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Effect of Fe doping concentration on photocatalytic performance of CeO$_2$ from DFT insight into analysis

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ABSTRACT
A series of CeO$_2$ based materials are analyzed using first-principles calculation. After geometry optimization, the calculated parameter of Ce$_3$O$_6$ is in good agreement with the experimental and theoretical results. The lattice constant of doped materials becomes increasingly smaller with the introduction of more Fe doping into the lattice owing to the small radii of impurity atoms. Other data relate to increase or decrease to some extent. As for electronic property, the energy band structure and partial density of states are explored and discussed. Due to the enhancement of the degree of hybridization between O atoms and metal atoms, there is a narrower band gap in Fe doped materials, indicating that lower energy can promote and achieve electronic transition from the valence band to the conduction band. Through the complex dielectric function composed of the real part and the imaginary part, the extinction coefficient, it is observed that they are responsive to light and electronic transition under visible light irradiation. On the other hand, we predict the photocatalytic behavior by discussing the extinction coefficient. Besides, the optical absorption spectrum and optical band gap are analyzed to further observe performance in photocatalysis. It is found that doping causes first the red shift of the absorption edge and then results in the red shift and enhancement of photocatalytic performance, which is consistent with our prediction. In addition, $E_{op}$ indicates that Fe is beneficial for the activity of CeO$_2$. The atomic number ratio of 3:1 (Fe:Ce) shows superior behavior compared to other materials.

I. INTRODUCTION
The past decade has witnessed a huge development in economy, bringing some problems at the same time, such as energy crisis and environmental problems accompanied by dyes and atmospheric carbon dioxide (CO$_2$). On the one hand, great efforts with the progressive research in experiment have focused on studying the conversion of water (H$_2$O) into hydrogen (H$_2$) as clean and sustainable energy. On the other hand, many papers reported the exciting technologies that are worthy to be carried out and of great significance for environmental governance. However, these cases take full advantage of the conversion of solar energy into chemical energy. Until now, metal-oxide based materials are of great interest because of their strong relevance to the important application in photocatalysts.

CeO$_2$, an n-type semiconductor, exhibits these properties including high stability and nontoxicity, and its effectiveness has been confirmed for three way automotive catalysis (TWC), solid oxide fuel cells (SOFC), as well as sensors. Especially, CeO$_2$ displays photocatalytic performance in the ultraviolet (UV) light region ($\lambda < 400$ nm). In analogy to TiO$_2$, CeO$_2$ with unique Ce 4f states shows the pattern of higher photocatalytic activity, which
means that CeO$_2$ can be expected to be an efficient photocatalytic material. However, the study on CeO$_2$ for visible-light photocatalysis is currently limited owing to the wide energy gap (3.000 eV), resulting in the difficulty of separation of the hole-electron pairs. Besides, fast charge carrier recombination is difficult to satisfy photocatalytic applications. In order to enhance the photocatalytic performance, fortunately, it has been reported that doping has the potential to improve photocatalysts, suggesting that it is associated with defect chemistry. Liu et al. reported a significant photocatalytic behavior for N doped CeO$_2$ in visible light, which is attributed to doping of N atoms. Moreover, doping of transition metal (TM) exhibits better activity. For instance, on account of the existence of Ce$^{3+}$ states, the absorption edge of CeO$_2$ nanoparticles has a red shift with increasing Co concentration. However, it is also found experimentally that efficiency of Co (6 mol. %) doped CeO$_2$ is identified as 89%, which is superior to those with other Co concentrations. Many reports, whether the theory or experimental investigations, have demonstrated that codoping also leads to decrease of the band gap, recombination rate, and improves photocatalytic activity. For example, (Ni, Co) codoped CeO$_2$ has been successfully synthesized using the hydrothermal technique and is realized as red shift in absorption. CeO$_2$, as fabricated from codoping of C and N, can be utilized as fascinating photocatalysts for application in comparison with pure CeO$_2$. In general, the crystalline phase is the crucial factor for achieving red shift of the absorption onset.

Most prominently, the photocatalytic activity also depends on the structure of photocatalysts, thus implying that the design of them is worthy of attention. For structure of photocatalysts, the improvement in design can not only enlarge the specific area and increase the active site, but also facilitate efficient photon utilization, resulting in higher separation of hole-electron pairs and a smaller recombination rate of photon-induced carriers. Thus, numerous works of research have gained considerable attention on the preparation and property of metal-doped metallic oxide (such as TiO$_2$, CeO$_2$) which gives rise to superior photocatalytic performance in the visible-light region. To strengthen the photocatalytic activity, the investigators have tried all kinds of ways to change the structure of the samples. The Fe doped CeO$_2$ film displays excellent methyl orange (MO) degradation in the visible-light region that corresponds to higher photocatalytic activity. (Al, Fe) codoped TiO$_2$ nanotubes, prepared by the hydrothermal method, with 0.25 (Al):0.75 (Fe) ratio leads to the maximum efficiency (79%) for humic acid (HA) removal. Other reports have demonstrated that ordered mesoporous Fe doped CeO$_2$ and CeO$_2$-TiO$_2$ composites offered tremendous opportunities to reduce CO$_2$ owing to enlarge the energy range of the photon excitation. Since Fe ions are easily introduced into the lattice of CeO$_2$, the modification of Fe ions in CeO$_2$ is believed to be a very promising strategy for photocatalysis. Previous reports focused on preparation methods and outline shape of the Fe doped CeO$_2$ by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM),

![FIG. 1. Calculation catalyst models of the doped structures with different Fe concentrations. (a) Ce$_2$O$_{34}$ structure, (b) Ce$_{31}$FeO$_{34}$ structure, (c) Ce$_{15}$FeO$_{32}$ structure, (d) Ce$_7$FeO$_{16}$ structure, (e) Ce$_7$FeO$_8$ structure, (f) Ce$_2$FeO$_8$ structure, and (g) CeFeO$_8$ structure.](image-url)
as well as x-ray diffraction (XRD) analysis\textsuperscript{33,34} and tested photocatalytic activity either by degradation reaction or by product generation.\textsuperscript{35-39}

Although there are a lot of investigations on ways to improve the performance of CeO\textsubscript{2}, very few studies have provided detailed explanation to dopant-induced enhancement of photocatalysts by analyzing the crystal structure, electronic structure, especially effect of activity on Fe ion concentration. However, there is a lack of explanation to dopant-induced enhancement of photocatalysts by extinction coefficient, and optical absorption of Fe doped CeO\textsubscript{2} structure, optical property containing the dielectric function, the crystal structure, electronic property from the energy band structure, optical property containing the dielectric function, the extinction coefficient, and optical absorption of Fe doped CeO\textsubscript{2} with summarized tables and plotted figures to learn the influence of Fe concentration on photocatalysis. On the basis of analysis, our results demonstrate that Fe doped CeO\textsubscript{2} with different dopant concentrations improves the photocatalytic performance. These results will provide new point of view through the analysis in Sec. III.

