

Supporting Information

Tandem Hydroperoxyl–Alkylperoxyl Radical Quenching by an Engineered Nanoporous Cerium Oxide Nanoparticle Macrostructure (NCeONP): Toward Efficient Solid-State Autoxidation Inhibitors.

Riccardo Amorati^{A*}, Yafang Guo^A, Bridgette Maria Budhlal^B, Carol Forance Barry^B, Dongmei Cao^C and Siva Sai Ramana Kumar Challa^{D*}

^ADepartment of Chemistry “G. Ciamician”, University of Bologna, Via Gobetti 83, 40129, Bologna, Italy; e-mail: riccardo.amorati@unibo.it

^BDepartment of Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, United States;

^CLouisiana State University, Shared Instrumentation Facility, 121 Chemistry and Material Building, 4048 Highland Rd. Baton Rouge, LA, 70809, United States

^DXheme, Inc., UMass Innovation Institute, Mt. Ida Campus of UMass Amherst, School of Applied Science, 100 Carlson Ave, Newton, MA. 02459, United States, e-mail: kumar@xhemeinc.com

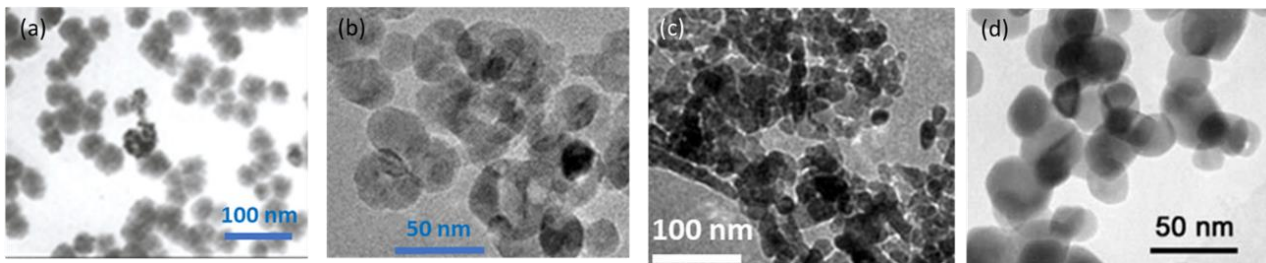


Figure S1. TEM images of (a) TiO₂ (Rutile), (b) TiO₂ (Anatase), (c) ZnO, and (d) ZrO₂ nanoparticles. The average particle sizes of TiO₂ (Rutile), TiO₂(Anatase), ZnO and ZrO₂ nanoparticles are 10-30 nm, respectively, indicating that they are non-porous spherical particles, unlike NCeONP.

