Nano-Size Effects on Decay Dynamics of Photo-Excited Polarons in CeO₂

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The study of polaron dynamics in complex materials has garnered significant attention owing to its implications for various technological applications, including catalysis, solid-state devices, and energy storage. This paper investigates the photo-excited electron and hole polaron dynamics in cerium dioxide (CeO₂) using time-resolved X-ray absorption spectroscopy, with an emphasis on the nano-size effect. Additionally, density functional theory and multiplet calculations have been utilized to reveal the photo-excited polaron dynamics in CeO₂ single crystal (SC) and nanocrystal (NC). The electron polaron is observed to decay into a deep trap site with a short duration of \approx 5 ps, while electrons in the traps stay for more than 1400 ps. The most significant observation is the behavior of holes in NC, which tends to stay longer (≈150 ps) compared to SC (<10 ps) suggesting hole existence more at the surface than at bulk. The fast dissociation of the electron polarons the prolonged lifetime of the electrons above the Fermi level and the enhanced hole lifetime at the surface are proposed to be among the various factors that influence the high reactivity of CeO₂.

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1. Introduction

Polarons, quasi-particles resulting from the coupling between charge carriers and lattice distortions, play a pivotal role in influencing various electronic and optical properties of material.^[1-3] Recent advances have highlighted the significance of metal oxides in essential processes like water splitting and CO2 reduction, underscoring their high reactivity. Among the diverse array of materials, cerium dioxide (CeO₂) stands out as a fascinating material for catalytic applications due to its excellent oxygen storage and transfer capabilities. Its efficiency in driving various chemical reactions makes CeO2 invaluable in research related to catalytic applications.^[4-9]

However, the utilization of metal oxides in photo-catalysis presents challenges attributed to the formation of polarons that can detrimentally impact the catalytic

activity.^[10] Therefore, understanding not only the formation but also the decay dynamics of these polarons becomes crucial. Notably, previous studies have shed light on the formation dynamics of polarons in metal oxides such as TiO_2 , hematite (α -Fe₂O₃), and NiO.^[11-14] However, the intricate realm of decay kinetics, notably within rare earth oxide such as CeO₂ has mainly remained undisclosed and less explored. Despite these challenges, understanding polaron decay is essential for optimizing photocatalytic performance and developing new high-performance materials. To study the electronic structural properties in CeO₂, it is necessary to evaluate transitions in 4f states of CeO₂ after photoexcitation through time-resolved X-ray-absorption spectroscopy (tr-XAS). Additionally, CeO₂ even in its ground state can stimulate charge transfer between O 2p and Ce 4f due to the presence of mixed valence states of Ce ions formed by oxygen vacancies. Tr-XAS reveals information about the formation of Ce4+ and Ce3+ oxidation states via Ce M5-edge XAS, which are further characterized by measuring the kinetic trace to reveal their decay dynamics.

The other challenge in studying catalytic reactions is the catalyst surface which is highly dynamic under reaction conditions. Conventional steady-state techniques might prove insufficient to examine these reactions. Fortunately, ultrafast (femtosecond to picosecond) and element-specific pump-probe experiments, such as tr-XAS using X-ray free-electron laser (XFEL), offer dynamic insights into catalyst behavior. This paper aims to explore www.advancedsciencenews.com

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Figure 1. a) The schematic illustration for the experimental setup of tr-XAS. b) Schematic for the subsequent transformation in the energy levels following photoexcitation in CeO_2 . c,d) Comparative analysis of the XAS spectra of CeO_2 (SC) at the (c) oxygen K-edge in GS, 0.3 ps ES, and 3.0 ps ES. (d) Ce M_5 -edge in its GS, 0.3 ps ES, and 3.0 ps ES. (We also conducted measurements for CeO_2 NC. The data appears to be quite similar in spectral shape and transient decay, more details can be found in Figure S4, Supporting Information).

the electron and hole polaron decay dynamics in CeO_2 with an emphasis on the impact of nano-size effects. This study investigates both CeO_2 single crystal (SC) and nanocrystal (NC). By utilizing advanced experimental techniques such as tr-XAS and coupling them with theoretical modeling, we seek to understand the fundamental mechanisms governing the formation and decay of these charged carriers. This research contributes to a deeper understanding of the photo-excitation processes in CeO_2 and fosters the development of enhanced photocatalytic materials.