II. CATALYST MODELS AND COMPUTATIONAL DETAILS

A. Catalyst models

In this work, pure CeO\textsubscript{2}, as important rare earth oxide with a fluorite structure of a space group Fm-3m, is built by using a supercell containing 32 Ce atoms and 64 O atoms, as shown in Fig. 1(a). The radius of the Fe ion is smaller than that of the Ce ion, which facilitates Fe into the lattice of CeO\textsubscript{2} and results in a solid solution. The supercell containing 96 atoms, 48 atoms, 24 atoms, and 12 atoms is utilized by changing the atomic cell along the three lattice parameters so as to construct Fe doped CeO\textsubscript{2}. Fe doped CeO\textsubscript{2}, which is involved at different doping rates, is modeled by substituting Ce atoms in pure CeO\textsubscript{2} with Fe atoms, as plotted.

| Structure       | Lattice constants (Å) | Net charge (e) | Bond order       |
|-----------------|-----------------------|----------------|------------------|
| Ce\textsubscript{2}O\textsubscript{64} | a = 10.846\textsuperscript{a} 10.920\textsuperscript{a} | Ce:1.230\textsuperscript{a} O:−0.620\textsuperscript{d} | Ce–O:0.220\textsuperscript{a} |
|                 | b = 10.846\textsuperscript{a} 5.480\textsuperscript{a}   | Ce:1.230\textsuperscript{a} O:−0.620\textsuperscript{d} | Ce–O:0.210\textsuperscript{a} |
|                 | c = 10.846\textsuperscript{a} 5.410\textsuperscript{a}   |                |                  |
| Ce\textsubscript{1}Fe\textsubscript{0}O\textsubscript{64} | a = 10.799\textsuperscript{b} | Ce:1.230\textsuperscript{b} Ce:1.240\textsuperscript{b} | Ce–O:0.220\textsuperscript{b} Fe–O:0.230\textsuperscript{b} |
|                 | b = 10.799\textsuperscript{b} | O:−0.570\textsuperscript{b} O:−0.610\textsuperscript{b} |                  |
|                 | c = 10.798\textsuperscript{b} | O:−0.620\textsuperscript{b} Fe:0.740\textsuperscript{b} |                  |
| Ce\textsubscript{1}5Fe\textsubscript{0}2O\textsubscript{32} | a = 10.741\textsuperscript{c} | Ce:1.230\textsuperscript{c} Ce:1.240\textsuperscript{c} | Ce–O:0.220\textsuperscript{c} Ce–O:0.220\textsuperscript{c} |
|                 | b = 10.741\textsuperscript{c} | O:−0.570\textsuperscript{c} O:−0.570\textsuperscript{c} |                  |
|                 | c = 5.384\textsuperscript{c} | O:−0.610\textsuperscript{c} O:−0.620\textsuperscript{d} | Fe:0.740\textsuperscript{d} |
| Ce\textsubscript{7}FeO\textsubscript{16} | a = 10.639\textsuperscript{d} | Ce:1.210\textsuperscript{d} Ce:1.230\textsuperscript{d} | Ce–O:0.210\textsuperscript{d} |
|                 | b = 5.338\textsuperscript{d} | Ce:1.250\textsuperscript{d} O:−0.570\textsuperscript{d} | Fe–O:0.230\textsuperscript{d} |
|                 | c = 5.338\textsuperscript{d} | O:−0.610\textsuperscript{d} Fe:0.750\textsuperscript{d} |                  |
| Ce\textsubscript{5}FeO\textsubscript{8} | a = 5.249\textsuperscript{e} 5.250\textsuperscript{e} | Ce:1.240\textsuperscript{e} O:−0.560\textsuperscript{e} | Ce–O:0.200\textsuperscript{e} Fe–O:0.240\textsuperscript{e} |
|                 | b = 5.249\textsuperscript{e} | Fe:0.770\textsuperscript{e} Ce:1.240\textsuperscript{e} |                  |
|                 | c = 5.249\textsuperscript{e} | O:−0.580\textsuperscript{e} Fe:0.960\textsuperscript{e} |                  |
| Ce\textsubscript{2}Fe\textsubscript{2}O\textsubscript{8} | a = 5.008\textsuperscript{f} | Ce:1.320\textsuperscript{f} O:−0.510\textsuperscript{f} | Ce–O:0.170\textsuperscript{f} Fe–O:0.240\textsuperscript{f} |
|                 | b = 5.091\textsuperscript{f} | Fe:0.730\textsuperscript{f} |                  |
|                 | c = 5.008\textsuperscript{f} |                  |                  |
| CeFe\textsubscript{3}O\textsubscript{8} | a = 4.806\textsuperscript{g} | Ce:1.55\textsuperscript{g} O:−0.470\textsuperscript{g} | Ce–O:0.090\textsuperscript{g} Fe–O:0.250\textsuperscript{g} |
|                 | b = 4.806\textsuperscript{g} | Fe:0.740\textsuperscript{g} |                  |
|                 | c = 4.809\textsuperscript{g} |                  |                  |

\textsuperscript{a}The present work.
\textsuperscript{b}Other calculation in 2 × 2 × 2 supercell from Ref. 54.
\textsuperscript{c}Other calculation from Ref. 55.
\textsuperscript{d}Other calculation in 1 × 1 × 1 supercell from Ref. 53.
\textsuperscript{e}Other calculation from Ref. 57.
\textsuperscript{f}Experiment from Ref. 56.
\textsuperscript{g}Other calculation from Ref. 58.
in Figs. 1(b)–1(g). For Ce$_{15}$FeO$_{34}$, Ce$_{15}$FeO$_{32}$, Ce$_{15}$FeO$_{36}$, Ce$_3$FeO$_8$, Ce$_2$Fe$_2$O$_4$, and CeFe$_2$O$_4$, the atomic number ratio (Fe:Ce) is 1:31, 1:15, 1:7, 1:3, 2:2, and 3:1, respectively, which will guarantee the study on photocatalytic behavior of different Fe concentrations.

