Size and Shape Effects on Charge Recombination Dynamics of TiO2 Nanoclusters

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Supporting Information

ABSTRACT: Investigation of charge carrier recombination dynamics is central to understanding and further enhancing the photocatalytic activity of water splitting and other photochemical reactions catalyzed by TiO2. In this study, we carried out nonadiabatic molecular dynamics calculations combined with real-time time-dependent density functional theory to investigate the effects of size and shape on charge recombination in TiO2 nanoparticles (NPs). Using the Wulff construction method, we considered both octahedral (10, 35, and 84 TiO2 units) and cuboctahedral (29, 78, and 97 TiO2 units) nanoclusters with size varying from 1 to 3 nm. Generally, the recombination rates decreased with increasing NP size. We rationalized the trend in terms of average transition energy, exciton binding energy (ΔEex), nonadiabatic coupling (NAC), and pure-dephasing time. The relaxation times increased with increasing NP size, as the NAC and ΔEex decreased. The cuboctahedral clusters showed smaller ΔEex compared to the octahedral clusters. For the octahedral clusters, the smaller NAC and shorter dephasing time contributed to longer relaxation, despite smaller transition energy, as the size increased. However, the influence of the NAC, transition energy, and dephasing time were intertwined for the cuboctahedral clusters. The smaller NAC of the 97-unit cluster rationalized its longer relaxation time compared to the 29-unit cluster, but the presence of a singly coordinated oxygen atom greatly reduced the transition energy, thus leading to a shorter relaxation time compared to the 78-unit cluster. Our results provide a detailed understanding on the effects of size and shape on the charge carrier dynamics in TiO2 nanoclusters, separating these effects from other factors, such as presence of defects, dopants, and adsorbates that are hard to control precisely in experiments.

1. INTRODUCTION

Titanium dioxide (TiO2) nanoparticles (NPs) have been at the focus of scientific research and applications in a variety of fields, including solar cells,1,2 environmental cleanup,3,4 and photocatalysis.5–8 The applications of TiO2 in photocatalysis constitute an active field of research,9,10 in particular due to its ability to generate H2 from water splitting under light irradiation as an alternative energy source to fossil fuels. Unfortunately, the rather large band gap (>3.0 eV) of the most common polymorphs of TiO2 (anatase, rutile, and brookite) requires ultraviolet radiation for electronic excitation. This hinders the practical use of TiO2 under sunlight, as only ∼10% of the incoming photons from sunlight have enough energy to be absorbed and hence to participate in the photocatalytic process. It is essential to increase the efficiency of photocatalytic TiO2 by enhancing the light absorption.

Many different strategies, from doping12–14 to nanostructuring15,16 have been suggested to reduce the band gap of TiO2 so as to enhance its photocatalytic efficiency. In particular, doping by different types of chemical elements such as nitrogen17 and fluorine18 has attracted much interest. However, it has been reported that reducing the band gap to the visible range by introducing defect states does not guarantee the enhanced catalytic activity.14,18 This is because doping induced defects can trap charges and act as charge recombination sites, accelerating electron and hole losses and inhibiting charge transfer to reactive sites for hydrogen/oxygen evolution and other reactions. Charge and energy losses motivate studies of the charge carrier dynamics as well as the band gap engineering.

Nanostructuring has also been used to enhance the photocatalytic activity of TiO2. Of particular relevance to the present study, new techniques have been developed aimed at controlling the size and shape of anatase nanoparticles to optimize their photocatalytic activity.19 However, it is difficult to differentiate the effects of NP size and shape from those introduced by synthesis conditions in experiments. On one hand, previous studies showed contradictory results of the size effect on the charge relaxation dynamics. Du et al.20 reported that larger TiO2 particles resulted in longer charge recombination times due to the longer diffusion length of electrons. In contrast, Nakade et al.21 reported that electron recombination lifetime was reduced with the increase of the particle size due to

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the existence of charge trap site and grain boundary. On the other hand, it was reported that the nanoparticles with (001) facets exhibited better photocatalytic activity than those with (101) facets.\textsuperscript{24–26} However, fluorine atoms acted as dopants or were adsorbed on the surface in order to stabilize the relatively unstable (001) facets of anatase NPs while introducing Ti$^{3+}$ states.\textsuperscript{27} The intertwined influences of the fluorine atoms and (001) nanostructure make it difficult to investigate the origin of the resulting change in reactivity whether it originates from the intrinsic properties of (001) facets, or the introduced Ti$^{3+}$ states, or interaction with the fluorine atoms.