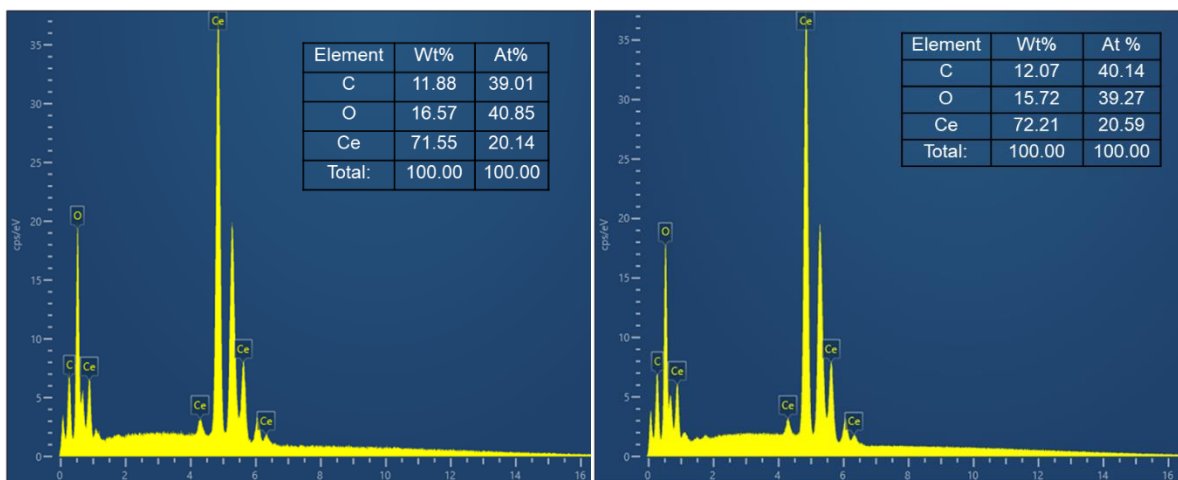


Figure S2. EDS spectra of NCeONP (left) and CeO₂ nanoparticles(right)

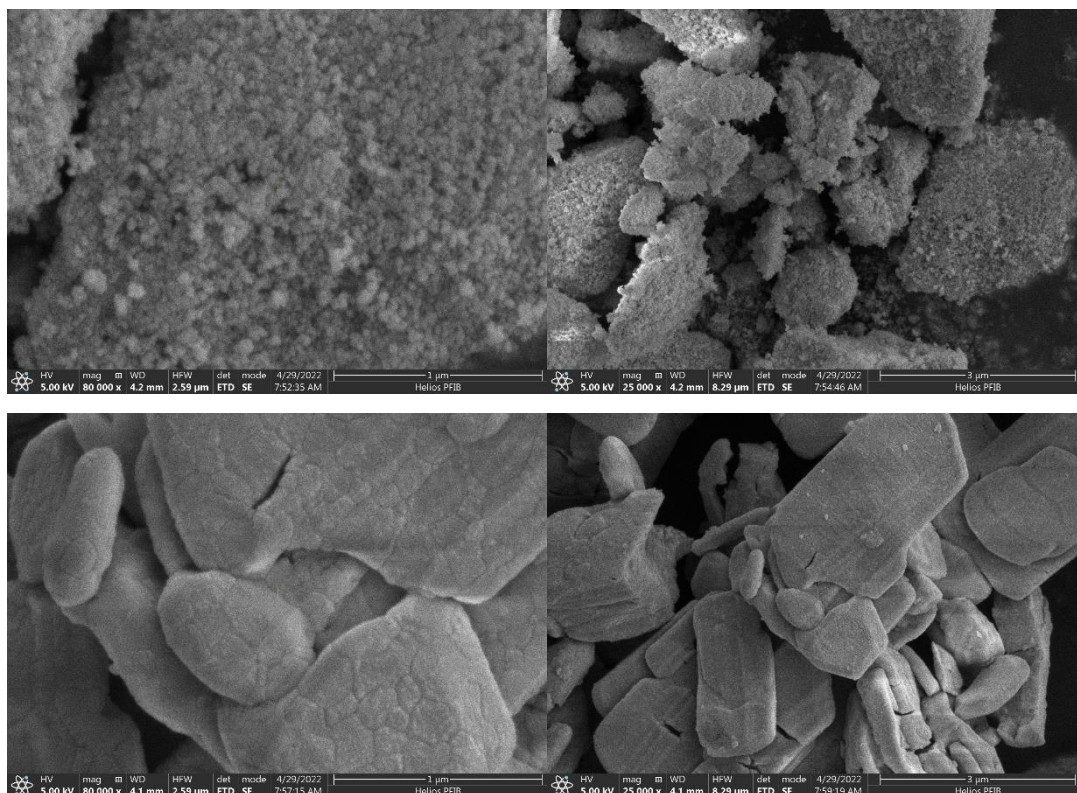


Figure S3. SEM Images of NCeONP (top two images) and CeO₂ nanoparticles (bottom two images)

