First-principles investigation on N/C co-doped CeO_2*

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The N and C doping effects on the crystal structures, electronic and optical properties of fluorite structure CeO_2 have been investigated using the first-principles calculation. Co-doping these two elements results in the local lattice distortion and volume expansion of CeO_2. Compared with the energy band structure of pure CeO_2, some local energy levels appear in the forbidden band, which may facilitate the light absorption. Moreover, the enhanced photo-catalytic properties of CeO_2 were explained through the absorption spectra and the selection rule of the band-to-band transitions.

Keywords: first-principles, N/C co-doped CeO_2, photo-catalytic activity

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1. Introduction

CeO_2 has become one of the most important potential materials since the late 1990s. With the feature of redox properties, low cost, and high photo-catalytic activity, CeO_2 has been widely used in the photo-catalysts field.[1] It has a wider application than TiO_2 due to its expanded UV absorption properties into visible-right region.[2] However, the major drawback of pure CeO_2 is a wide band gap of 3.2 eV, which limits its light absorption to a narrow range of the solar spectrum.[3] To take advantage of common light sources, the non-mental doped CeO_2 with enhanced visible-light-sensitive properties has attracted more and more attention.

Doping atoms into CeO_2 at substitutional or interstitial position of the semiconductor crystal structure to improve its performance has been reported in much literature. A large number of reports have confirmed that doping with non-metal elements such as nitrogen (N), carbon (C), and sulfur (S) gives promising results for improving the visible-light photo-catalysis. Liu *et al.*[4] observed an improved photo-catalytic activity from the N/C doped TiO_2 and found that the enhanced photo-catalytic activity is attributed to the N/C doping which extends the light absorption of TiO_2 into the visible light region. Chen *et al.*[5] revealed that the visible light absorptions of N/C/S doped TiO_2 are red shifted, and display the additional electronic states of the dopants, which explains the visible-light absorption of $TiO_{2-x}N_x$, $TiO_{2-y}C_y$, and $TiO_{2-z}S_z$.

Recently, more and more scholars have tried to dope non-metal elements into CeO_2 and improve its photo-catalytic activity. Yu *et al.*[6] reported that the N-doped material exhibited higher catalytic activity than the undoped one, which could open the door for designing new highly catalytic activity catalysts. Wu *et al.*[7] synthesized N doped CeO_2 by one step solvothermal route, and found that doping of N into CeO_2 can greatly enhance the photo-catalytic efficiency of CeO_2 under visible light irradiation. Mao *et al.*[8] successfully synthesized N-doped CeO_2 through a wet-chemical route, and the sample showed a visible-light absorbance shift compared to pure CeO_2. Meanwhile, the results also suggested that the N doping level could be controlled.

The aim of this paper is to confirm the influence of N/C co-doping on the optical absorption spectra and other properties of CeO_2, which are described in correlation with the photo-catalytic activity. In the present work, the results of the geometry structure, band structure, and density of states are presented, and the influence of N/C dopant and the optical absorption properties including the band gap energy are discussed, aiming at providing some profound theoretical illustrations for the related experimental research on N/C co-doped CeO_2.

2. Calculation model and method

Pure CeO_2 has cubic fluorite-type structure ($Fm3m$), containing four Ce and eight O atoms in the supercell. Aiming to refrain from the interaction between the two images of the displaced atom which is due to the periodic boundary condition, we model the properties by using a $2\times2\times1$ supercell with 48 sites in the calculations derived from the ideal fluorite structure. For the C or N single-doped CeO_2, an O atom in the center of the supercell is substituted by one C atom (C-CeO_2) or one N atom (N-CeO_2). For the N/C co-doped CeO_2, two O atoms within the supercell are substituted by one C atom and

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one N atom, respectively. The doped models of 2×2×1 CeO_2 supercell used in the calculations are shown in Fig. 1.