B. Computational details

To analyze the behavior of pure and Fe doped CeO$_2$, all calculations are computed with the Cambridge Serial Total Energy Package (CASTEP) code applying the density functional theory (DFT). Generalized gradient approximation (GGA) adds the consideration of simulating the exchange-correlation interaction employing Perdew-Burke-Ernzerhof potential of solid (PBEsol) functional. However, the ultrasoft pseudopotential is employed to describe the interactions between the electrons and ions. For geometry optimization, other calculations including the electronic structure and optical property of pure and Fe doped CeO$_2$, the Brillouin zone is sampled with 2 × 2 × 2 and 4 × 4 × 4 Monkhorst-Pack grids, respectively. A set of a cut-off value of 500 eV can lead to the plane wave basis expansion, and the calculation is converged until energy convergence is set to 2 × 10$^{-5}$ eV. The 2s 2p 3s 3p 4s 3d$^1$ electrons of oxygen, cerium, and iron are considered as valence electrons, respectively. Furthermore, a 4 × 4 × 4 k-grid was used to calculate the dielectric functions. For DFT, there is some difficulty in simulating accurately the electronic structure and on-site coulomb repulsion. Thus, U = 5 eV and U = 4 eV aim to describe Ce 4f states and Fe 3d states, so as to overcome this limitation. The lattice constants of pure CeO$_2$ are 10.846 Å in Table I, and the energy band gap is 2.919 eV, which are close to the theoretical (lattice constants of pure CeO$_2$) and experimental (lattice constant: 5.410 Å from Ref. 56, energy gap: 3.000 eV from Ref. 19) values reported in our previous work. This means that our calculation is reasonable.

III. RESULTS AND DISCUSSION

A. Model structures

By optimizing the different Fe doped CeO$_2$ supercell models, the lattice constant, charge as well as bond order are summarized in Table I, and bond length (including Ce–O and Fe–O bond) and cell volume are given in Table II. The calculated lattice constants of different doped models after doping (before doping) are a = b = 10.779 Å, c = 10.778 Å (a = b = c = 10.846 Å) for Ce$_{31}$FeO$_{64}$, a = b = 10.741 Å, c = 5.838 Å (a = b = 10.846 Å, c = 5.423 Å) for Ce$_{15}$FeO$_{32}$, a = 10.639 Å, b = c = 5.338 Å (a = 10.846 Å, b = c = 5.423 Å) for Ce$_7$FeO$_{16}$, a = c = 5.008 Å, b = 5.091 Å (a = b = c = 5.423 Å) for Ce$_2$Fe$_2$O$_8$ and a = b = 4.806 Å, c = 4.809 Å (a = b = c = 5.423 Å) for CeFe$_2$O$_4$, respectively, showing a small difference except for Ce$_2$Fe$_2$O$_8$ and CeFe$_2$O$_4$. In addition, the lattice constant of Ce$_7$Fe$_2$O$_8$ is a = b = c = 5.249 Å (a = b = c = 5.423 Å), in agreement with Ref. 58. The changes of bond length can result in the change of lattice constants. It is clear that Fe doped CeO$_2$ at a lower doping level exhibits slight discrepancy with respect to the Ce–O bond, which seems that Fe doping has no evident influence on the bond length; however, the decrease of the bond length is remarkable for Ce$_2$Fe$_2$O$_8$ and CeFe$_2$O$_4$, as described in Table II. Ce$_{15}$FeO$_{34}$, Ce$_{15}$FeO$_{32}$, and CeFe$_2$O$_4$ display thirteen types of bond length (ten Ce–O and three Fe–O bond lengths), ten types of bond length

### TABLE II. Calculated bond length [d$_{Ce-O}$ (Å), d$_{Fe-O}$ (Å)] and cell volume (Å$^3$) of pure and Fe doped CeO$_2$ marked by *a* for structures of pure CeO$_2$ and doped CeO$_2$ with different Fe concentrations. Other marks represent theoretical and experimental data from references.

| Structure       | Bond length [d$_{Ce-O}$ (Å)] | Bond length [d$_{Fe-O}$ (Å)] | Cell volume (Å$^3$) |
|-----------------|-------------------------------|-------------------------------|-------------------|
| Ce$_{31}$O$_{64}$ | Ce–O: 2.348                  | Fe–O: 2.124                  | 1276.006          |
| Ce$_{15}$FeO$_{34}$ | Ce–O: 2.372                  | Fe–O: 2.125                  | 1259.189          |
| Ce$_{31}$FeO$_{64}$ | Ce–O: 2.316                  | Fe–O: 2.126                  | 1259.189          |
| Ce$_{15}$FeO$_{32}$ | Ce–O: 2.331                  | Fe–O: 2.139                  | 621.172           |
| Ce$_{7}$FeO$_{16}$  | Ce–O: 2.360                  | Fe–O: 2.140                  | 303.210           |
| Ce$_2$FeO$_{4}$    | Ce–O: 2.321                  | Fe–O: 2.141                  | 144.658           |
| Ce$_2$Fe$_2$O$_8$  | Ce–O: 2.279                  | Fe–O: 2.090                  | 127.695           |
| CeFe$_2$O$_4$     | Ce–O: 2.225                  | Fe–O: 2.038                  | 111.045           |

*a* The present work.

*b* Other calculation from Ref. 57.

*c* Other calculation from Ref. 58.
(eight Ce–O and two Fe–O bond lengths) and six types of bond length (four Ce–O and two Fe–O bond lengths). Besides, the bond length of the Ce–O bond, Fe–O bond, and the cell volume shrinks in comparison with the corresponding-scale CeO$_2$ apart from the individual Ce–O bond. These exhibit lattice distortion on account of the factors in the following:

1. First, given the different atomic radius between Fe atom (1.720 Å) and Ce (1.820 Å), the Fe–O bond length is smaller relative to the Ce–O bond length, which promotes the lattice constant, the cell volume to reduce size, resulting in the lattice deformation to some extent.

2. Moreover, Table I shows redistribution of electron by the introduction of a dopant, which is a key factor of the above and alters the dipole moments at the same time.

3. Most Ce–O bonds have been decreased and few bonds increase for the supercell of multifarious Ce–O bonds, based on facts that the change of structure causes different bond lengths to make structure stability. However, electron has redistributed after introducing Fe into CeO$_2$ (see Table I, Fig. 2).