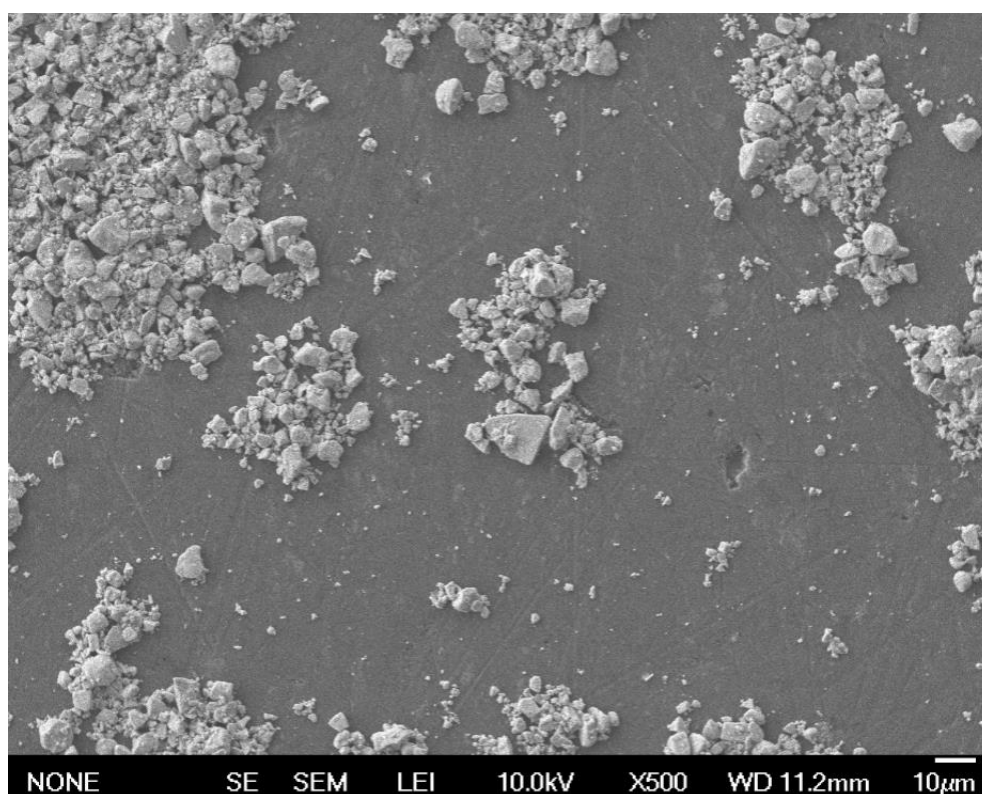


Figure S4. Low-resolution SEM image of NCeONP.