2. Results and Discussion

2.1. Results

Figure 1a illustrates the measurement geometry employed in our tr-XAS experiment to probe the photoexcited state of CeO_2 . The photoexcitation process was initiated using an optical pump laser (267 nm, 100 fs pulse width), and was probed by an XFEL (near the oxygen K-edge (525–538 eV) and Ce M_5 –edge

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(878-891 eV) with a pulse width of 50 fs). The monochromatized X-rays were normalized by an I₀ monitor and focused on the sample position using Kirkpatrick-Baez mirrors. The measurements were performed in the total electron yield (TEY) mode using a micro-channel plate (MCP) detector. The relative time between the pump and probe beam was controlled with an optical delay line and the spatial and temporal overlap (delay = 0) was set using fluorescence observed on a thin cerium-doped yttrium aluminum garnet (YAG) crystal. Figure 1b illustrates the generalized pump-probe scheme used to study the photoexcitation process in CeO₂. 267 nm pump laser excites an electron from the valence band (VB) (O 2p) to the conduction band (CB) (Ce 4f) creating a hole in the VB. XFEL serves as a probe to measure these photoexcited holes and electrons at different delay times. The excited electrons shift the energy level of Ce 4f by -0.15 eV. This scheme allows us to extract information about hole formation in the VB using the oxygen K-edge, and the Ce⁴⁺ and Ce³⁺ oxidation state via the Ce M5-edge. In Figure 1c,d, we have compared the ground state spectra (GS) with the excited state spectra (ES) measured at a delay time of 0.3 and 3.0 ps at the oxygen K- and Ce M_5 -edges. The observed-state spectra (OS) encompass the ES and the GS since the pump laser can only excite a limited portion of the sample. Therefore, the ES can be derived from the GS and OS by estimating the absorption coefficient (α) using Equations 1–3 provided below.

$$OS(\lambda, t) = (1 - \alpha) \quad GS(\lambda, 0) + \alpha ES(\lambda, t) \Rightarrow$$
$$ES(\lambda, t) = \frac{1}{\alpha} OS(\lambda, t) - \frac{1 - \alpha}{\alpha} GS(\lambda, 0)$$
(1)

$$OS(\lambda, t) - GS(\lambda, 0) = TR(\lambda, t) = \alpha ((ES(\lambda, t) - GS(\lambda, 0)) (2))$$

$$ES(\lambda, t) = \frac{1}{\alpha} TR(\lambda, t) + GS(\lambda, 0)$$
(3)

By analyzing the XAS spectrum at the oxygen K-edge (Figure 1c), it is revealed that the ES spectra exhibited similar spectral features with GS, except an overall shift of -0.15 eV with a slight broadening of the whole spectrum. To understand these changes in the 0.3 and 3.0 ps ES (Figure 1c), we fitted the ES using the GS spectra with additional spectral broadening and an energy shift of -0.15 eV, which showed a good agreement with the experiment. Whereas, the ES at 0.3 and 3.0 ps at the Ce M5 -edge (Figure 1d) showed obvious changes in the amplitude of Ce³⁺ and Ce⁴⁺ states. These changes in the ES can be related to both charge transfer and energy shift. Since the ground state at CeO₂ already takes a mixed state, it is difficult to investigate the charge transfer and energy shift effects at excited states. Therefore, to understand the origin of these differences, we calculated the charge transfer multiplet (CTM) simulation by including the charge transfer effect and the energy shift effect using the CTM4XAS package.^[15] Using the equation $c \times [Ce^{4+}] + (1-c) \times [Ce^{3+}]$, where c is constant, we were able to fit CTM simulation into 0.3 and 3.0 ps ES at Ce M₅-edge. (For more minute details related to the process to obtain CTM simulations of ES spectra, please follow Figure S2, Supporting Information) An abrupt increase in the Ce³⁺ peak at 882.6 eV was observed at 0.3 ps. This can be interpreted as excited electrons are transferred into the Ce3+ state. The swift decay of this Ce³⁺ state at 3.0 ps signifies that the localized electrons transfer from the Ce atom to elsewhere. Returning to the overall energy shift of -0.15 eV at both the oxygen K-edge and Ce M₅-edge, this shift can be attributed to the change in the anti-bonding energy level due to structural deformation or to charge redistribution above the Fermi level.^[16]