Likewise, the origin of the photocatalytic activity of nanoparticles is largely unknown and likely to be the result of many factors, including morphology, size, and the inevitable presence of point defects and/or adsorbates. To overcome experimental limitations, theoretical studies can be used to investigate the effects arising from the finite size and shape of the TiO$_2$ NPs. However, modeling TiO$_2$ NPs of an experimentally relevant size using first-principles electronic structure methods is still computationally challenging. To overcome this difficulty, many studies have used TiO$_2$ bulk polymorphs\textsuperscript{28–29} and surfaces.\textsuperscript{30,31} Those studies have provided a large amount of useful information, but the effects arising from the finite size and shape of TiO$_2$ NPs are still missing. To help close the gap between such periodic models and small nanocluster models, some studies\textsuperscript{31–33} have provided information on the stability and exciton binding energy depending on the size and shape of TiO$_2$ NPs, but understanding of the charge carrier dynamics of excited electron and hole is still lacking. In this context, we report an investigation of the effect of finite size and shape on the charge carrier dynamics of TiO$_2$ NPs. In this paper, we study the charge recombination dynamics in TiO$_2$ NPs with varying size in the 1–3 nm range. Generally, we observe decreased recombination rates with increased NP size and rationalize this trend by analyzing the electronic structure, nuclear dynamics, charge density, and electron–phonon coupling.

2. COMPUTATIONAL DETAILS

The simulations were performed with nonadiabatic molecular dynamics (NAMD) formulated within the framework of real-time time-dependent density functional theory (TDDFT) in the Kohn–Sham formulation.\textsuperscript{34,35} The light electrons are treated quantum mechanically, using ab initio DFT, while the heavier and slower nuclei are treated (semi)classically. The electron–nuclear interactions are modeled using NAMD. In particular, the charge recombination dynamics was studied using decoherence induced surface hopping (DISH)\textsuperscript{36} which includes loss of coherence induced by coupling to quantum phonons. Decoherence is essential for the slow charge recombination which involves a single quantum transition across a large energy gap. DISH was implemented within TD-DFT in the Pyxaid software package.\textsuperscript{37,38} The methodology has been tested and applied successfully to the electron transfer and relaxation dynamics of a broad range of materials such as perovskites,\textsuperscript{39} quantum dots,\textsuperscript{40} graphene,\textsuperscript{41} carbon nanotubes,\textsuperscript{42} 2D materials,\textsuperscript{43} metallic nanoclusters,\textsuperscript{44} etc.

The electronic structure and adiabatic MD trajectories were computed with the Vienna Ab initio Simulation Package (VASP)\textsuperscript{50} program using a converged plane-wave basis set. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{51} and projector-augmented wave (PAW) pseudopotentials\textsuperscript{52,53} were used. Additionally, we performed PBE+$U$ calculations, with $U = 3.3$ eV to both Ti and O atoms, because it is well-known that the electronic structure of transition metal oxides can be influenced by DFT functionals. Although more advanced electronic structure methodologies,\textsuperscript{54,55} such as (screened)-hybrid DFT functionals, and GW and Bethe–Salpeter theories can provide a more accurate description of the electronic structure of the systems under investigation, they are computationally quite more demanding and thus cannot be combined with NAMD that requires thousands of electronic structure calculations. Vacuum layers of 10 Å were inserted in the $x$, $y$, and $z$ directions in order to avoid spurious interaction between adjacent NP images. The structures were fully relaxed until the calculated forces between ions was smaller than 0.01 eV/Å. Only the Gamma k-point was used, since NPs are zero-dimensional systems. The NPs were then heated to 300 K through repeated velocity rescaling. 1 ps adiabatic MD trajectories with a 1 fs atomic time step were produced and used to perform the NAMD simulations with the Pyxaid package.\textsuperscript{37,38} 100 initial conditions were sampled randomly from the first 500 fs of the trajectories, and NAMD simulations were performed starting from each initial condition and using 2000 random number sequences to sample the surface hopping probabilities.