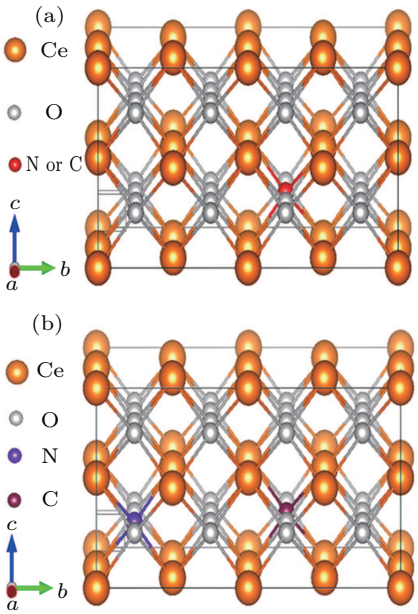


Fig. 1. (color online) 2×2×1 supercell of (a) N- or C-doped CeO_2 (b) N and C co-doped CeO_2.

The density functional theory (DFT) has been successfully applied to the first-principles calculation of ground state properties of various materials.[9] The exchange–correlation function is described by the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE).[10,11] In our calculation, the electronic wave functions are expanded in a plane wave basis set with energy cut-off 330 eV.[12,13] The pseudo atomic calculation is performed for Ce $4f^1 5s^2 5p^6 5d^1 6s^2$, O $2s^2 2p^4$, N $2s^2 2p^3$, and C $2s^2 2p^2$.[14] The convergence thresholds for the maximum energy change, the maximum force, the maximum stress, and displacement tolerances are set to 2.0×10^{-6} eV/atom, 0.05 eV/Å, 0.1 GPa, and 0.002 Å, respectively.

After the structural optimization, the electronic band structures, electron density, partial density of states (PDOS), and absorption spectra of C-doped, N-doped, and N/C co-doped CeO_2 are calculated respectively. The polarization of the polycrystalline model is used to calculate the optical properties of the systems and the scissor theory is used to modify the results.

3. Results and discussion

3.1. Structural parameters

Firstly, the 2×2×1 CeO_2 supercells with substitutional N, C, N/C atoms are optimized. The lattice parameters are summarized in Table 1. The calculated lattice parameter of pure CeO_2 is $a = 5.50$ Å, which is close to $a = 5.40101$ Å reported in the reference.[15] Calculation results suggest that the doping impurities lead to the lattice distortion of CeO_2 and the structure expands slightly. After the process of doping, the CeO_2 volumes are 167.18 $Å^3$, 167.91 $Å^3$, and 167.79 $Å^3$, respectively. The cubic lattice parameter is in great agreement with that of N-doped CeO_2 in the literature.[16] Compared with the Ce–O bond length of 2.38 Å in pure CeO_2, the Ce–N bond length is increased to 2.41 Å and the Ce–C bond length is increased to 2.46 Å. The expanded unit cell can be attributed to the increase in the concentration of Ce^{3+} active clusters.[17]

Table 1. The lattice constant and volume of CeO_2 before and after doping.

	a/Å	*b*/Å	*c*/Å	*V*/$Å^3$
Experimental	5.50	5.50	5.50	166.99
Theoretical	5.41	5.41	5.41	158.34
N-CeO_2	5.52	5.52	5.48	167.18
C-CeO_2	5.51	5.51	5.52	167.91
N/C-CeO_2	5.48	5.52	5.53	167.79

3.2. Charge populations

To explain the chemical environment of the different systems, the electronic populations of the doped CeO_2 are calculated. Table 2 shows the charge populations of the doped elements.

From Table 2, it can be found that N and C obtain electrons. Compared with N/C co-doped CeO_2, N-doped CeO_2 has fewer electrons and C-doped CeO_2 has more electrons. As a result, the electrons from N and C atoms co-doped in CeO_2 can interact with each other, which may have a synergistic effect on the electronic structure of CeO_2, and further affect the photo-catalytic activity of CeO_2.

Table 2. Charge populations of N and C in CeO_2.