Figure 2a presents the experimental transients (difference between OS and GS) obtained at the oxygen K-edge, corresponding to the time delay of 0.3 and 3.0 ps. The transients observed at the oxygen K-edge are a result of energy shift and broadening at the peaks, which is also corroborated by theoretical transients (solid lines). Figure 2b shows the experimental transients at Ce M₅-edge, along with fitted CTM transients obtained by subtracting GS CTM spectra from the ES CTM spectra at 0.3 and 3.0 ps. Further detailed explanation of the inclusion of CTM transient can be found in Figure S3 (Supporting Information). The P region in Figure 2b, represents Ce³⁺ which displays a rapid rise at 0.3 ps, followed by a fast decline at 3.0 ps. In contrast, the Q region retains a significant intensity until 3.0 ps. The Q region can be attributed to a charge redistribution over the Fermi level or the structural deformation followed by polaron formation. This feature is noted to endure significantly longer than the charge localization in the P region. The measured kinetic traces at 882.6 eV (P, Ce³⁺) and 884 eV (Q, Ce⁴⁺) are shown in the top and bottom panels of Figure 2c, respectively.^[17] The P feature exhibits fast decay dynamics with a time constant of ≈ 2 ps. In contrast, Q shows decay dynamics with a time constant of 0.7, 10, and 1400 ps, with amplitudes in a ratio of 0.25:0.25:0.5. The short time constant of 0.7 ps might be ascribed to polaron formation. The time constants of 10 ps (2 ps) pertain to the polaron disintegration into electrons (holes), during which the polaron undergoes decay while the electrons (holes) become trapped at the defect sites. The process of the trapped electrons returning to the GS is determined to take more than 1400 ps. The dynamics in the regions P and Q can be explained in two points.

- 1) Changes observed in the XAS spectra where the kinetic traces are measured: The process primarily involves charge transfer and localization of electrons. In context to our data, changes in Ce³⁺ and Ce⁴⁺ regions indicate variation in oxidation state due to the charge transfer process.
- 2) Charge phonon coupling where holes and electrons can interact with lattice vibrations (phonons): The presence of broadening and shift in our data can be largely correlated with the charge phonon interactions. The formation of polarons where electrons and holes become coupled with lattice vibrations can lead to specific changes in XAS spectra and can influence the behavior of kinetic traces collected over the region of P and Q.

To investigate the impact of material size on the behavior of charged carriers of CeO₂, we measured kinetic traces of XAS intensities on the lower energy side of the main peak in the oxygen K–edge. We measured delay times up to 40 ps with a step size of 0.5 eV in photon energies from \approx 526 to 529 eV. The kinetic trace mappings reveal that holes are captured at gap states and then decay (**Figure 3a**). Notably, the NC exhibits short-lived hole signals (<10 ps), followed by long-lived holes of \approx 150 ps. On the contrary, in the case of SC, there are no such long-lived signals. (The quantitative kinetic traces of NC and SC at 526.8 eV are shown





Figure 2. The comparative analysis of transient XAS spectra at the ES with fitted TR spectra at 0.3 and 3.0 ps for a) oxygen K-edge and b) Ce M_5 -edge. c) Kinetic traces of transient XAS at the metal edges indicate charge localization. The traces show abrupt changes upon photoexcitation, with faster decay observed at *P* (Ce³⁺ at 882.6 eV) compared to Q (Ce⁴⁺ at 884 eV). The calculated decay time constant using the S-1 equation is 2 and 1400 ps at *P* and *Q*, respectively. The error bar represents standard errors.

in Figure 3b). Surprisingly, the electron lifetime at 882.6 eV (for $\rm Ce^{3+})$ remains unaffected regardless of material size.

