Supporting information

Promoting Surface Oxygen Vacancies on Ceria via Light Pretreatment to Enhance Catalytic Ozonation

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Table S1. Surface area, particle size, crystallinity, surface adsorption and defect concentration of commercial ceria as supplied, following calcination, following reduction and following light pre-treatment.

Ceria Catalyst	BET Surface Area (m²/g)	Average Size (nm)[a]	Crystallite Size(nm)[b]	TOC after Adsorption (mg/L)[c]	O_v Concentration[d]
Commercial	57	23	22	87	1.20×10^{20}
Calcined	51	26	25	88	1.25×10^{20}
Reduced	51	26	25	87	1.59×10^{20}
Light Pre-treated	57	22	23	86	1.75×10^{20}

[a] Measured from HRTEM imaging

[b] Calculated based on Scherrer equation[1] using the full width at half maximum (FWHM) of the (111) reflection in the XRD patterns

[c] Measured from TOC analysis ($TOC_0 \approx 90$ mg/L for initial SA concentration of 150 mg/L)

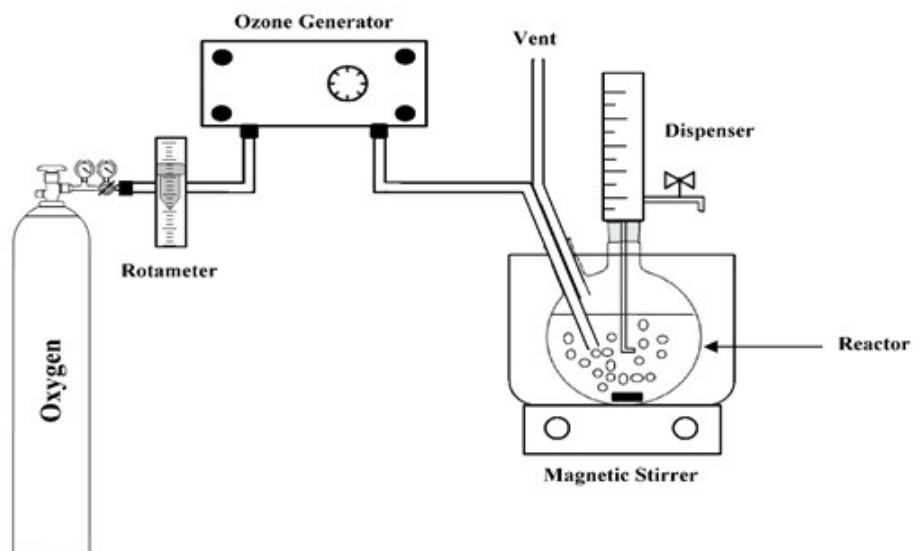[d] Calculated based on the grain size using Raman spectra[2]

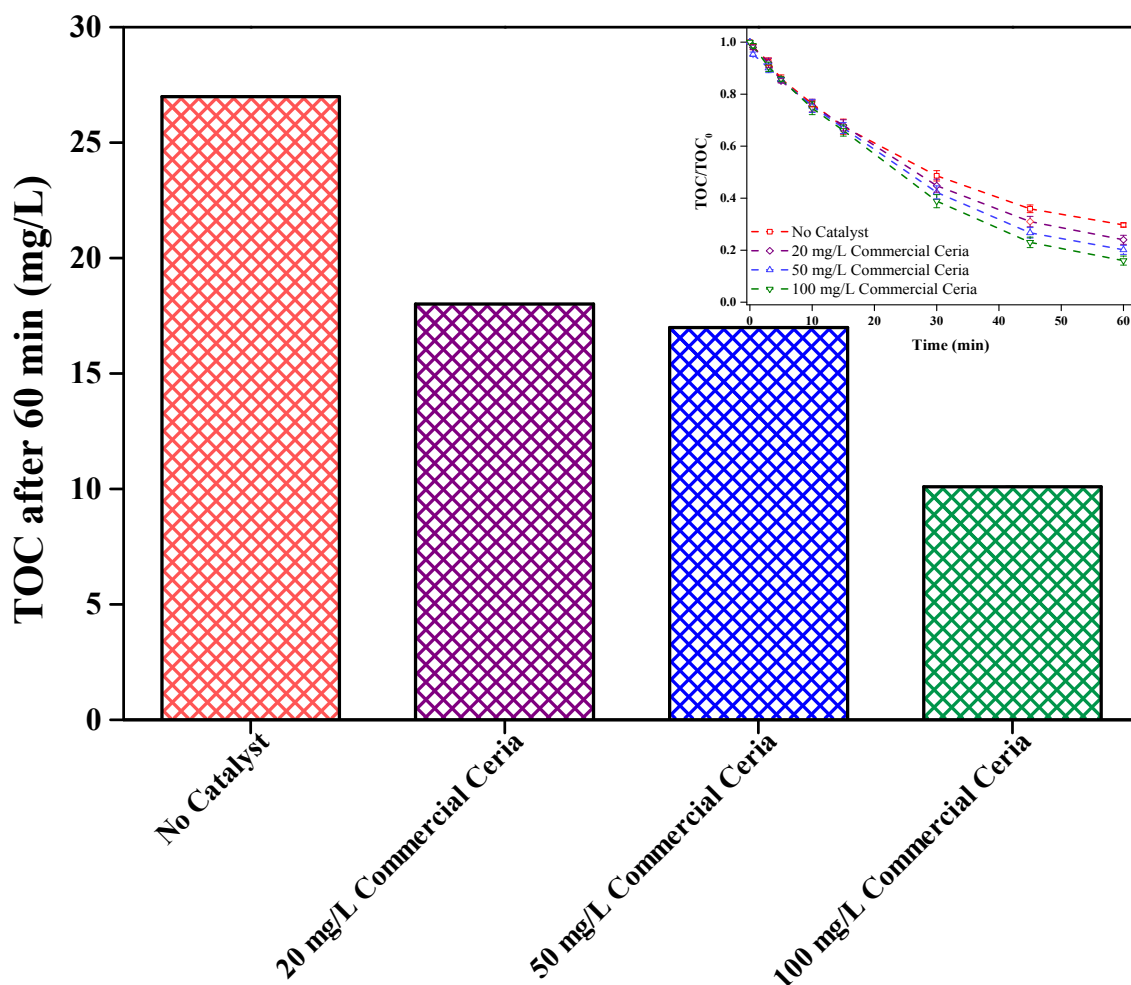**Fig. S1.** Schematic diagram of catalytic ozonation setup.

Fig. S2. The influence of ceria catalyst loading on residual TOC concentration at 60 min during catalytic ozonation. Inset: SA mineralization with time (measured by TOC). Reaction conditions: $[SA]_0 = 150$ mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.