3. RESULTS AND DISCUSSION

To investigate the size and shape effect on the electron–hole recombination dynamics of TiO$_2$ NPs, we modeled three octahedral clusters (O$_h$) which have only (101) facets and three cuboctahedral clusters (C$_h$) which have both (101) and (001) facets. The clusters were constructed using the Wulff method\textsuperscript{36,57} by cutting bulk polymorph in order to maintain its (101) or (001) facets as shown in Figure 1. The isomers used here are known to be the most stable structures by the previous studies.\textsuperscript{31–33} Barnard et al.\textsuperscript{31} suggested these atomic structures by considering relative stabilities of (TiO$_2$)$_n$ anatase-like particles exhibiting the lowest energy surfaces with $n$ up to 455 units, employing a self-consistent tight-binding approach. Then, the results were further supported by DFT calculation using a variety of functionals\textsuperscript{52,53} such as PBE, PBE0, and B3LYP with all electron basis sets. Also, these structures remained stable during our molecular dynamics simulations at
ambient temperature. Thus, these structures provide a faithful representation of the geometric and electronic structure of experimentally synthesized nanoparticles used to probe photocatalytic water splitting. Here, the size of NPs was determined by the largest distance within each NP: 1 nm (TiO$_2$)$_{10}$ < 1.2 nm (TiO$_2$)$_{29}$ < 2.0 nm (TiO$_2$)$_{35}$ ≈ (TiO$_2$)$_{78}$ < 2.2 nm (TiO$_2$)$_{84}$ < 3.0 nm (TiO$_2$)$_{97}$ < 2.2 nm (TiO$_2$)$_{78}$ < 3.0 nm (TiO$_2$)$_{84}$ (Table 1). The NP size grew with increasing number of TiO$_2$ units with the exception of (TiO$_2$)$_{97}$, which was regarded smaller than (TiO$_2$)$_{78}$ and (TiO$_2$)$_{84}$ due to its larger (001) facet relative to the (101) facet. Table 1 also contains information on dynamics properties, including the relaxation time, which is a measure of the recombination rate, the transition energy defined as the energy difference corresponding to (de)-excitation, nonadiabatic coupling that characterizes electron–phonon interactions and depends on overlap of wave functions between a given pair of states, and pure-dephasing time representing elastic electron–phonon scattering. These quantities will be discussed below during analysis of the NAMD simulation results.

The clusters contain singly coordinated oxygen atoms, as marked with black circles in Figure 1. The clusters always exhibit two singly coordinated oxygen atoms at the head and the tail. The COh clusters show no particular trend. The 29-unit cluster has one singly coordinated oxygen atom at the left side. No such atoms are observed for the 78-unit cluster, and the total of eight such atoms are seen at the top and bottom of the 97-unit cluster. The 151-unit cluster has no singly coordinated oxygen atoms once again. These singly coordinated oxygens could significantly influence the electronic structure of the NPs and affect the recombination dynamics. Therefore, we investigated the density of states (DOS) of each TiO$_2$ NP (Figure 2).

The DOS shown in Figure 2 demonstrates that the highest occupied molecular orbital (HOMO) arises mainly from atomic orbitals of O atoms and the lowest unoccupied molecular orbital (LUMO) stems from Ti atoms, as known. Several unexpected states, which were not found in the bulk TiO$_2$ model, were observed between the valence band and the Fermi energy in all clusters, except for (TiO$_2$)$_{78}$, as marked with black dotted rectangles. They were also observed in the results of the PBE+U calculations, which showed a somewhat increased energy gap between these states and the conduction band minimum (Figure S1): 2.05–2.50 eV (10 unit), 2.05–2.27 eV (35 unit), and 2.03–2.04 eV (84 unit) for O$_h$ clusters and 2.29–2.69 eV (29 unit), 2.23–2.56 eV (78 unit), and 1.59–2.01 eV (97 unit) for CO$_h$ clusters. To find out the origin of these states, we investigated the charge density distribution patterns for the states between HOMO–1 and LUMO+3, as shown in Figure 3.

The charge density distributions demonstrate that these hole trap states are localized on the singly coordinated oxygen atoms. No trap states are seen in (TiO$_2$)$_{78}$, which contains no singly coordinated oxygen atoms (Figure 1). Previous studies reported that a neutral oxygen vacancy provided two excess electrons to reduce Ti$^{4+}$ to Ti$^{3+}$, and as a result defect states appeared around 1.0 eV below the conduction band minimum. The singly coordinated oxygen atom can be understood as the opposite of the oxygen vacancy. The atom

<table>
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<th>average transition energy (eV)</th>
<th>nonadiabatic coupling (meV)</th>
<th>pure-dephasing time (fs)</th>
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<td>169.0</td>
<td>1.38</td>
<td>1.37</td>
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</table>

Table 1. Nonradiative Relaxation Time, Average Transition Energy between HOMO and LUMO, Average Absolute Nonadiabatic Coupling, and Pure-Dephasing Time

Figure 2. Density of states (DOS) for TiO$_2$ NPs. Black, blue, and red lines represent total DOS and partial DOS of Ti and O atoms, respectively. The dotted rectangles highlight the states originating from the singly coordinated oxygen atoms (Figure 1).
creates a defect state above the valence band due to the presence of an unstable unpaired electron. Contrary to HOMO−1 and HOMO, the electron densities of the states between LUMO and LUMO+3 were fairly delocalized in the centers of all considered cluster. The charge densities calculated with PBE+U also validate the above conclusions (Figure S2).