To gain a qualitative understanding of the aforementioned effects (in Figure 2), ab initio calculations were conducted by introducing an additional electron to the supercell of CeO_2 (Figure 4a).^[18] Polaron formation is manifested in terms of structural distortion (Figure 4a), localized electron density (Figure 4b), and density of state (Figure 4c). This led to an increase of $\approx 2.8\%$

in the average atomic distance between Ce and oxygen atoms, causing the oxygen atoms to move away from the Ce atom (Figure 4a). Changes in electron density by an additional electron are visualized in Figure 4b.^[19]

Furthermore, our calculations suggest that the localized electron makes a new polaronic state, positioned at 0.4 eV below the conduction band (Figure 4c), which is consistent with previous reports.^[20] In addition, density functional theory (DFT)

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Figure 3. Comparative analysis of the hole and electron behavior in the CeO_2 NC and SC a) The mapping of holes traced after photoexcitation via oxygen K-edge in CeO_2 NC and SC b) The kinetic trace of the hole (that of electron shown in inset) in CeO_2 NC and SC.



Figure 4. a) The structural deformation resulting from the presence of an additional electron in the Ce atom, as calculated using DFT. A bond length increase of + 2.8% is determined. b) Electron density map of a polaron. c) Projected density of states (PDOS) for GS, atoms near electron polaron sites (red), and atoms far from electron polarons (grey and blue). d) The density of state (DOS) calculations for slab (upper panel) and bulk (lower panel) were performed using DFT, illustrating the increased oxygen 2p valence band at the slab as a result of surface structure.

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calculations were performed using Quantum Espresso to better understand the longer lifetime of holes in NC compared to SC.^[21,22] The oxygen 2p projected density of states was calculated on a slab ($1 \times 0 \times 0$) and bulk ($3 \times 1 \times 1$ supercell) configuration. (Additional details regarding calculations can be found in the Methodology section.) An increase in DOS near the valence band maximum was observed in the case of slab calculations (upper panel Figure 4d), whereas, the bulk showed no such DOS (lower panel Figure 4d).^[23]

2.2. Discussion

Our study on electron carrier behavior uncovers two discernible observables: overall spectral shifts (-0.15 eV) and electron transfer to a Ce atom (resulting in Ce³⁺). The former originates from excited electrons above the valence band and the Fermi level, while the latter from additional electron localization to a Ce atom (polaron formation). The spectral shift exhibits a long lifetime, whereas the electron localization demonstrates a fast decay, which implies that the decayed electrons are captured by trap sites and remain there for an extended time.

Another observation in our study is the size effect (SC or NC) on the lifetime of holes. The holes at the VB in NC exhibit surface-sensitive behavior with lifetimes of \approx 150 ps compared to SC (<10 ps). This difference in behavior aligns with previous reports related to TiO₂,^[24,25] supporting the validity of our approach. Therefore, it would be reasonable to suggest that within 150 ps, hole polarons are captured by surface trap sites.^[26] However, in the case of SC, this signal should be much smaller due to the smaller surface area. Therefore, these effects are further amplified in smaller crystals due to a higher surface-to-volume ratio.