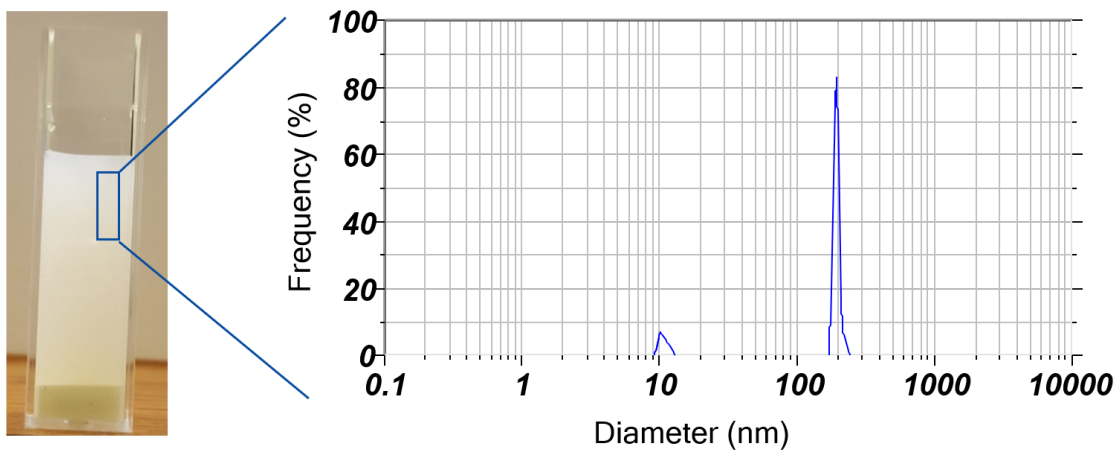
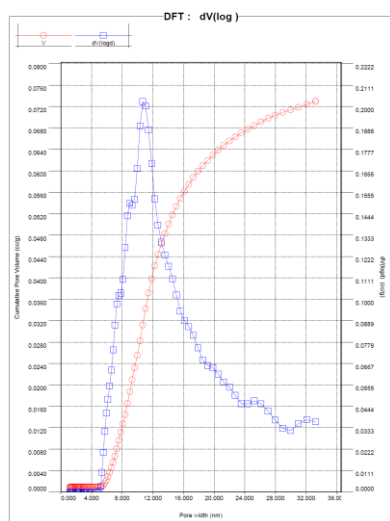
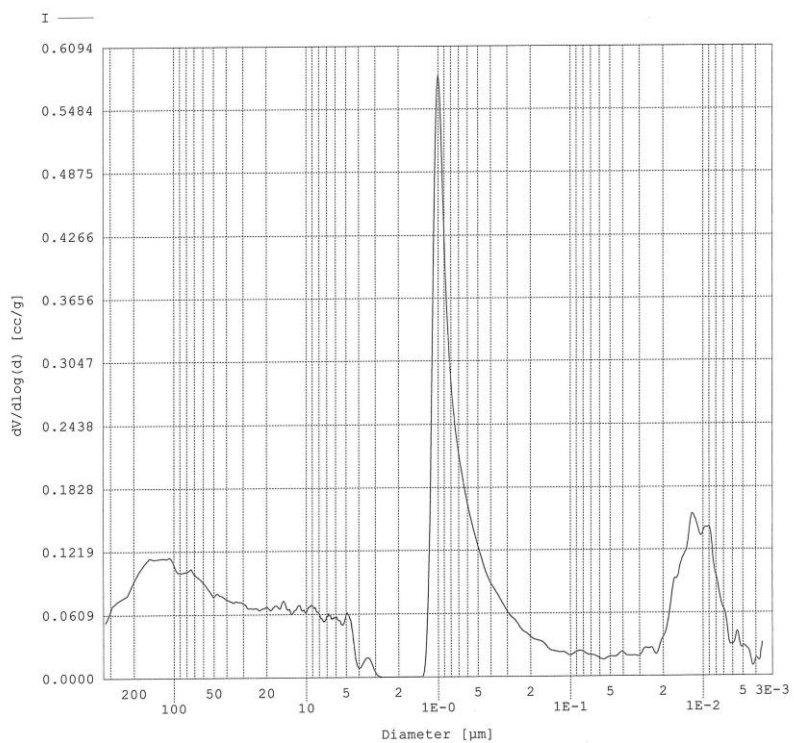


Figure S5: DLS spectrum of the supernatant of NCeONP in water.



DFT method summary	
Pore volume =	0.073 cc/g
Surface area =	29.285 m ² /g
Lower confidence limit =	1.193 nm
Fitting error =	0.962 %
Pore width (Mode) =	10.682 nm
Moving point average :	off

Figure S6. NCeONP-Porosity and surface area measurements using Nitrogen BET measurements showing nanoporosity.



MERCURY INTRUSION POROSIMETRY (MIP) DATA SUMMARY

TOTAL INTRUSION VOLUME (cc/g)	TOTAL SURFACE AREA (m ² /g)	VOLUME MEDIAN PORE DIAMETER (μm)	BULK DENSITY (g/mL)	APPARENT DENSITY (g/mL)	% POROSITY
0.37	27.37	0.9864	1.72	4.82	64.3

Figure S7. NCeONP-Porosity and surface area measurements using Mercury Intrusion Porosimetry (MIP) measurements showing micropores.