Following a photoexcitation, and prior to charge recombination, the excited electron relaxes rapidly to the LUMO, while the created hole relaxes rapidly to the HOMO. The NAMD simulations included the electron states from LUMO to LUMO+3 and the hole states from HOMO to HOMO−1. We expect the nonadiabatic coupling (NAC) leading to electron−hole recombination would be reduced as the particle size increases because the wave function overlap between the electron states at the center of cluster and the hole traps localized on the singly coordinated oxygen atoms decreases. Indeed, the NAC averaged for all possible transitions from HOMO−1 and HOMO to LUMO through LUMO+3 decreased, 7.73 > 4.42 > 3.03 > 2.25 > 1.66 > 1.37 expressed in meV, as the number of TiO2 unit in the NPs increased, (TiO2)10 < (TiO2)29 < (TiO2)35 < (TiO2)78 < (TiO2)84 < (TiO2)97 (Table 1).

We also calculated the exciton binding energy (ΔEex) defined as $E_{gap} - O_{gap}$ where $E_{gap}$ is the electronic gap defined as the energy difference between the vertical ionization potential and the vertical electron affinity and $O_{gap}$ is optical gap approximated by the difference between the LUMO and HOMO energies (Figure 4). The exciton binding energy shows how strongly the electron and hole are bound together. A large exciton binding energy indicates strong electron−hole that can lead to rapid electron−hole recombination. As the size of NPs increased, both $O_{gap}$ and $E_{gap}$ decreased, although they were somewhat underestimated due to known self-interaction error of the PBE functional. $O_{gap}$ (in eV) decreased as 2.054 > 2.049 > 2.028 in the (TiO2)10, (TiO2)35, and (TiO2)84 clusters, respectively, and 2.285 > 2.229 > 1.593 in the (TiO2)29, (TiO2)78, and (TiO2)97 COh clusters, respectively. Similarly, $E_{gap}$ (in eV) decreased as 5.614 > 3.873 > 3.309 for the Oh clusters and 4.087 > 3.249 > 2.450 for the COh clusters. The exciton binding energy decreased as the size of NPs increased because $E_{gap}$ decreased more rapidly than $O_{gap}$. The trend suggests that the electron−hole recombination rate decreases as the NP size increases. Also, the observed longer relaxation time in the COh clusters containing (001) surfaces, compared to the Oh clusters containing no such surfaces, can be related to the smaller $\Delta E_{ex}$ of COh than Oh due to their smaller $E_{gap}$ and larger $O_{gap}$. However, this difference should become negligible as the NP size increases considering that the $\Delta E_{ex}$ of the Oh NPs decreases more rapidly than that of the COh NPs.

Then, we investigated the nonradiative electron−hole relaxation dynamics using the NAMD simulation (Figure 5). We considered all possible excitations of electron from HOMO−1 and HOMO to LUMO through LUMO+3 as the active space. Assuming that the overall decay is exponential, as observed in experiments, we fitted the 500 fs of NAMD data with the expression $P(t) = 1 - \exp(-t/\tau)$ to obtain the relaxation time $\tau$. In all cases, the data were represented by straight lines very well (Figure 5). The nonradiative lifetime was hundreds of picoseconds, in agreement with the time-resolved photoluminescence data for TiO2 nanostructures. The relaxation time increased with the particle size, as expected. Specifically, the relaxation time of the Oh structures increased from 15.2 ps to 175.9 and 384.3 ps as the particle size increased.

Figure 3. Charge densities of HOMO−1 to LUMO+3 orbitals in the (TiO2)ₙ nanoparticles

Figure 4. Optical ($O_{gap}$) and electronic ($E_{gap}$) gaps and exciton binding energy ($\Delta E_{ex}$) calculated for the octahedral (black line) and cuboctahedral (red line) nanoparticles.
charge density shown in the Supporting Information, we can anticipate somewhat slower dynamics because the energy gaps between the hole trap states and conduction band minimum increased somewhat, while the orbital localizations remained unchanged, suggesting similar NAC magnitudes.

