Mechanistic aspects of photo-induced formation of peroxide ions on the surface of cubic Ln$_2$O$_3$ (Ln = Nd, Sm, Gd) under oxygen

Xiao-Lian Jing, Qing-Chuan Chen, Chong He, Xue-Quan Zhu, Wei-Zheng Weng*, Wen-Sheng Xia, Hui-Lin Wan*

Electronic supplementary information (ESI)

Fig. S1. XRD patterns of the prepared Ln$_2$O$_3$ samples: a) Nd$_2$O$_3$, b) Sm$_2$O$_3$ and c) Gd$_2$O$_3$. 
Fig. S2. Plot of intensity ratio of the Raman peaks at 844 cm\(^{-1}\) (\(\nu_{(\text{O}^{-})}\)) and 359 cm\(^{-1}\) (\(\nu_{(\text{Gd}^{3+}-\text{O}^{2-})}\)) on a cubic Gd\(_2\)O\(_3\) 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 \(\mu\)m in diameter) at 150 \(^{\circ}\)C for 90 min.
Fig. S3. A) the Raman spectrum of the Nd peroxide linkage formed by irradiating cubic Nd$_2$O$_3$ under flowing O$_2$ with 325 nm laser at room temperature, B) The Raman spectrum of Nd$_2$O$_2$(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 \( ^{18}\text{O}_2^2^- \) and \((^{18}\text{O}^{16}\text{O})_2^2^-\) peroxide ions

For a diatomic molecule A-B, the fundamental vibration frequency \( (\nu) \) 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

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

The fundamental vibration frequency \( (\nu) \) for the \( ^{16}\text{O}_2^2^- ,^{18}\text{O}_2^2^-\) and \((^{18}\text{O}^{16}\text{O})_2^2^-\) peroxide ions are given by the following equations

\[
\nu_{^{16}\text{O}_2^2^-} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{^{16}\text{O}_2}}} \\
\nu_{^{18}\text{O}_2^2^-} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{^{18}\text{O}_2}}} \\
\nu_{(^{18}\text{O}^{16}\text{O})_2^2^-} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{(^{18}\text{O}^{16}\text{O})}}} 
\]

Based on the band position for the fundamental vibration frequency of the \( ^{16}\text{O}_2^2^- \) peroxide ion \( (\nu_{^{16}\text{O}_2^2^-}) \) at 833 cm\(^{-1}\), band positions for the \( ^{18}\text{O}_2^2^- \) and \((^{18}\text{O}^{16}\text{O})_2^2^-\) peroxide ions can be calculated using the following equations

\[
\nu_{^{18}\text{O}_2^2^-} = \nu_{^{16}\text{O}_2^2^-} \sqrt{\frac{\mu_{^{18}\text{O}_2}}{\mu_{^{16}\text{O}_2}}} = 0.943 \times 833 = 786 \text{ cm}^{-1} \\
\nu_{(^{18}\text{O}^{16}\text{O})_2^2^-} = \nu_{^{16}\text{O}_2^2^-} \sqrt{\frac{\mu_{^{18}\text{O}^{16}\text{O}}}{\mu_{^{16}\text{O}_2}}} = 0.972 \times 833 = 810 \text{ cm}^{-1}
\]