The bond order is considered as a tool of measurement of covalent property. Fe doping below 50% doping rate suggests that the covalent property of the Ce–O bond is slightly weaker or stronger in contrast to the corresponding pure CeO$_2$. In contrary, the systems over 50% doping rate cause very weak covalency of the Ce–O bond, especially for CeFe$_2$O$_8$. Doping, whether below 50% or over 50% doping rate, induces strong covalency of the Fe–O bond. The observations can be made from the distribution maps of valence electron density in Fig. 2 to reproduce chemical bonds and covalent property. The covalent bond has been confirmed by the color electron density scale, and the covalency of the Ce–O, Fe–O bond is consistent with analysis by bond order. However, covalency of Ce–O is strong for Ce$_2$Fe$_2$O$_8$ and CeFe$_3$O$_8$, which is different from the conclusion mentioned before, predicting that this phenomenon is due to the enhanced degree of the hybridization between Ce and O atoms [see partial density of states (PDOS) from them in Sec. III C]. Table I and Fig. 2 both are indicative of the redistribution of electron, which motivates the change of the electron structure. However, the optical property is involved in excellent photocatalytic performance owing to sensitivity to the electron structure.

B. Energy band structures

Figure 3 shows the energy band structure of Ce$_{32}$O$_{64}$ and doped CeO$_2$ with different Fe concentrations using DFT, where the Fermi level is set at 0.000 eV. Note that the computed energy gap ($E_g$) is 2.919 eV, which is in good agreement with that reported in Ref. 57, which is lower than the experimental value (3.000 eV) due to the underestimation of the GGA. However, the limitation has no influence on both analysis and comparison in the following. However, Ce$_{32}$O$_{64}$ has a direct band gap, suggesting that fast recombination of electron-hole pairs.

From Ce$_{31}$FeO$_{64}$, Ce$_{15}$FeO$_{32}$, and Ce$_7$FeO$_{16}$ in Fig. 3, the energy gap is decreased from 2.919 eV to 2.017 eV, 1.848 eV, and 1.582 eV.
with increasing Fe concentration. The $E_g$ narrowing is not only caused by the decrease between the valence band (VB) and the conduction band (CB), but also by the creation of Fe impurity states in the vicinity of the Fermi level and CB (Ce 4f). As shown in Fig. 3, it is found that there are indirect band gaps and two isolated states, including one empty band and one band occupied by the localized states, which easily occur in the transfer from VB to CB step by step due to low transition energy and prolonged carrier lifetime. $E_g$ between the narrower CB (Ce 4f) and wider CB (Ce 5d) is almost unchanged. Though there is an isolated band at 4.000–7.000 eV, it is not expected to achieve absorption of visible light. The calculated $E_g$ of Ce$_3$FeO$_8$ and Ce$_2$Fe$_2$O$_8$ is 1.339 eV and 0.800 eV, being 1.580 eV (54%) and 1.913 eV (66%) narrower than that of pure CeO$_2$; however, there is almost no $E_g$ for Ce$_2$Fe$_2$O$_8$. The isolated states appear either in the forbidden band, or in about 3.500–8.000 eV of the three models, and is a negative shift between 12.500 eV and 20.000 eV in comparison to the undoped CeO$_2$. Ce$_3$FeO$_8$ with direct band gap and Ce$_2$Fe$_2$O$_8$, which can reduce transfer energy from VB to CB, with indirect energy gap extend carrier lifetime. Here, long carrier lifetime is related to low electron-hole recombination, which results in weak photon emission caused by the radiation of optical transition. The performance of Ce$_3$Fe$_2$O$_8$ is difficult to be predicted only by energy band structure. Moreover, the valence bands of the three systems are broadened, making more carriers participate in the photocatalytic performance. The models may emerge as the process that the electron is excited to the isolated states and go further to the conduction band utilizing lower energy photon, i.e., visible light. In the view of energy band analysis, it is necessary to further discuss the effect on Fe concentration.

C. Partial density of states of pure and Fe doped CeO$_2$

Having been investigated the structures and energy band structures of pure and doped CeO$_2$ with different Fe concentrations, the electronic structure is continued to be studied for more details for partial density of states (PDOS), including the entire models and the individual atom, so that these can provide more references for variation of photocatalytic performance. Here, the black dotted line is considered as the Fermi level, as shown in Figs. 4–7. It can be seen from Fig. 4 that VB for Ce$_3$O$_4$ is mainly concentrated in the energy region between −18.000 eV and −13.000 eV, in −4.000 eV −0.000 eV, which is contributed by Ce 5p, O 2s and Ce 4f, Ce 5d,
FIG. 4. Partial density of states of the Ce$_{32}$O$_{64}$ structure. Black dotted lines represent the Fermi level at 0.000 eV.

FIG. 5. Partial density of states of the (a) Ce$_{31}$FeO$_{64}$ structure and (b) Ce$_{15}$FeO$_{32}$ structure. Black dotted lines represent the Fermi level at 0.000 eV.
FIG. 6. Partial density of states of the (a) Ce$_7$FeO$_{16}$ structure and (b) Ce$_3$FeO$_8$ structure. Black dotted lines represent the Fermi level at 0.000 eV.

O 2p, respectively. CB originates from Ce 5p, Ce 4f, Ce 5d and a small amount of O 2p, O 2s. It is noticed that the hybridization, whether VB or CB, is caused by Ce 5d, Ce 4f, and O 2p in high VB and low CB regions, which affirms the formation of bonding states and antibonding states.

Figures 5(a) and 5(b) are demonstrated for PDOS for Ce$_{31}$FeO$_{64}$ and Ce$_{15}$FeO$_{32}$, suggesting that the electron structures have altered owing to Fe doping into CeO$_2$. The bottom of VB comes from Ce 5p, O 2s and a small contribution of O 2p in the range (i.e., 0.000 eV–15.000 eV), which is involved in two parts: (1) the hybridized states of Ce 4f and O 2p in the narrow CB; (2) the mixed states of Ce 5d, Ce 5p, O 2p with the hybridization between Ce atom and O atom. Fe 3s and Fe 3p, with low density of states, can be ignored. It is found that VB near the Fermi level consists of Ce 4f, Ce 5d, O 2p, and Fe 3d states. As expected, there is hybridization among Ce atom, Fe atom, and O atom (i.e., Ce 4f and O 2p, Ce 5d and O 2p, Fe 3d and O 2p). With the increase of Fe concentration, the wide CB range shifts from about 12.000 eV to 15.000 eV or more. In addition, the two new peaks (0.000 eV–2.500 eV) are represented by Fe 3d states at both Fermi level and the bottom of Ce 4f states. Compared with pure CeO$_2$, VB near the Fermi level is detected to be markedly broadened, resulting in higher performance of photocatalysts.