The operating conditions such as initial solution pH, ozone concentration, initial contaminant concentration and catalyst dosage could have significant impacts on the removal efficiency of catalytic ozonation. Fig. S2 shows the effect of catalyst dosage on the mineralization of SA during the catalytic ozonation process. As shown in Fig. S2, increasing the amount of catalyst leads to higher SA mineralization. The number of surface-active sites will increase with increasing catalyst dosage which can facilitate ozone decomposition and potentially produce more hydroxyl radicals.[3]
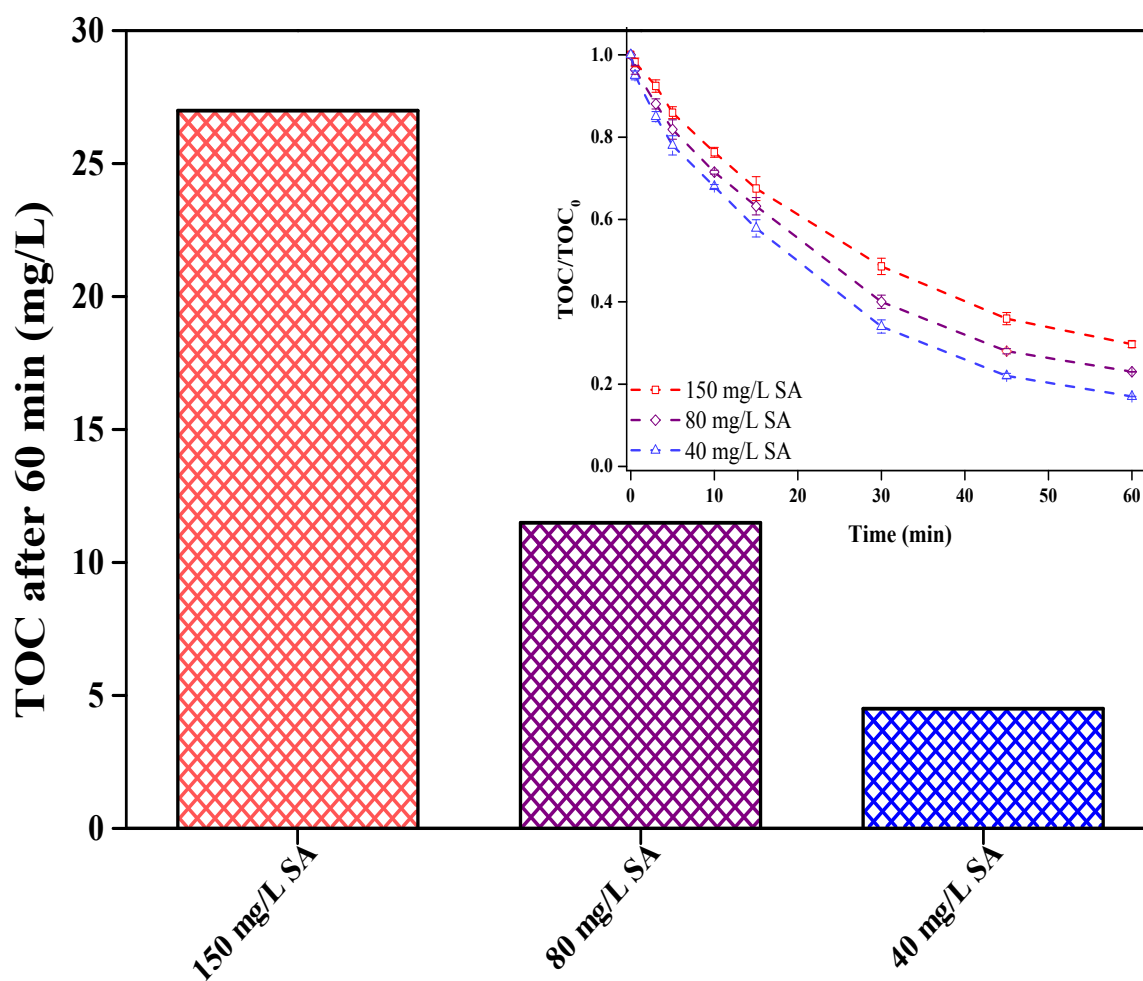
Fig. S3. The influence of initial SA concentration on residual TOC concentration at 60 min during catalytic ozonation. Inset: SA mineralization with time (measured by TOC). Reaction conditions: oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.

A second important operating condition which can affect the catalytic ozonation efficiency is initial organic pollutant concentration. Fig. S3 illustrates the influence of SA concentration on SA mineralization. It is clear from the figure that an increase in initial SA concentration reduces removal efficiency. This phenomenon can be explained by the fact that the formation of intermediates and by-products will increase with increasing initial organic pollutant concentration which leads to competition between intermediates and initial pollutants for ozone and hydroxyl radical consumption. The competition can hamper the degradation of organic pollutants.[3,4]
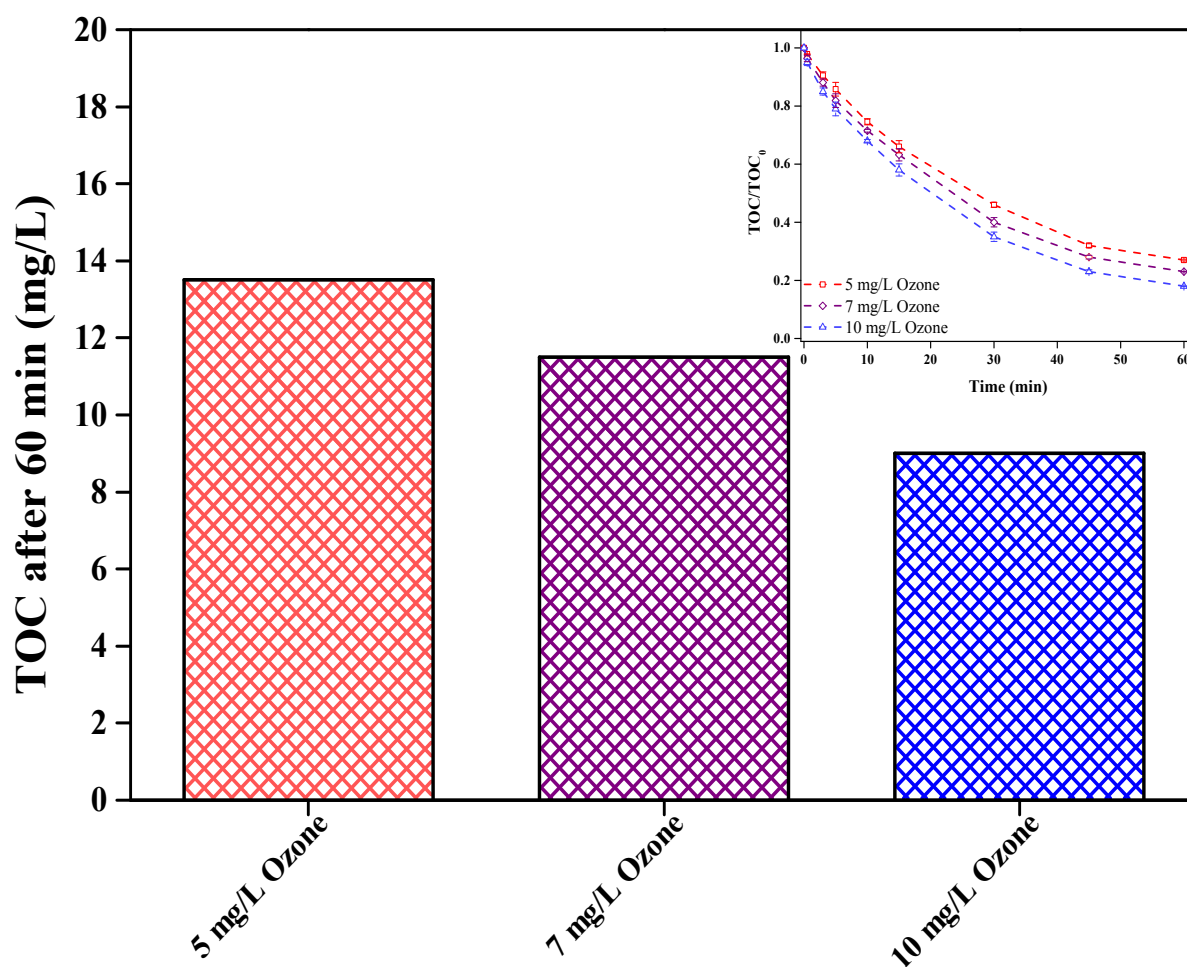
Fig. S4. The influence of ozone concentration on residual TOC concentration at 60 min during catalytic ozonation. Inset: SA mineralization with time (measured by TOC). Reaction conditions: $[SA]_0 = 80$ mg L^{-1}; oxygen flowrate = 800 mL min^{-1}.