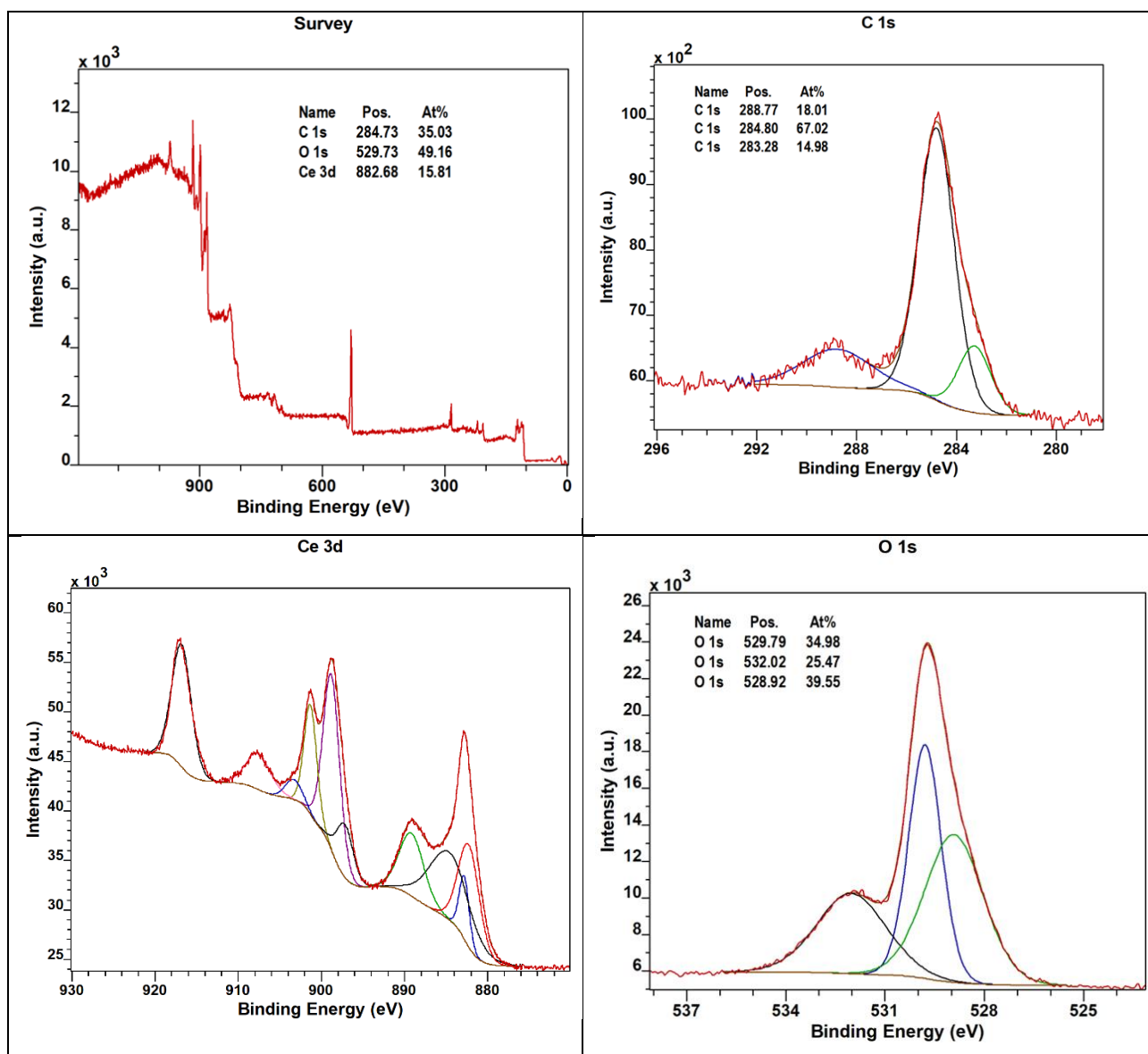


Figure S8. XPS spectra of NCeONP macrostructures

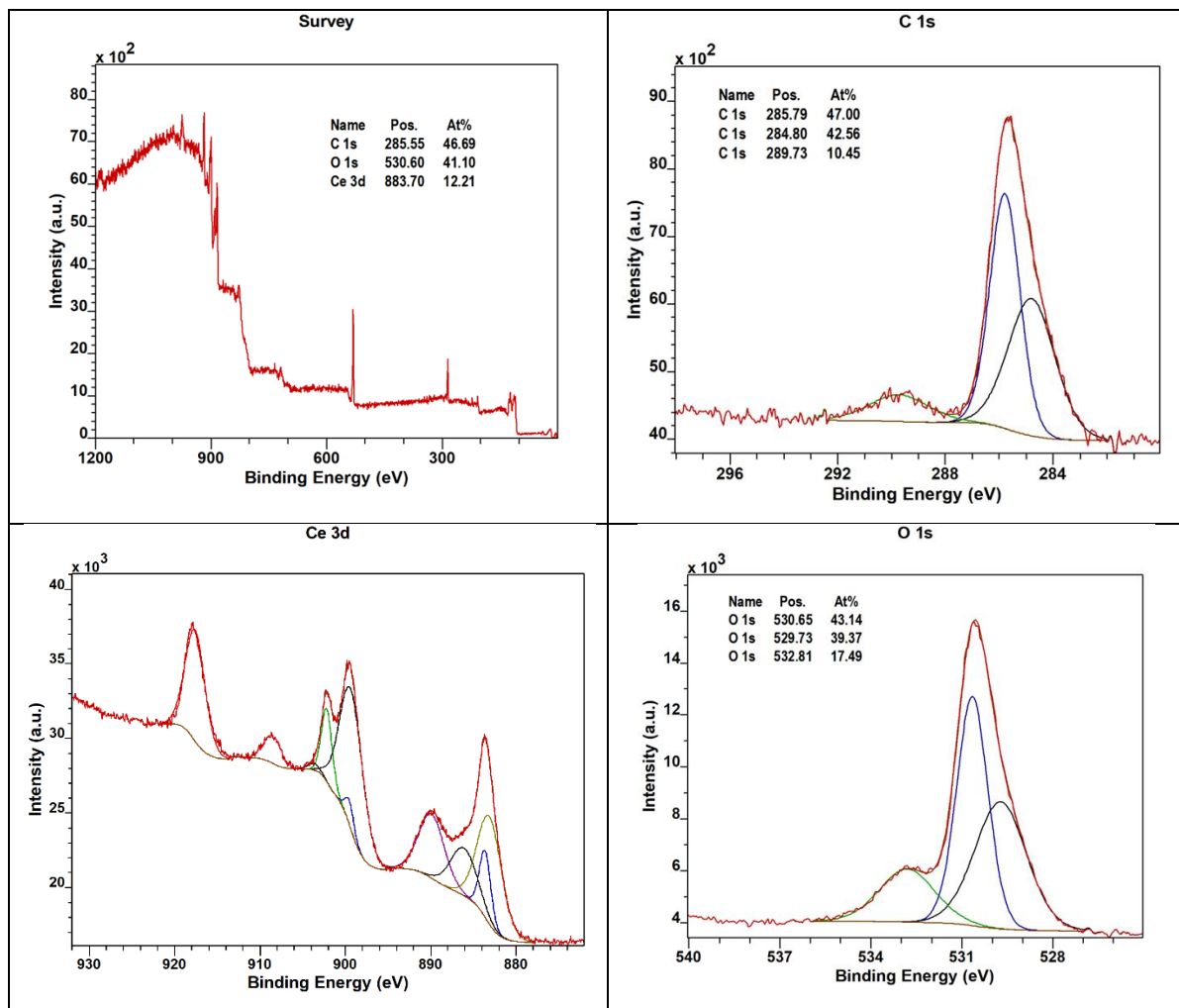


Figure S9. XPS spectra of CeO₂ nanoparticles

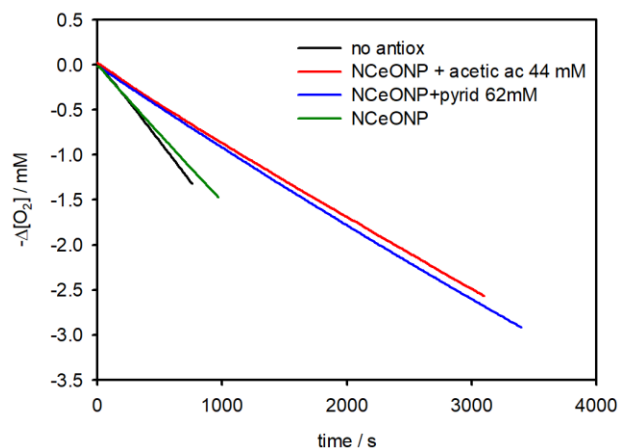
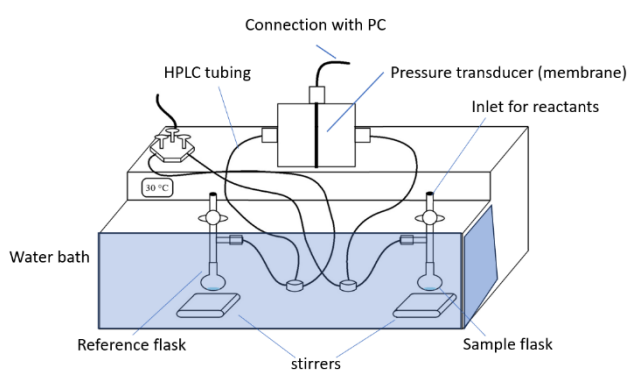