The influences of NAC, transition energy, and pure-dephasing time on the electron–hole recombination are intertwined. For example, the shorter dephasing time and smaller NAC of (TiO$_2$)$_{29}$ contributed to its longer relaxation time relative to (TiO$_2$)$_{109}$ despite the smaller transition energy. On the other hand, the larger transition energy and smaller NAC of (TiO$_2$)$_{35}$ contributed to the slower recombination relative to (TiO$_2$)$_{29}$ despite the longer dephasing time. A similar argument can be applied to explain the slower recombination of (TiO$_2$)$_{78}$ than (TiO$_2$)$_{35}$. Likewise, shorter dephasing time and larger transition energy of (TiO$_2$)$_{84}$ contributed to its longer relaxation time compared to (TiO$_2$)$_{97}$, considering similar NAC values.

The relaxation time and the transition energy were significantly affected by the presence of the singly coordinated oxygen atom. The charge densities of the hole trap states were highly localized at the singly coordinated oxygens, while LUMO to LUMO+3 were relatively delocalized at the center of the NPs. As the NP size increases, the physical distance between the electron and hole also increases, suggesting that the NAC responsible for the charge recombination decreases. At room temperature, the energies of the hole traps localized on the singly coordinated oxygen atoms showed a strong fluctuation, as shown in Figure S3. The (TiO$_2$)$_{78}$ cluster showed much smaller energy fluctuations compared to the others. In sufficiently large clusters the singly coordinated oxygen atoms can lead to efficient and long-lived charge separation. In applications that rely on charge separation, such as photocatalysis, the singly coordinated oxygen atoms are beneficial. At the same time, in photovoltaic applications that require efficient charge transport, the localized trap states created by the singly coordinated oxygen atoms should be avoided.

Overall, the rate of the nonradiative electron–hole recombination decreased with increasing TiO$_2$ NP size for both O$_h$ and CO$_h$ symmetries, as observed in the experiments. Generalizing the reported results to other transition metal oxides, we note that the charge recombination rate is governed by two competing effects. As the NP size increases, the decreasing transition energy (band gap) favors faster recombination, while decreasing NAC reduces the recombination rate. The relative importance of each factor can vary for different transition oxides. Because the calculated rates decrease very significantly with increasing NP size for the systems under investigation, we can expect a similar trend for other transition metal oxides. For large clusters the lifetime should depend on the amounts of defects, such as singly coordinated oxygen atoms, or dopants, such as nitrogens and fluorines, rather than on cluster size.

4. Conclusions

We have investigated the effects of size and shape on the charge carrier dynamics of TiO$_2$ nanoparticles, using nonadiabatic molecular dynamics and real-time time-dependent density functional theory. Our results have demonstrated that the charge recombination time increases with increasing particle size due to decreasing nonadiabatic coupling and exciton binding energy. The cuboctahedral clusters showed smaller exciton binding energies compared to the octahedral clusters,
rationalizing longer relaxation times. For the octahedral clusters, the decreasing nonadiabatic coupling and pure-dephasing time contributed to the longer relaxation time with increasing cluster size, despite decreasing transition energy. The influences of the nonadiabatic coupling, transitions energy, and pure-dephasing time were more complex for the cuboctahedral clusters. The smaller nonadiabatic coupling of \((\text{TiO}_2)_{29}\) contributed to its longer relaxation time compared to \((\text{TiO}_2)_{29}\) despite a longer pure-dephasing time. At the same time, \((\text{TiO}_2)_{29}\) contained no singly coordinated oxygen atoms, which reduced significantly the average transition energy of \((\text{TiO}_2)_{29}\), making \((\text{TiO}_2)_{29}\) relax faster than \((\text{TiO}_2)_{29}\). The magnitudes and trends in the relaxation times show good agreement with the available experimental data.\(^{20}\) The reported results isolate the size and shape effects from other factors affecting the charge recombination dynamics, such as presence of dopants, defects, and adsorbates that cannot be fully controlled in experiments. The detailed atomistic insights into the energy relaxation and charge recombination processes advance fundamental understanding of photoinduced dynamics in nanoscale materials for solar energy harvesting and utilization.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free on charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b00691.

Density of states and charge densities of key orbitals calculated with the PBE+U method, and evolution of the orbital energies in the \((\text{TiO}_2)_{29}\) nanoparticles [PDF]

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**Notes**

The authors declare no competing financial interest.

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