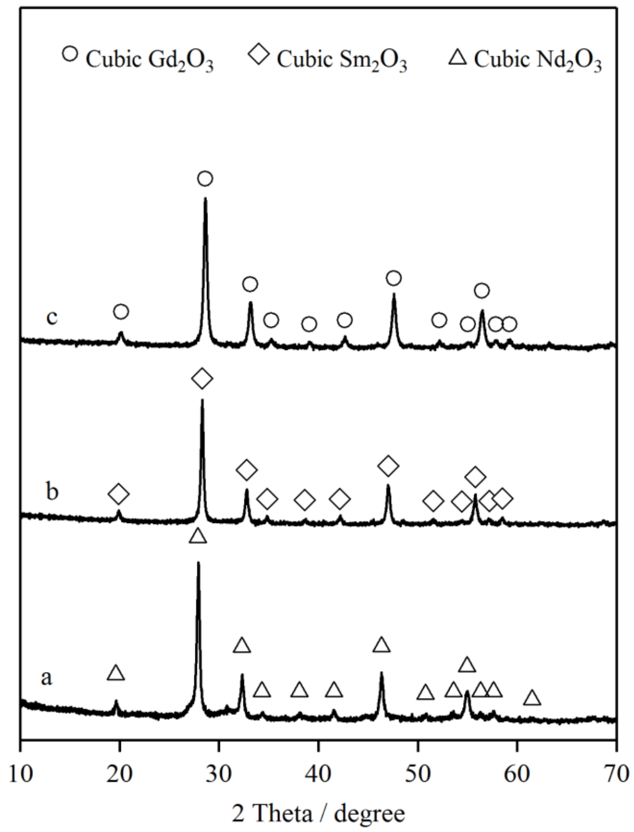

Fig. S1. XRD patterns of the prepared Ln_2O_3 samples: a) Nd_2O_3, b) Sm_2O_3 and c) Gd_2O_3.

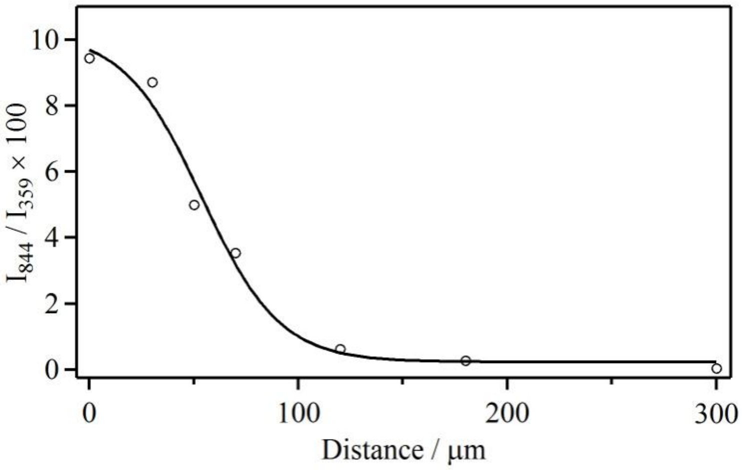

Fig. S2. Plot of intensity ratio of the Raman peaks at 844 cm^{-1} ($\nu_{(O-O)^{2-}}$) and 359 cm^{-1} ($\nu_{(Gd^{3+}-O^{2-})}$) on a cubic Gd_2O_3 against the distance from the center of the laser beam after the sample under O_2 was continuously irradiated with a focused 325 nm laser beam (~ 3 μm in diameter) at 150 °C for 90 min.

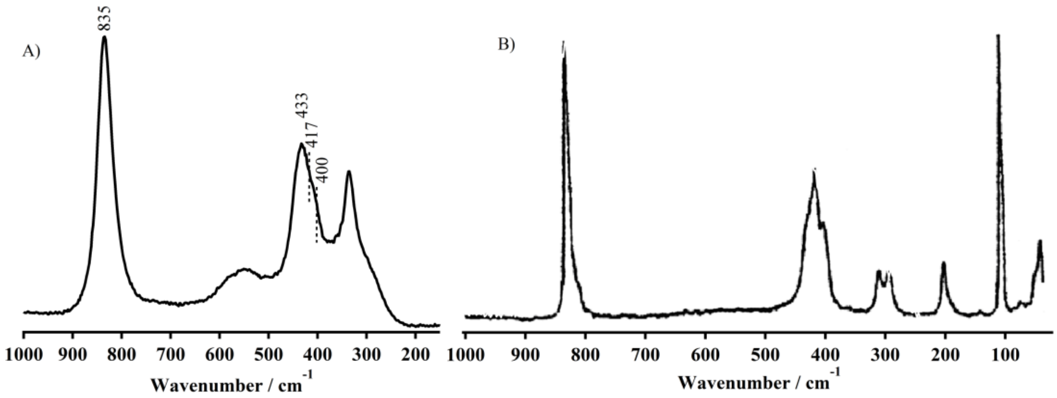

Fig. S3. A) the Raman spectrum of the Nd peroxide linkage formed by irradiating cubic Nd_2O_3 under flowing O_2 with 325 nm laser at room temperature, B) The Raman spectrum of $Nd_2O_2(O_2)$ (neodymium (III) oxide peroxide) reported by A. M. Heyns and K. J. Range (*J. Raman. Spectrosc*., 1994, **25**, 855).

Calculation of the band positions for the $^{18}O_2^{2-}$ and $(^{18}O^{16}O)^{2-}$ peroxide ions

For a diatomic molecule A-B, the fundamental vibration frequency (ν) of a chemical bond between atom A and B could be approximated by a harmonic oscillator:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where

k is the spring constant for the bond; and

μ ($\mu = \frac{M_A \times M_B}{M_A + M_B}$, M is the mass of the atom) is the reduced mass for diatomic molecule A-B.

The fundamental vibration frequency (ν) for the $^{16}O_2^{2-}$, $^{18}O_2^{2-}$ and $(^{18}O^{16}O)^{2-}$ peroxide ions are given by the following equations

$$\nu_{^{16}O_2^{2-}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{^{16}O_2}}}$$

$$\nu_{^{18}O_2^{2-}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{^{18}O_2}}}$$

$$\nu_{(^{18}O^{16}O)^{2-}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{^{18}O^{16}O}}}$$

Based on the band position for the fundamental vibration frequency of the $^{16}O_2^{2-}$ peroxide ion ($\nu_{^{16}O_2^{2-}}$) at 833 cm^{-1}, band positions for the $^{18}O_2^{2-}$ and $(^{18}O^{16}O)^{2-}$ peroxide ions can be calculated using the following equations

$$\nu_{^{18}O_2^{2-}} = \nu_{^{16}O_2^{2-}}\sqrt{\frac{\mu_{^{16}O_2}}{\mu_{^{18}O_2}}} = 0.943\ \nu_{^{16}O_2^{2-}} = 0.943 \times 833 = 786\ cm^{-1}$$

$$\nu_{(^{18}O^{16}O)^{2-}} = \nu_{^{16}O_2^{2-}}\sqrt{\frac{\mu_{^{16}O_2}}{\mu_{^{18}O^{16}O}}} = 0.972\ \nu_{^{16}O_2^{2-}} = 0.972 \times 833 = 810\ cm^{-1}$$