Fig. S4 shows the removal of SA for different ozone concentrations. TOC removal increases with increasing ozone concentration. There is a direct relationship between ozone concentration and the degradation of SA (Fig. S4). An increase in ozone concentration enhances the direct reaction between ozone and the contaminants as well as the decomposition rate of ozone into hydroxyl radicals.[3,4] Therefore, a higher ozone concentration can improve the degradation of the organic contaminants.
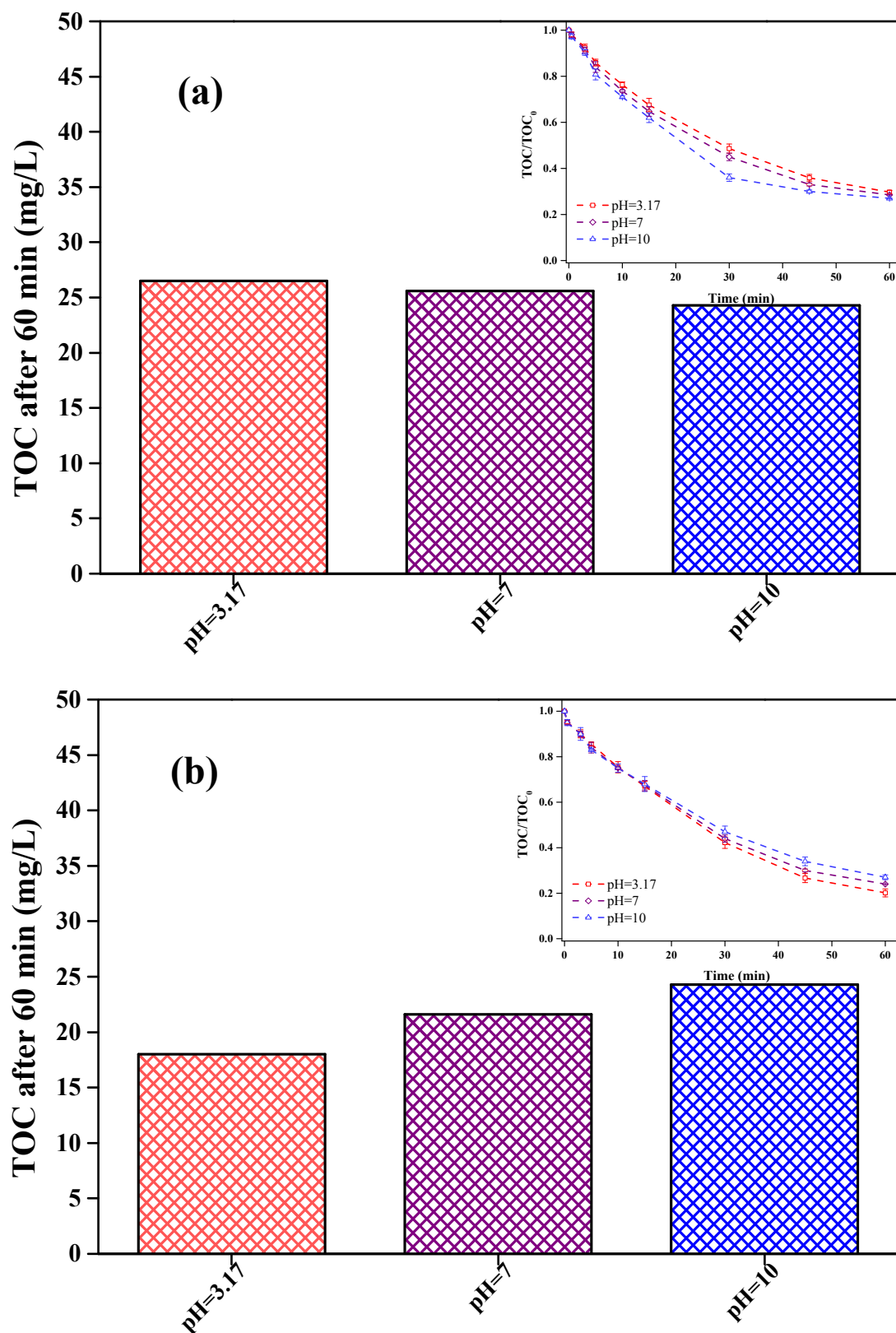
Fig. S5. The influence of initial solution pH on residual TOC concentration at 60 min for **(a)** the non-catalytic ozonation process; Inset: SA mineralization with time (measured by TOC) and **(b)** the catalytic ozonation process using 50 mg L^{-1} of commercial ceria; Inset: SA mineralization with time (measured by TOC). Reaction conditions: $[SA]_0$ = 150 mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.

Solution pH is a key parameter in aqueous ozone chemistry and can influence both the kinetics and pathways of ozone reactions. Fig. S5a shows the influence of initial pH on the mineralization of SA. TOC removal of SA increases with increasing pH (Fig. S5a). However, no distinct difference in the mineralization rate was observed at the final reaction time (60 min). However, SA mineralization (i.e. TOC removal) can reach a constant value at a lower reaction time when single ozonation is conducted under a basic pH relative to an acidic pH. It is well known that ozone decomposition is dependent on pH and increases with solution pH.[4] The decomposition rate of ozone can be facilitated by OH^- at higher solution pH and consequently, the degradation rate of organic pollutants can be increased.