In the previous study, Cresi et al.,^[20] verified the formation of photoexcited electron polarons within 0.3 ps. However, the decay kinetics of these polarons were not observed. Their investigations revealed two complementary transients in visible light absorption spectroscopy: an immediate bleaching dip followed by a fast rise (300 fs), for which they presumed polaron formation. Our results substantiate this observation, corresponding to a timescale of 0.7 ps in our study. Furthermore, our experiments directly show Ce^{3+} with rapid decay (<4 ps). Unexpectedly, we also identified an additional long-lasting state (>1400 ps). Notably, our findings regarding the short decay time of polarons (<4 ps) contrast with the previously reported value of 310 ps.^[20] This discrepancy may be due to the referenced studies only measuring data for short periods of time (<3 ps). In comparison with another previous report, Singh and co-workers^[27] assigned a rise time of 10 ps in their experiment to the electron trapping time for various trap sites, which aligns with our observation of a rapid decay at ≈4 ps. In another report, Jennifer et al., revealed that dye-sensitized electron injection into CeO₂ nanoparticles shows mid-IR signals appearing within 0.5 ps after 430 nm photoexcitation.^[28] These signals were assigned to the injected electrons which had been trapped in defect states. This is consistent with our findings showing a trapping time of 2-4 ps. Additionally, the combined effects of electron relaxation within CeO₂ and back-electron transfer to the dye lead to faster electron decay compared to the decay time observed in our study (>1400 ps).

While there are many reports on the measurement of absorption-edge spectra focusing mainly on metal oxides and their theoretical investigations,^[29] our results emphasize the ability of tr-XAS using XFEL to directly probe into the interplay between electronic and structural dynamics in photoexcited rare earth CeO₂. Aligning this approach with theoretical calculations provided valuable insights into the behavior of 4f electrons, which is essential for the design of next-generation rare earth-based catalytic materials.^[30] Moreover, our research highlights that this approach can be effectively applied to study metal oxides and rare earth oxides, giving a significant leverage to researchers aiming to understand other materials by making slight modifications to improve efficiency and functionality.

3. Conclusion

We unveiled the intricate polaron dynamics by employing the pump-probe tr-XAS technique at the oxygen K- and the Ce M₅edges. Our observations reveal a rapid electron polaron formation within 0.7 ps, followed by fast electron decay (<10 ps) and long-lived remnant effects (>1400 ps). Based on these two observations, the electron is supposed to escape from the Ce atom in <10 ps but does not immediately return to the GS. Instead, it remains trapped for more than 1400 ps in presumed defect before returning to the GS. Second, we observed that holes in NC compared to SC tend to exhibit longer durations (≈150 ps) and are primarily located near the surface providing an explanation for the holes as a result of surface-sensitive species. Leveraging this surface sensitivity, the behavior of the holes at the surface can be exploited using species that can be adsorbed onto the surface of material and trap holes. By advancing our comprehension of polaron behavior, this study contributes to harnessing unique characteristics of CeO₂ for technological advancements and lays a foundation for studying carrier dynamics in other advanced materials.

4. Experimental Section

XAS Measurements: A CeO₂ (001) single crystal was purchased from MTI Corp., USA whereas, the CeO₂ nanocrystal (less than 25 nm) was purchased from Sigma–Aldrich. All the measurements were taken in the ultra-high vacuum condition of 10⁻⁸ mbar. The tr-XAS spectra were measured at the Soft X-ray Spectroscopy and Scattering (SSS) beamline at the Pohang Accelerator Laboratory X-ray Free Electron Laser (PAL-XFEL).^[31] The samples were excited with 267 nm (4.66 eV) optical laser at a fluence of 20 mJ cm⁻². The measurement was carried out in the electron yield (EY) mode using a microchannel plate detector at a normal incident angle. Comprehensive information regarding the experimental setup employed in this study is provided in the Supporting Information. The reference numbers^[32–37] corresponds to DFT references used in the supporting information.

Optical Laser Pump: The Ti:sapphire laser of wavelength 267 nm (4.66 eV) with a pulse duration of 100 fs focused to an area of 100 μ m in FWHM. The fluence of the pump laser was 20 mJ cm⁻². No significant change was observed in the transient features and lifetime behaviors in the fluence range of 10–30 mJ cm⁻². Laser fluence below 10 mJ cm⁻² induced a very weak signal in the transients that were too weak to obtain a sufficient signal-to-noise ratio, while within the range of 50 mJ cm⁻² did not cause damage to the sample.

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Supporting Information

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

catalyst, polarons, pump-probe, XFEL

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