Figure S10. Left. Schematic diagram of the O₂ uptake recording apparatus. Right. O₂ consumption during the autoxidation of styrene (4.3 M) initiated by AIBN (25 mM) at 30 °C in MeCN without any inhibitors (black line), in the presence of 0.25 mg/mL of NCeONP with 44 mM acetic acid (red) or 62 mM pyridine (blue).

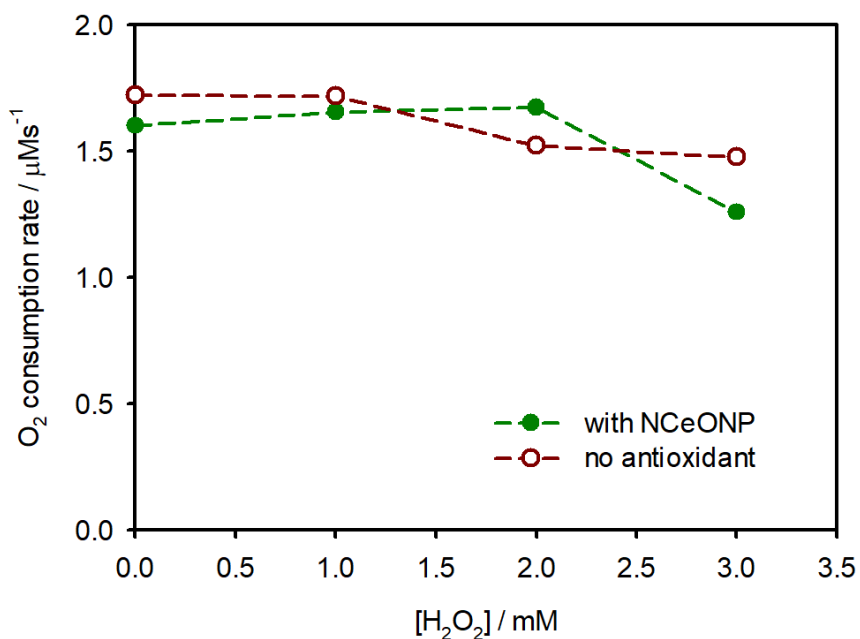


Figure S11. Slope of O₂ consumption during the autoxidation of styrene (4.3 M) initiated by AIBN (25 mM) at 30 °C in MeCN in the presence of increasing amount of hydrogen peroxide, without or with NCeONP (0.25 mg/mL).