The SA TOC removal during catalytic ozonation at different solution pH values is provided in Fig. S5b. As can be seen, the SA TOC removal decreases with increasing solution pH in the presence of a catalyst. In addition to influencing ozone decomposition rate, the solution pH can change the chemical structure of SA as well as the surface charge of the ceria.[5] During catalytic oxidation, the density of surface active sites is influenced by both the initial pH and the point of zero charge (pH_{PZC}), which is almost 6 for CeO_2.[5] When the pH is near the pH_{PZC} of the catalyst, most of the surface hydroxyl groups will be at a neutral state. Otherwise, protonated or deprotonated surface hydroxyl groups predominate when the pH of the aqueous solution is below or above the pH_{PZC}. Additionally, there are more salicylate anions which possess a negative charge than the SA at higher solution pH.[6] The repulsion force between two negative charges may reduce the mineralization of SA at higher solution pH. Acidic solution pH exhibits the best performance in the presence of a catalyst.
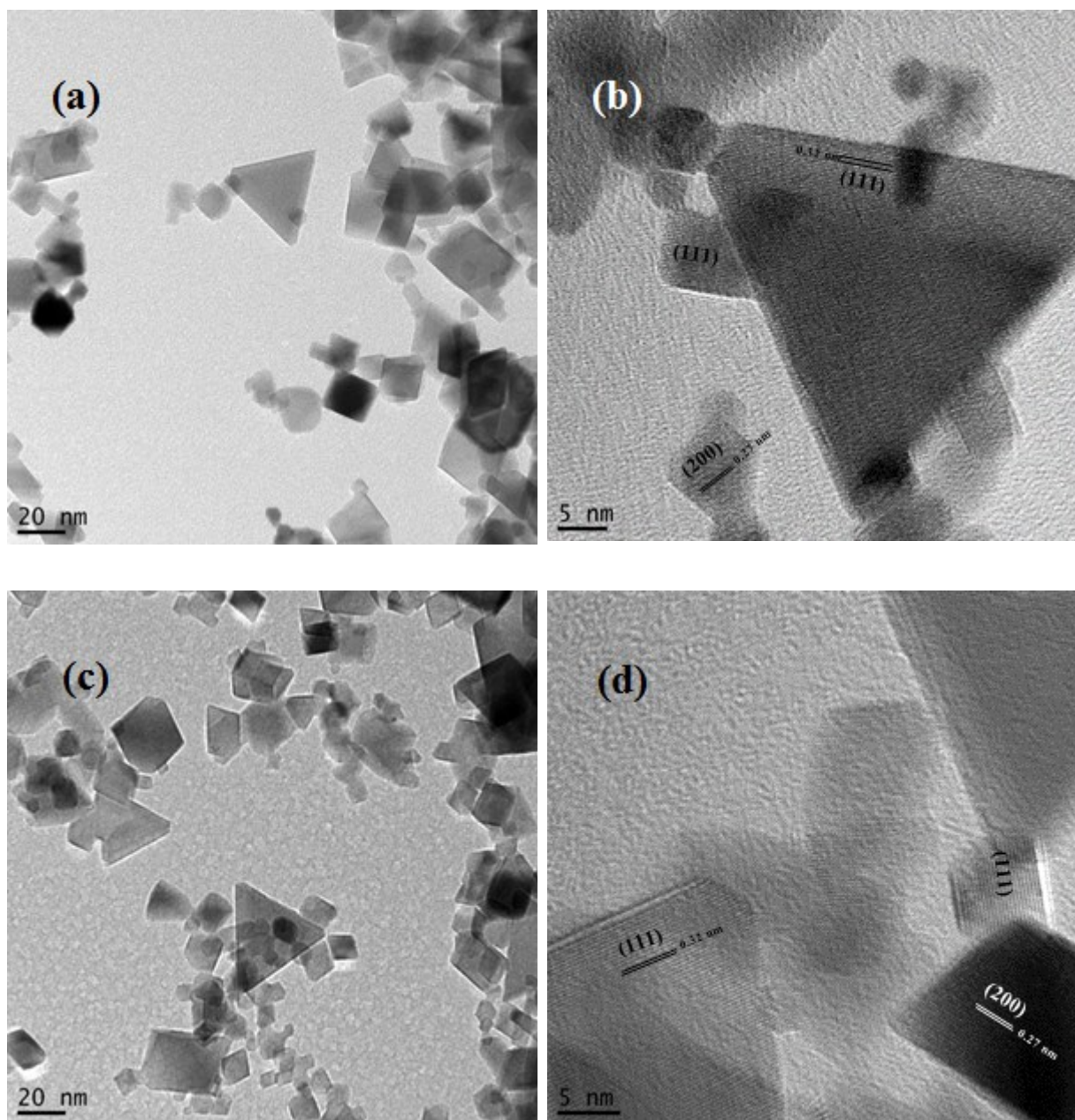
Fig. S6. HRTEM images of **(a** and **b)** calcined ceria, and **(c** and **d)** reduced ceria.
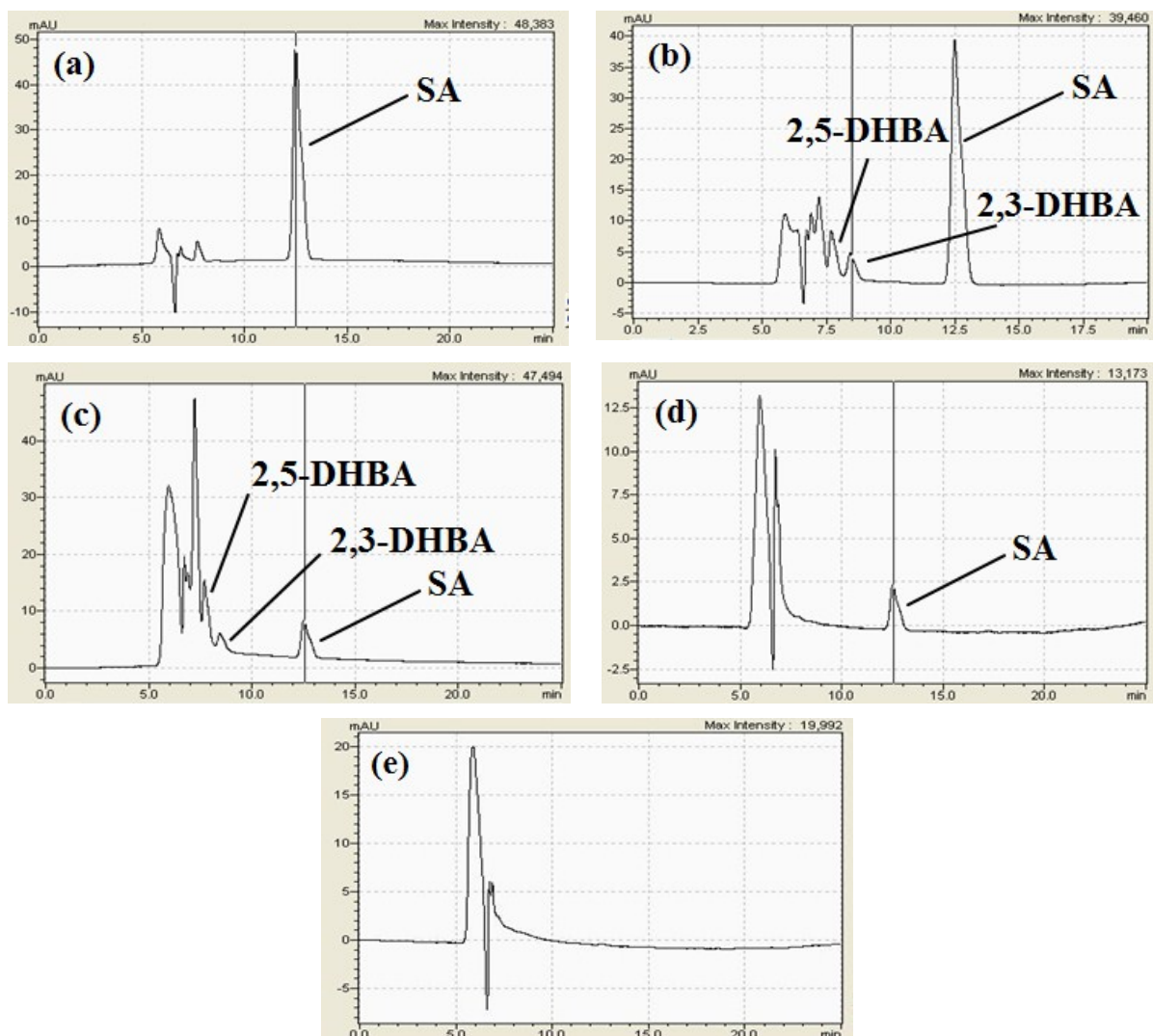
Fig. S7. HPLC analysis of degradation of SA (retention time = 12.5 min) into 2,5-DHBA (retention time = 7.6 min) and 2,3-DHBA (retention time = 8.5 min)at wavelength of 254 nm at reaction time of **(a)** t = 0 , **(b)** t = 1 min, **(c)** t = 5 min, **(d)** t = 10 min and **(e)** t = 15 min. Reaction conditions: [SA]$_0$ = 150 mg L^{-1}; catalyst loading = 50 mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.
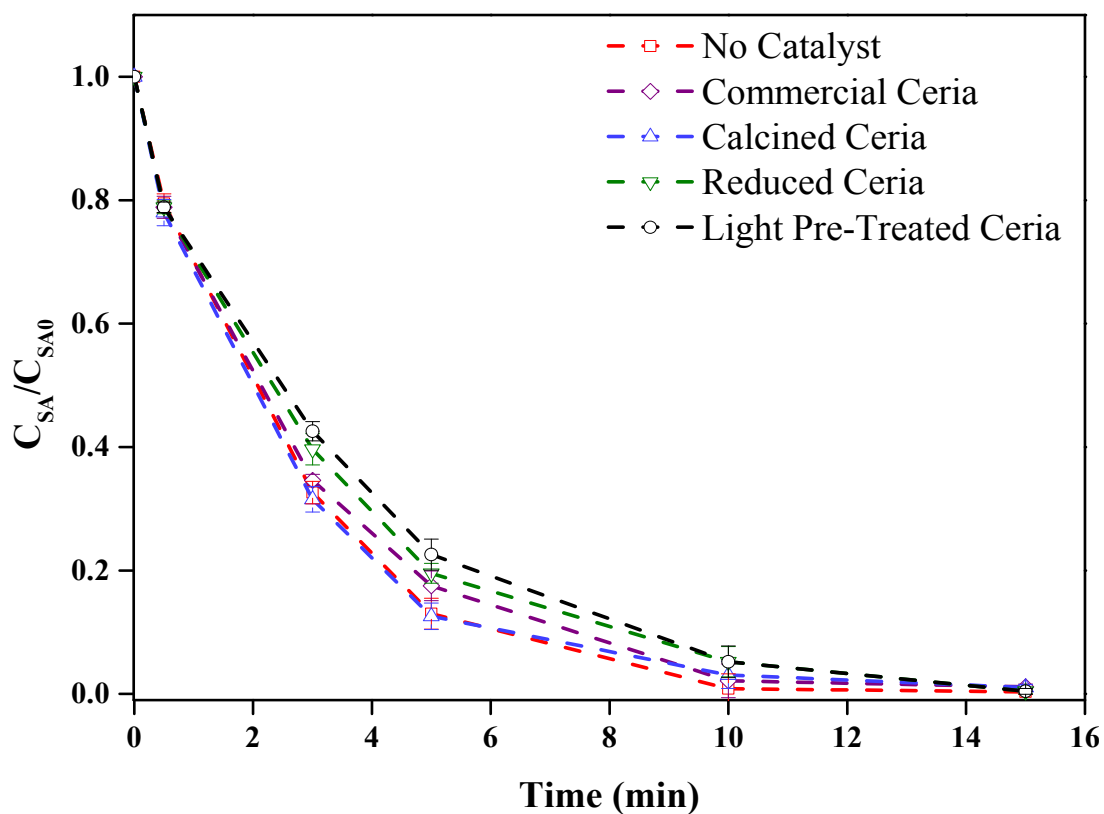
Fig. S8. The influence of ceria catalyst pre-treatment (neat, calcined, hydrogen-reduced, light pre-treated) on SA molecule degradation (measured by HPLC) with time during catalytic ozonation. Ozonation in the absence of a catalyst is provided as a control. Reaction conditions: $[SA]_0 = 150$ mg L^{-1}; catalyst loading = 50 mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.