The bottom of VB and the wide CB are comprised almost entirely of the same atomic states, as shown in Figs. 6(a) and 6(b). However, Fe 3s and Fe 3p are enhanced with the increase of Fe concentration between 10.000 eV and 15.000 eV. Similar to the first two models, both Ce$_2$FeO$_{16}$ and Ce$_3$FeO$_8$ are comprised of Ce 4f, Ce 5d, O 2p, and Fe 3d states for the highest VB and Ce 4f, O 2p states for the narrow CB, respectively. As mentioned before, the hybridization interaction contributes to VB and CB, showing covalency to some extent and especially being in good agreement with Tian et al. for Ce$_3$FeO$_8$. There are impurity states in the forbidden states, which will serve to extend absorption range. From PDOS in Figs. 7(a) and 7(b), with introducing more Fe, the electron structures have been changed a lot relative to pure CeO$_2$, though the composition of states and the type of hybridization are similar to other doped structures. It is obvious that, the splitting states are located in the range from −20.000 eV to −12.500 eV either for Ce 5p states or for O 2s states, which is due to spin-orbit interaction. Especially, Ce 5d splitting states for CeFe$_3$O$_8$, corresponding to the isolated band in the band structure, not only depends on the spin-orbit interaction, but also is ascribed to the crystal field. From the band structure of Ce$_2$Fe$_2$O$_8$, there is almost no E$_g$ and the top of VB crosses the Fermi level, which gives rise to the appearance of a free electron. Amazingly, more Fe concentration to a great extent can make...
VB of two models wider, which is beneficial for photoexcited electron for CeFe₂O₈. However, because of the metallic characteristics, we have difficulty in the predictions about photocatalytic activity for Ce₂Fe₂O₈.

It is observed that Fe 3d states, located in the vicinity of the Fermi level, have been changed and increased in terms of density little by little with increasing Fe doping. There is the hybridization with Fe 3d and O 2p orbitals, which results in the formation of bonding states. It is interesting that, with respect to states near the bottom of CB (Ce 4f states), they are mainly dominated by Fe 3d, together with a small contribution from O 2p, and the density of O 2p, Fe 3d states exhibits enhanced trend, showing antibonding states in the range (1.000 eV–2.500 eV). The strong covalent bond depends on unoccupied antibonding states, thus the hybridization created positive effects that strengthens Fe–O bonds, reinforces material stability, and are beneficial for the separation of excited carriers. Based on the above analysis, Fe doped CeO₂ is good for the improvement of photocatalytic activity in the visible light region by VB to Fe 3d, Fe 3d to CB transition for Ce₁₁FeO₄₄, Ce₁₅FeO₃₂, Ce₇FeO₁₆, and Ce₃FeO₈. As for CeFe₂O₈, there may be the same transition from VB to CB, and it may show very strong absorption. What’s more, there is difficulty in predicting the photocatalytic property of Ce₂Fe₂O₈. In a word, Fe doping can boost the photogenerated electron and hole to achieve the purpose of photocatalysis reaction.

**D. The complex dielectric function of pure and Fe doped CeO₂**

Generally, optical properties are associated with the electronic structure, which are also the most important properties for pure and Fe doped CeO₂ in our work. The complex dielectric function ε(ω) can describe the interaction between incident photon and electron in materials. The transition of electron can be identified on the basis of band structures and PDOS. The complex dielectric function ε(ω) possesses two parts, i.e.,

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), \]

where \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) denote the real and imaginary parts of the complex dielectric function. \( \varepsilon_1(\omega) \) exhibits the polarization owing to the electronic field and \( \varepsilon_2(\omega) \) shows absorption caused by the transition of electron. Thus, the dielectric function can explore the response of pure and Fe doped CeO₂ to the incident photon energy (\( E = h\nu \)).
The imaginary part of the complex dielectric function $\varepsilon_2(\omega)$ is shown by using the following equation:

$$
\varepsilon_2(\omega) = \frac{8\pi^2e^2}{\omega^2m^2} \sum_n \sum_{n'} \int_{BZ} \left| p_{kn}^n \right|^2 f_{kn}(1 - f_{kn'}) \times \partial \left( E_{kn} - E_{kn'} - \hbar \omega \right) \frac{\partial^3 k}{2\pi^3},
$$

(2)

Here, $f_{kn}$ and $p_{kn}^n(k)$ express the Fermi-Dirac function and the momentum dipole-matrix element. $E_{kn}(k)$, $m$, and $e$ denote the energy, mass, and charge of the electron in the materials, respectively.

On the basis of the imaginary part of the complex dielectric function, the real part of the complex dielectric function $\varepsilon_1(\omega)$ is derived by employing the Kramers–Kronig (K–K) relation, as shown in the following:

$$
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega',
$$

(3)

where $p$ represents the Cauchy principal value.

1. The real part of the complex dielectric function of pure and Fe doped CeO$_2$

Figure 8 shows the real part of the complex dielectric function for pure and Fe doped CeO$_2$. It is clear from Fig. 8 that the primary peak has a red shift with increasing Fe concentration, meanwhile, which relates to the increase and decrease of intensity ranging from 0.000 eV to 5.000 eV. Compared with the first peak, the second and third peaks exhibit weaker response to incident photon in 7.500 eV–11.000 eV and 15.000 eV–25.000 eV. $\varepsilon_1(\omega)$ corresponds to the positive or negative in higher energy region than 25.000 eV. The real part becomes negative between 10.000 eV and 15.000 eV and gradually gets the values greater than zero. In particular, for Ce$_2$Fe$_2$O$_8$ and CeFe$_3$O$_8$, there are negative values in the lower energy range above visible light energy, indicating that the vector wave $k$ is imaginary in terms of K–K relation, where the wavefunction is reflected in the corresponding range, corresponding to screening incident photon.