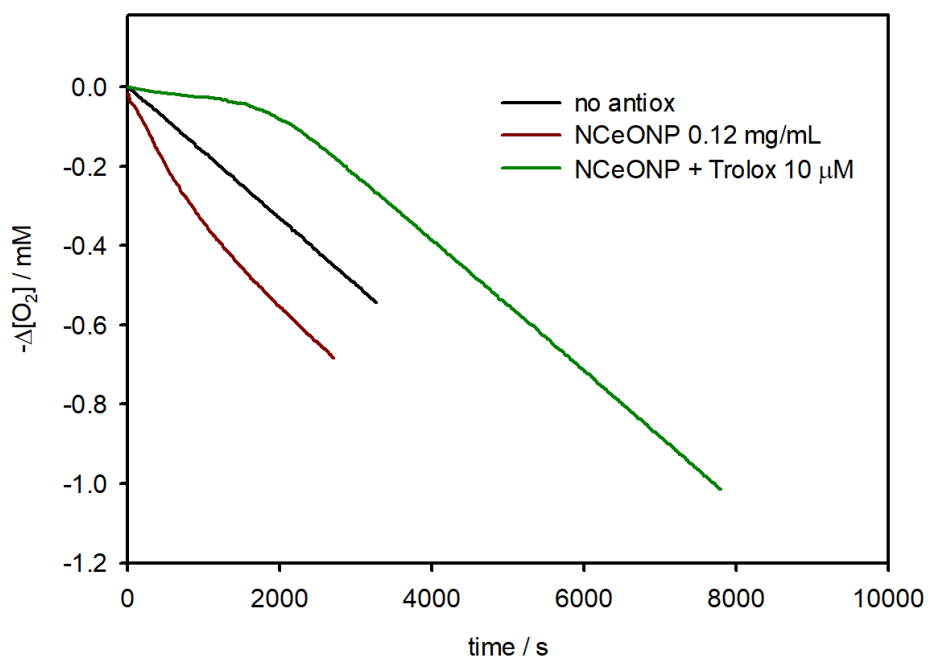


Figure S12. O₂ consumption during the autoxidation of tetrahydrofuran (3.1 M) initiated by AAPH (25 mM) at 30°C in water at pH 7.4 ($R_i = 8.8 \times 10^{-9} \text{ Ms}^{-1}$)

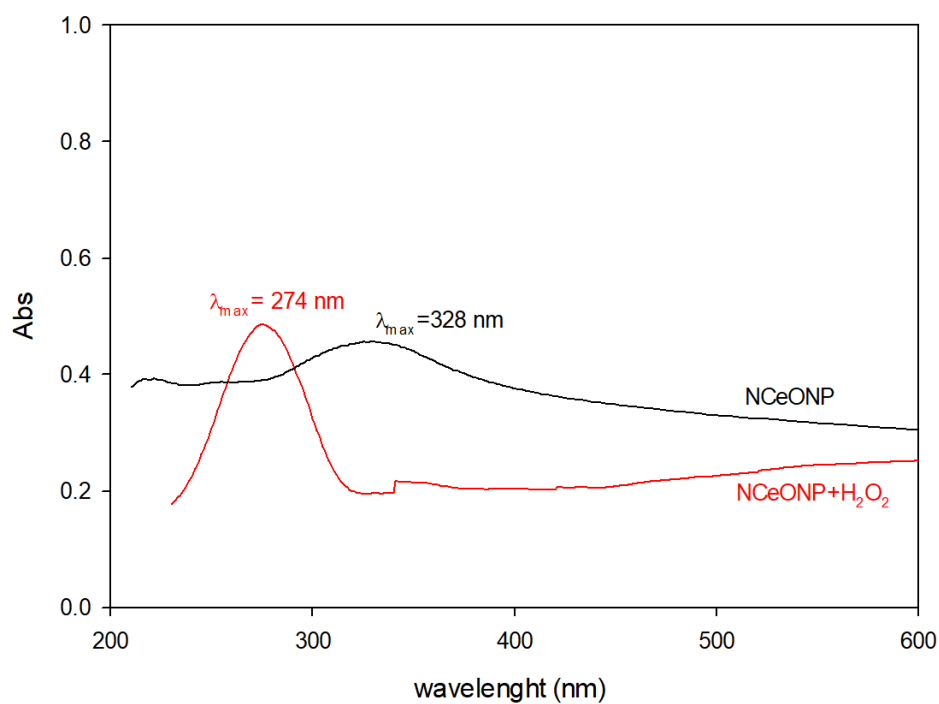


Figure S13. Spectra of NCeONP (0.9 mg/mL) in MeCN without (black) and with the addition of H₂O₂ 1 mM, dispersed by sonication.