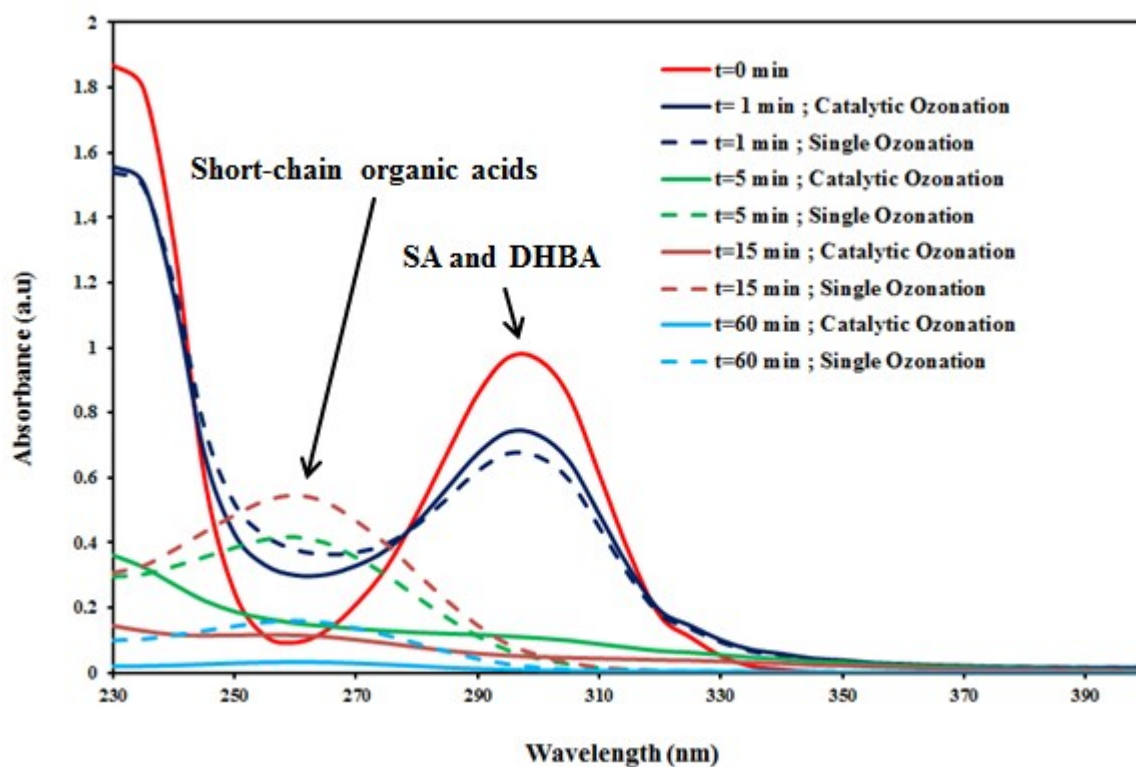
Fig. S9. UV absorbance of SA and its intermediates during ozonation and catalytic ozonation. Reaction conditions: $[SA]_0 = 40$ mg L^{-1}; catalyst loading = 100 mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 5 mg L^{-1}.
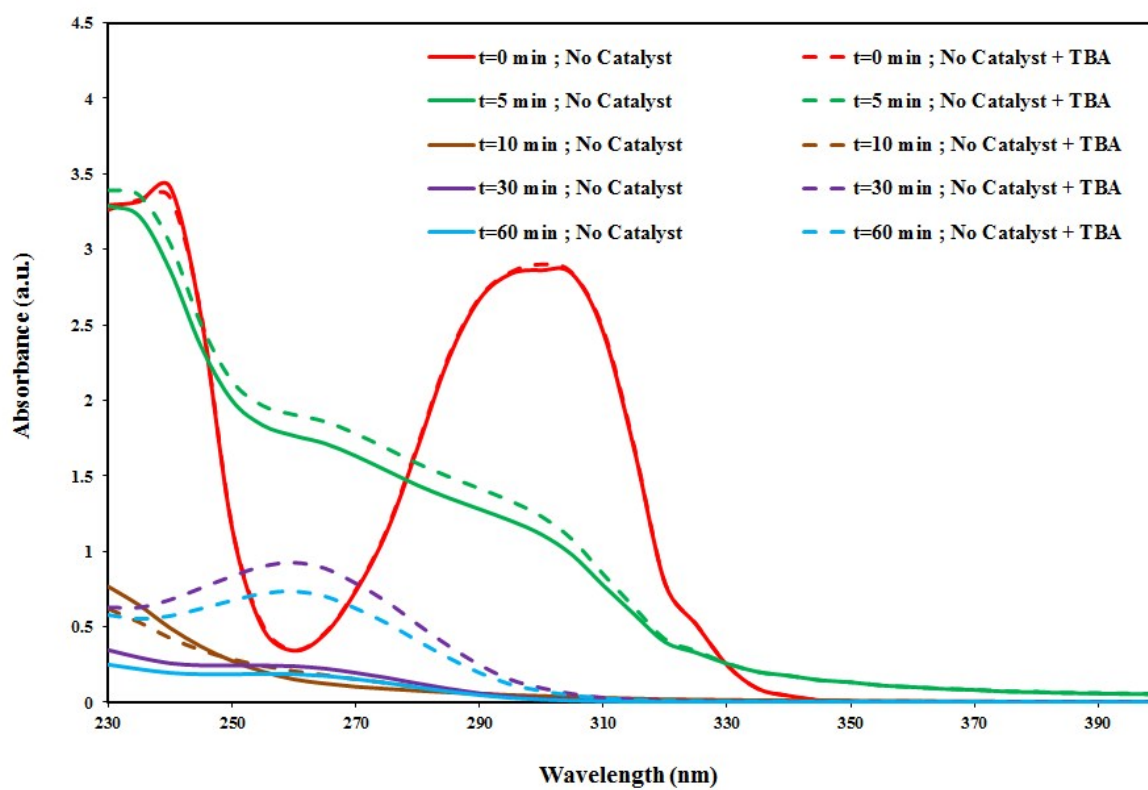
Fig. S10. UV absorbance of SA and its intermediates during ozonation in the absence and presence of TBA (radical scavenger). Reaction conditions: $[SA]_0 = 150$ mg L^{-1}; $[TBA]_0 = 100$ µL; oxygen flowrate $= 800$ mL min^{-1}; ozone concentration $= 7$ mg L^{-1}.
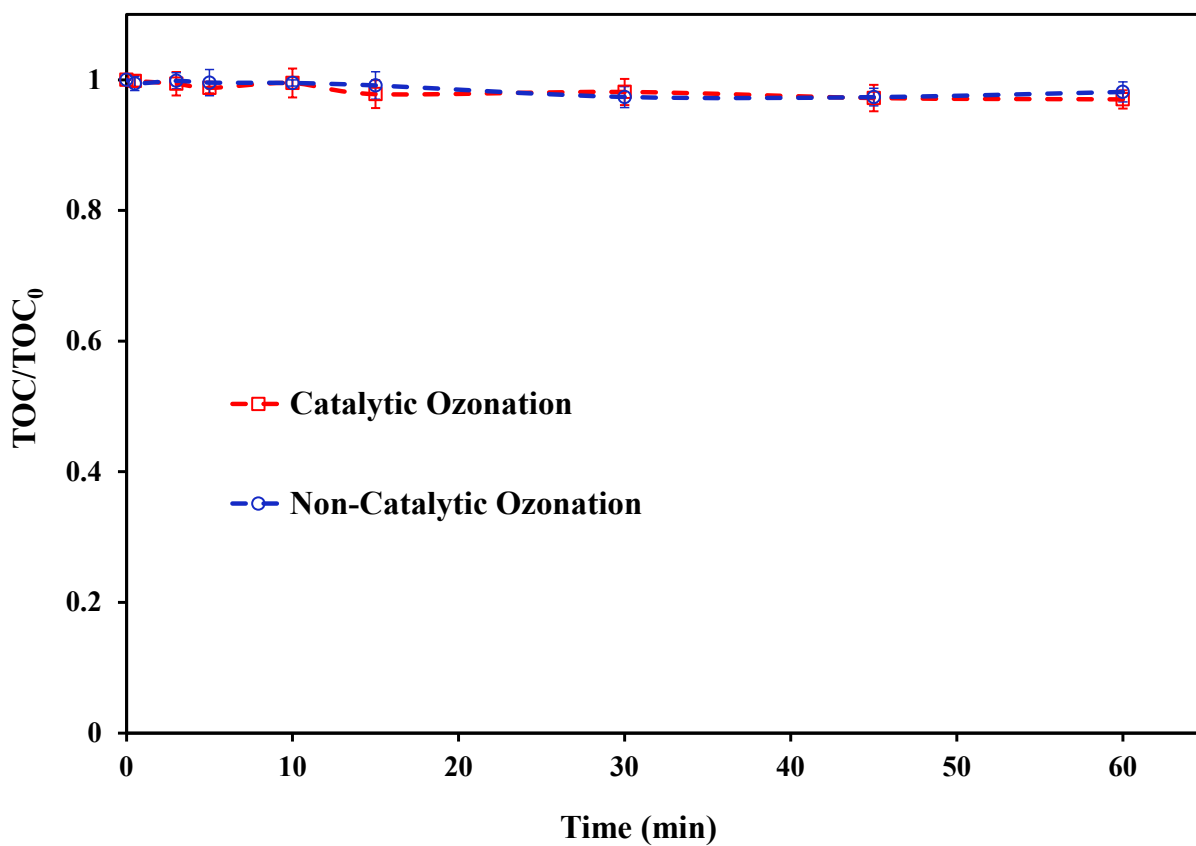
Fig. S11. Mineralization of TBA (measured using TOC) with time in non-catalytic and catalytic ozonation processes. Reaction conditions: $[TBA]_0$ = 100 µL; neat commercial ceria loading = 50 mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.