The calculated values, the real part of the complex dielectric function when $\omega$ is equal to zero (i.e., $E = 0$), are 6.000 for Ce$_{32}$O$_{64}$, 6.200 for Ce$_{31}$FeO$_{64}$, 7.000 for Ce$_{15}$FeO$_{32}$, 7.800 for Ce$_7$FeO$_{16}$, 8.800

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**FIG. 8.** The real part $\varepsilon_1(\omega)$ of the complex dielectric function. (a) Ce$_{32}$O$_{64}$ structure, (b) Ce$_{31}$FeO$_{64}$ structure, (c) Ce$_{15}$FeO$_{32}$ structure, (d) Ce$_7$FeO$_{16}$ structure, (e) Ce$_3$FeO$_8$ structure, (f) Ce$_2$Fe$_2$O$_8$ structure, and (g) CeFe$_3$O$_8$ structure.
TABLE III. Calculated value of the band gap $E_g$ from the band structure in Fig. 3, the real part $\varepsilon_1(0)$ of the complex dielectric function and the maximum value $\varepsilon_{1\text{Max}}(\omega)$ with respect to the real part of the complex dielectric function.

|          | Ce$_{32}$O$_{64}$ | Ce$_{31}$FeO$_{64}$ | Ce$_{15}$FeO$_{32}$ | Ce$_{7}$FeO$_{16}$ | Ce$_{3}$FeO$_{8}$ | Ce$_{2}$Fe$_{2}$O$_{8}$ | CeFeO$_{8}$ |
|----------|------------------|---------------------|----------------------|--------------------|------------------|------------------------|------------|
| $E_g$    | 2.919            | 2.017               | 1.848                | 1.582              | 1.339            | 0.000                  | 1.006      |
| $\varepsilon_1(0)$ | 6.000            | 6.200               | 7.000                | 7.800              | 8.800            | 14.000                 | 20.000     |
| $\varepsilon_{1\text{Max}}(\omega)$ | 14.000           | 12.500              | 12.000               | 13.500             | 15.500           | 21.500                 | 29.000     |

for Ce$_2$FeO$_8$, 14.000 for Ce$_2$Fe$_2$O$_8$, as well as 20.000 for CeFeO$_8$ as summarized in Table III, respectively. The static dielectric constant $\varepsilon_1(0)$ is strongly related to the band gap of the corresponding material, which is consistent with Penn’s model \[\varepsilon_1(0) = 1 + \left(\frac{h\omega_p}{E_g}\right)^2\] where $h\omega_p$ is the plasma energy.\(^{68}\) As for the maximum of the primary peak, there is a change from slight difference to significant discrepancy (i.e., stronger response of light in a certain range) in comparison with pure CeO$_2$, as depicted in Table III and Fig. 8. The case expresses the strong optical response of Fe doped CeO$_2$ on account of the condition that an increasing number of Fe atoms substitutes Ce atoms in the lattice of pure CeO$_2$.

2. The imaginary part of the complex dielectric function of pure and Fe doped CeO$_2$

The imaginary part of the complex dielectric function is involved in optical absorption and electronic transition of the corresponding materials. It can clearly been seen from Fig. 9 that the imaginary part $\varepsilon_2(\omega)$ curves of each structure exhibits existence of three peaks, including the low energy (0.000 eV–7.500 eV), the
middle energy (7.500 eV–15.000 eV), and the high energy (17.500 eV–30.000 eV). The secondary and third peaks are mainly due to the process from CB (O 2p, Fe 3d) to CB (Ce 5d) and from the lowest VB (O 2s, Ce 5p) to (Ce 5d). However, since more Ce atoms are replaced by Fe atoms, the secondary and third peaks are increasingly lower intense to about 2.000 expect for a small difference. Figure 9 manifests that the primary peak may have a deep influence on the photocatalytic performance in visible light irradiation, which is related to the transition from VB (O 2p, Fe 3d) near the Fermi level to CB (Ce 4f). However, it is worth mentioning that the impurity states (Fe 3d) are momentarily occupied, so as to finally move to CB (Ce 4f). Furthermore, the density for primary peaks of Ce$_2$Fe$_2$O$_8$ and CeFe$_3$O$_8$ is very strong in contrast to pure CeO$_2$. It is demonstrated that Fe doping can improve activity in visible light owing to the red shift of the threshold value of optical response.

E. The extinction coefficient of pure and Fe doped CeO$_2$

The extinction coefficient, as the function of photon energy, is the imaginary part of the complex refractive index, i.e.,

$$N(\omega) = n(\omega) + ik(\omega),$$

$$n(\omega) = \frac{\sqrt{2}}{2} \left[ \sqrt{\varepsilon_2(\omega) + \varepsilon_1(\omega)} + \varepsilon_1(\omega) \right]^{\frac{1}{2}},$$

$$k(\omega) = -\frac{\sqrt{2}}{2} \left[ \sqrt{\varepsilon_2(\omega) + \varepsilon_1(\omega)} + \varepsilon_1(\omega) \right]^{\frac{1}{2}},$$

in which $n(\omega)$ is the refractive index and $k(\omega)$ is the extinction coefficient, respectively, which are computed from the complex dielectric function. In general, the extinction coefficient can be used as the criterion of degree of incoming radiation. Although, it is also realized that the comparison between $n(\omega)$ and $k(\omega)$ decide whether light can propagate in a certain region, our work focuses more on optical absorption instead of this case by the extinction coefficient. In fact, there is the proportional relation between the extinction coefficient and the absorption coefficient $\alpha(\omega)$, i.e.,

$$k(\omega) = \frac{\alpha(\omega)\lambda}{2\pi}.$$

FIG. 10. The extinction coefficient of pure and Fe doped CeO$_2$: (a) Ce$_{32}$O$_{64}$ structure, (b) Ce$_{31}$FeO$_{64}$ structure, (c) Ce$_{31}$FeO$_{32}$ structure, (d) Ce$_{31}$FeO$_{16}$ structure, (e) Ce$_{32}$FeO$_{8}$ structure, (f) Ce$_{2}$Fe$_{2}$O$_{8}$ structure, and (g) CeFe$_{3}$O$_{8}$ structure.
Thus, to some degree, the extinction coefficient provides indirectly some reference to the absorption behavior.