To examine the impact of TBA addition on the TOC values during the SA degradation experiments, control experiments examining the effect of ozonation on TBA degradation were performed. The findings are provided in Fig. S11. As can be seen, the TBA does not undergo degradation over 60 minutes during both non-catalytic and catalytic ozonation reactions. Consequently, changes to the TOC during SA degradation experiments where TBA is present as a hydroxyl radical scavenger, are due to SA degradation alone. To account for the additional TOC introduced into the system upon TBA addition we measured the TOC of the solution before and after adding the TBA with the difference corresponding to the TBA. The TBA TOC was then subtracted from the overall TOC value during the course of the SA degradation reaction.
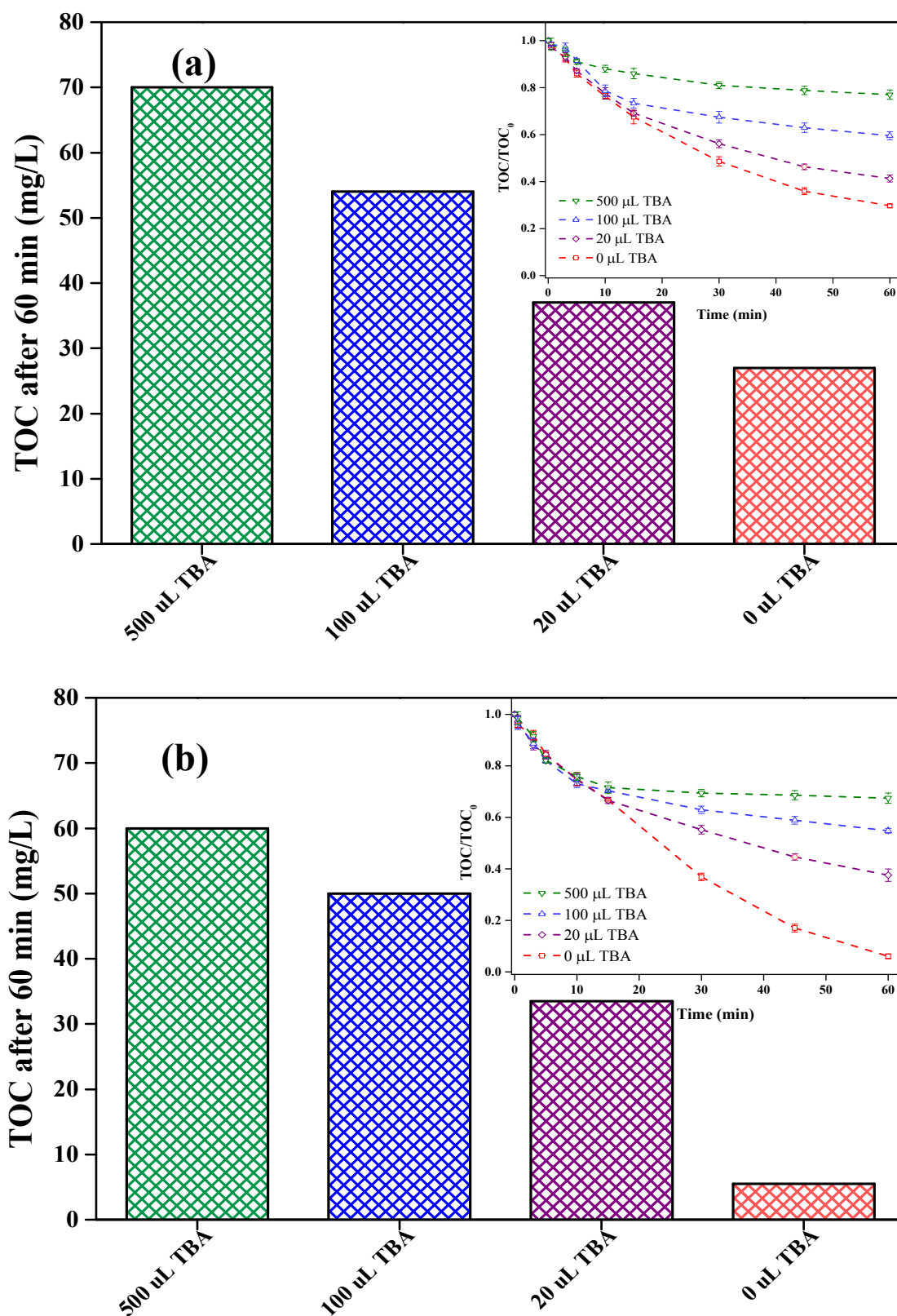
Fig. S12. The influence of TBA concentration on residual TOC concentration at 60 min for **(a)** the non-catalytic ozonation process; Inset: SA mineralization with time (measured by TOC) and **(b)** the catalytic ozonation process using 50 mg L^{-1} of commercial ceria; Inset: SA mineralization with time (measured by TOC). Reaction conditions: $[SA]_0 = 150$ mg L^{-1}; oxygen flowrate = 800 mL min^{-1}; ozone concentration = 7 mg L^{-1}.
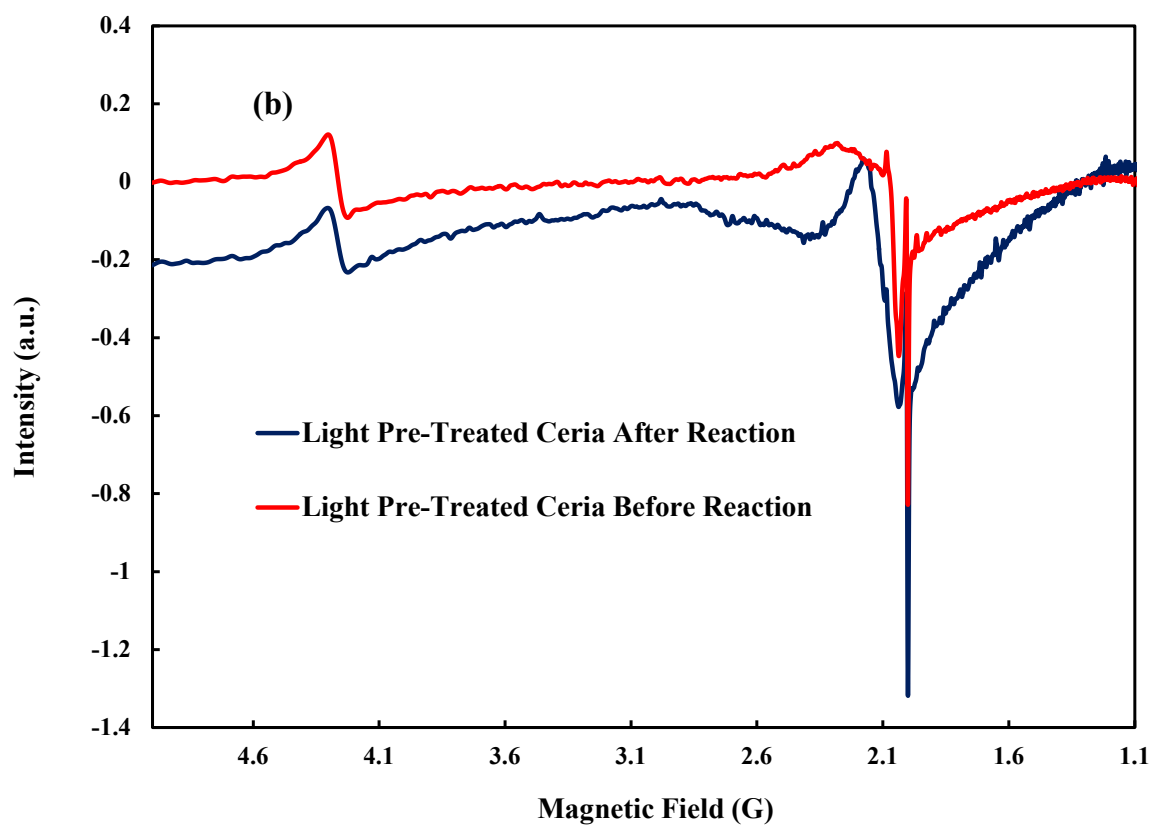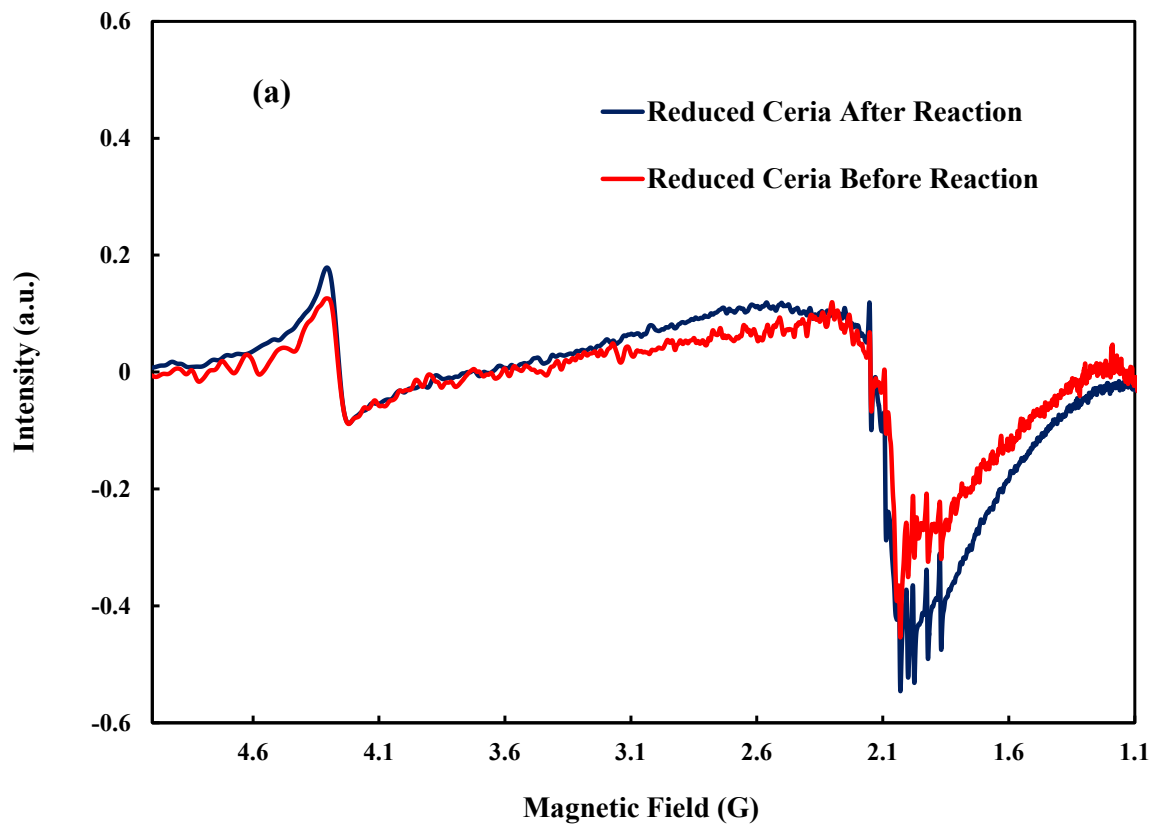
Fig. S13. EPR spectra at 120 K of ceria before and after reaction; **(a)** hydrogen-reduced ceria and **(b)** light pre-treated ceria.

References

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