Figures 10(a)–10(g) present the extinction coefficient of the pure and Fe doped CeO\(_2\) with different Fe concentrations. For these materials, the threshold energy is shifted from 2.600 eV of Ce\(_{32}\)O\(_{64}\) to the lower energy region (i.e., 2.200 eV, 2.100 eV, 1.900 eV, 1.500 eV, 0.750 eV, and 0.800 eV), as described in Fig. 10, indicating that the optical absorption similarly relates to the red shift at the same time. In the 0.000 eV–5.000 eV region, the peaks will reflect the fact that the material can absorb more photon in the specific energy range. In accordance with insets in Figs. 10(a)–10(g), with the enhancement of Fe doping, the extinction coefficient increases gradually and shows range extension in visible light region (1.600 eV–3.200 eV). In addition, the curve of the extinction coefficient exhibits an obvious peak observed at 2.250 eV with a peak intensity of 2.300 and is found to be at 2.200 eV with a peak intensity of 2.800 [corresponding to Figs. 9(f) and 9(g)], leading to strong absorption. According to the plotted figures, it is predicted that, in the visible light region, the absorption edge of the materials mainly have a red shift rather than a significant increase of intensity due to the slight change for Ce\(_{32}\)O\(_{64}\), Ce\(_{31}\)FeO\(_{64}\), and Ce\(_{15}\)FeO\(_{32}\). From Ce\(_2\)FeO\(_8\) to Ce\(_3\)FeO\(_8\), compared with the former, the systems are involved in range extension and enhancement of the absorption behavior. However, when the atomic number ratio is equal to or more than 1:1, the intensity of their peaks increases sharply besides the red shift of the threshold energy for Ce\(_2\)FeO\(_8\) and CeFeO\(_8\), showing that optical absorption will be very strong. On the basis of the above analysis, these will be further demonstrated in Sec. III F.

### F. The optical absorption of pure and Fe doped CeO\(_2\)

#### 1. The optical absorption spectrum

The optical absorption spectrum has significant impact on studying photocatalytic behavior that is crucial for photocatalyst. Figure 11 summarizes the drawing of the optical absorption against wavelength in 100 nm–900 nm. As mentioned by Goubin,\(^{18}\) strong ultraviolet absorption capacity can be regarded as the intrinsic nature of pure CeO\(_2\). It is observed that the absorption in the ultraviolet region, whether pure or Fe doped CeO\(_2\), is strong and only relates to increase or decrease in the certain range. In our work, we

![Fig. 11. The optical absorption spectrum of pure and Fe doped CeO\(_2\): (a) Ce\(_{32}\)O\(_{64}\) structure, (b) Ce\(_{31}\)FeO\(_{64}\) structure, (c) Ce\(_{15}\)FeO\(_{32}\) structure, (d) Ce\(_7\)FeO\(_{16}\) structure, (e) Ce\(_3\)FeO\(_8\) structure, (f) Ce\(_2\)Fe\(_2\)O\(_8\) structure, (g) Ce\(_3\)FeO\(_8\) structure, and (h) Ce\(_7\)Fe\(_2\)O\(_{16}\) and Ce\(_3\)Fe\(_2\)O\(_{16}\) structure.](image-url)
pay more attention to the degree of absorption capacity in the visible light region (i.e., 400 nm–600 nm).

As expected from Sec. III E, for Ce$_{31}$FeO$_{64}$, Ce$_{13}$FeO$_{32}$, as well as Ce$_2$FeO$_{3}$ with lower impurity concentration, the absorption edge moves toward longer wavelength with increasing Fe doping concentration (i.e., optical absorption distributed from 400 nm to 550 nm). Thus, doping with lower Fe concentration merely causes the extension of the absorption from ultraviolet light to visible light. As seen from Figs. 11(e)–11(g), the higher Fe doping rate not only results in the further red shift of the absorption edge, so as to promote photocatalysis, but also causes the enhancement of optical absorption in 400 nm–600 nm. It is clear that, for the three materials, there is a hump at approximately 450 nm, 540 nm, and 550 nm, respectively, and subsequently decreases with wavelength. Optical absorption intensity is 10$^5$ cm$^{-1}$ when the atomic number ratio (Fe:Ce) increases to 3:1, which is optimum photocatalytic efficiency in comparison with other materials expect for Ce$_3$Fe$_2$O$_{64}$ and Ce$_{15}$Fe$_{32}$O$_{64}$. Based on Figs. 11(g) and 11(h), the slight difference can be acquired even though Fe is introduced into the lattice of pure CeO$_2$, so that it can demonstrate that the atomic number ratio (Fe:Ce) of 3:1 can exhibit excellent catalytic performance. It is obvious that the result is consistent with the prediction by the extinction coefficient. However, optical absorption is in connection with these factors in the following:

(i) Because all atoms in the models are relaxed, Fe doping into CeO$_2$ makes the original structure change to a certain degree, which is called defect.

(ii) Doping leads to the redistribution of charge, the formation of the covalent bond (Fe–O bond), and the change of the electron structure. According to the electronic energy band structure and PDOS, narrowing $E_g$, which is ascribed to the interaction between Fe atoms and O atoms, is a key factor for photocatalysis. Therefore, the lower transition energy is beneficial for transition from VB to CB, though the phonon provide assistance to electrons involved in the indirect gap. On the ground of PDOS, the broadened VB shows that more electrons will be excited in Fe doped CeO$_2$, either with direct band gap or with indirect band gap, when the incident light is radiated into Fe doped systems. In addition, the impurity states (Fe 3d) between VB and CB make electron easy to jump to CB (Ce 4f) on account of the fact that the electron has been excited into Fe 3d.

2. The optical band gap

The optical band gap is an important tool to estimate optical absorption property of the materials. There is a relationship between the absorption coefficient ($\alpha$) and the optical band gap ($E_{opt}$) expressed as$^{22,23}$

$$\alpha = \frac{A(h\nu - E_{opt})^n}{h\nu},$$

(8)

where $A$ is the constant ($A \neq 0$), $h$ and $\nu$ represent the Planck constant and frequency, respectively. As for the value of $n$, $n$ depends on different transitions, such as $n = 1/2$ for allowed direct transition, $n = 2$ for allowed indirect transition, $n = 1/3$ for direct forbidden transition, and $n = 3$ for indirect forbidden transition. However, this work pays attention to the optical absorption behavior induced by electron transition. Therefore, the value of $n$ is equal to 1/2 and 2 corresponding to direct and indirect transitions in our simulated materials. For the estimation of $E_{opt}$, Eq. (8) needs to be processed as follows:

$$\alpha(h\nu - E_{opt})^n = (h\nu - E_{opt})^n$$

(9)

$$\alpha(h\nu - E_{opt})^n = (h\nu - E_{opt})^n$$

(10)

when $(\alpha h\nu)^n$ is equal to zero, the result of $A(h\nu - E_{opt})$ is also zero. It means that the specific value ($h\nu$) represents the optical band gap energy, which is determined by extrapolating the linear region of the curve plot. Figure 12 displays the plots of $(\alpha h\nu)^n$ vs ($h\nu$) and $(\alpha h\nu)^n$ vs ($h\nu$) in which the intercept of the dashed-dotted line with energy axis is $E_{opt}$, where $(\alpha h\nu)^3 = 0$ or $(\alpha h\nu)^2 = 0$. The $E_{opt}$ is 2.910 eV for Ce$_{31}$Fe$_{64}$O$_{64}$ (experimental value: 2.940 eV$^{30}$), 2.070 eV for Ce$_{13}$FeO$_{64}$, 1.920 eV for Ce$_{15}$FeO$_{32}$, 1.640 eV for Ce$_2$FeO$_{64}$, 1.600 eV for Ce$_2$FeO$_{64}$, and 0.830 eV for Ce$_6$FeO$_{64}$, which shows that the steep absorption edge was obviously shifted to a wider absorption range with increasing impurity atom concentration and $E_{opt}$ gets small. As shown in Fig. 12. The estimated band gap energy of Fe doped CeO$_2$ was less than that of Ce$_{31}$Fe$_{64}$O$_{64}$, resulting in greater optical absorption, so that more photon-generated carriers are excited by visible-light irradiation and then migrated to the surface to participate in reaction.

Especially, there is no $E_g$ of Ce$_{32}$Fe$_3$O$_{64}$. However, $E_{opt}$ (0.660 eV) of Ce$_{21}$Fe$_3$O$_{64}$ is weaker than that of Ce$_{32}$Fe$_3$O$_{64}$, which is due to the fact that the process over the Fermi level shows that there are free electrons in Ce$_{21}$Fe$_3$O$_{64}$. In the regard, some electrons did not participate in the process from a filled band to an empty one by photon absorption. Furthermore, Fig. 13 (the left side) shows that the electron (O 2p) of VB is first excited to impurity states (Fe 3d) and subsequently move toward CB (Ce 4f). Of course, the excited electron will go through a recombination process of hole-electron pairs described in Fig. 13 (the left side). Fig. 13 also describes the recombination process of direct and indirect band gaps. Hence, for Ce$_{32}$Fe$_3$O$_{64}$ and Ce$_6$FeO$_{64}$, the recombination process of hole-electron pairs can be achieved as long as electron releases energy in the form of photon, showing a short lifetime. However for Ce$_2$FeO$_{64}$, the lifetime of carrier is longer in comparison with Ce$_{32}$Fe$_3$O$_{64}$, because this recombination need go through Fe 3d states. On the contrary, as for the indirect gap, the given phonon has played an indispensable role in the recombination, such process cannot only depend on the emitting photon. Thus, this case will give rise to going into overtime of the journey from CB to VB for other materials. Given this fact that Fe doping improves photocatalytic performance, the mechanism of excitation is described as follows:(1) The electrons of the valence band are excited into Fe 3d due to optical radiation; (2) On the basis of the electronic structure, the imaginary part of the complex dielectric function and optical absorption spectrum, electrons have participated in the transition from Fe 3d to Ce 4f; (3) specific oxidation reactions and reduction reaction take place on the surface of materials to achieve photocatalysis. The gap from Fe 3d to Ce 4f is narrower in comparison with that from O 2p to Ce 4f of CeO$_2$. Thus, this process takes place subsequently after the completion of the first stage. As mentioned above, phonon is required in the transition either from O 2p to Fe 3d or from Fe 3d to Ce 4f, except for CeO$_2$ and Ce$_6$FeO$_{64}$. It is concluded that Ce$_2$Fe$_3$O$_{64}$ or the atomic number ratio of 3:1 is most suitable as an effective photocatalytic material.
FIG. 12. The optical absorption edge and optical band gap of pure and Fe doped CeO$_2$. (a) Ce$_{32}$O$_{64}$ structure, (b) Ce$_{31}$FeO$_{64}$ structure, (c) Ce$_{15}$FeO$_{32}$ structure, (d) Ce$_7$FeO$_{16}$ structure, (e) Ce$_3$FeO$_8$ structure, (f) Ce$_2$Fe$_2$O$_8$ structure, and (g) CeFe$_3$O$_8$ structure.

IV. CONCLUSIONS

In summary, our work shows that, to gain a comprehensive study about the photocatalytic performance of CeO$_2$ with different Fe concentrations, the structure, electronic structure, optical property (including the complex dielectric function, the extinction coefficient, optical absorption, etc.) are considered by using CASTEP based on the DFT+U method. We have built models of Fe doped CeO$_2$ by introducing Fe into pure CeO$_2$. For the structure of CeO$_2$, the parameters tabulated in Tables I and II are in good agreement with that of the experimental finding and theoretical results. After Fe doping, the lattice constant and the charge of O atoms become small. The bond order of the metal-oxygen bond and the charge (Fe atoms, O atoms) relate to the increase or decrease to some extent. Particularly, these results get smaller with more and more Fe concentration. The bond length (Ce–O bond, Fe–O bond) shows a similar phenomenon, which is due to the fact that Fe atoms have small atom radii. Though distribution maps of valence electron density of Ce$_2$Fe$_2$O$_8$ and CeFe$_3$O$_8$ exhibit the strong interaction between the
Ce atom and O atom, the covalency is weak, indicating that the maps exhibit higher hybridization. The electronic energy band structure shows that the pure and Fe doped CeO2 have a band gap ranging from 2.919 eV to 0.800 eV, i.e., the direct band gap for Ce2O3 and CeFeO3, and the indirect band gap for Ce31FeO8, Ce15FeO32, Ce2FeO10, Ce2Fe2O5, and CeFe2O8, which increases the lifetime of carriers for other models. From the PDOS, the degree of hybridization between metal atoms and O atoms has been enhanced, such as Ce 4f–O 2p, Ce 5d–O 2p, and Fe 3d–O 2p. It is clearly found that two Fe 3d states distribute both near the Fermi level and the bottom of Ce 4f states. It is observed that the VB become broad with increasing Fe concentration. On account of this fact, more electrons from VB will be involved in excitation and transition. Differently, there is nearly no Eg partially VB over the Fermi level for Ce2Fe2O8, suggesting that it exhibits metal characteristic and possess free electron.

The real and imaginary part of the complex dielectric function and the extinction coefficient are calculated and discussed. The dielectric function suggests that Fe doping shows an increasingly strong response to light with more concentration under visible light. Given these analyses, the red shift and strong absorption. The optical band gap shows evidence for photocatalysis in visible light. Given these analyses, the atomic number ratio of 3:1 is suitable for acting as excellent photocatalytic materials. For the photocatalytic mechanism, the excited electron can take part in the transition from VB to impurity states (Fe 3d) and subsequent one from Fe 3d to CB step by step. Finally, we hope that these calculated results can promote further photocatalysis investigations.

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