Species		s	p	d	f	Total	Charge/*e*
N-CeO_2	N	1.80	3.79	0.00	0.00	5.59	–0.59
C-CeO_2	C	1.64	3.02	0.00	0.00	4.66	–0.66
N/C-CeO_2	N	1.74	3.94	0.00	0.00	5.68	–0.68
	C	1.68	2.94	0.00	0.00	4.62	–0.62

3.3. Band structures and partial density of states

The energy band calculations are important in the study of the photo-catalytic properties of CeO_2.[18] The band structures and partial density of states (PDOS) near the Fermi level of pure, N, C, and N/C doped CeO_2 are shown in Fig. 2.

Figure 2(a) reveals that the band gap of CeO_2 is 1.961 eV. Due to the Perdew–Burke–Ernzerhof generalized gradient approximation to electronics and electronic exchange correlation function, the value is smaller than the experimental one of $E_g = 3.2$ eV. However, the treatments also contribute to the doped systems and the same calculation parameters. Because we only focus on the relative change of the electronic and optical properties of the systems, so the calculation results are comparable. It is obvious that the conduction band of CeO_2 is composed of Ce-4f orbital, and the valence band is mainly composed of O-2p and Ce-4f orbitals.

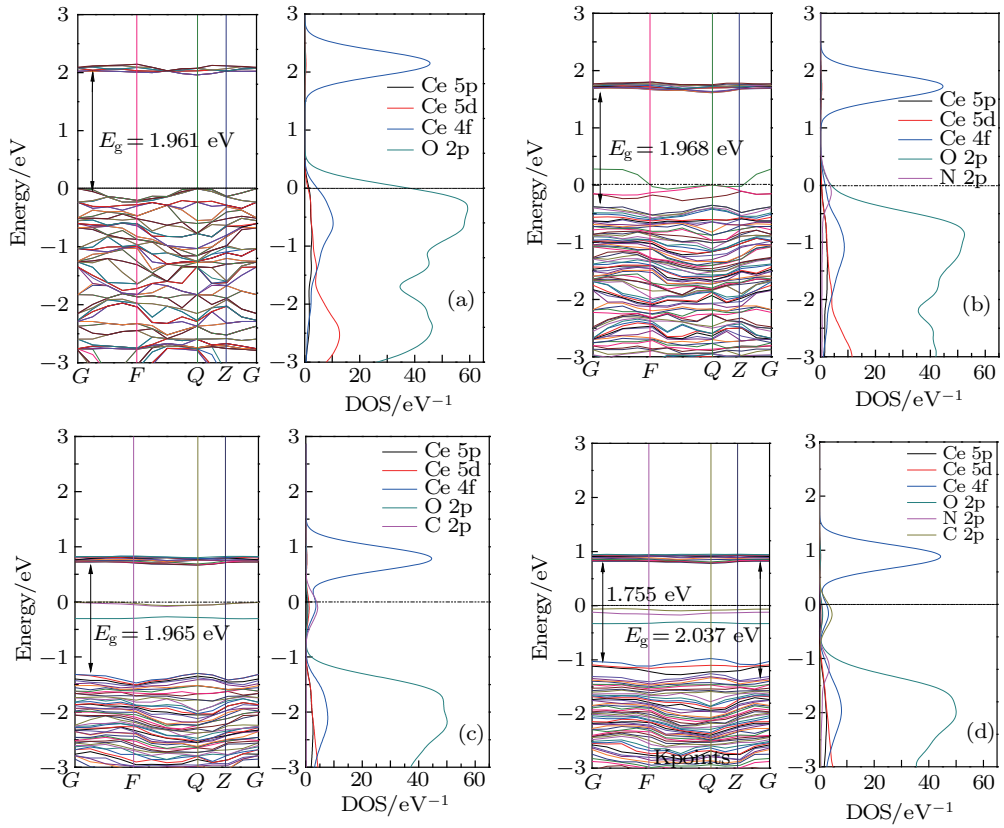


Fig. 2. (color online) Band structures and PDOS for (a) pure, (b) N-doped, (c) C-doped, (d) N/C co-doped CeO_2.

Figure 2(b) shows the band structure and partial density of states of N-doped CeO_2. It is evident that the calculated forbidden band width ($E_g = 1.968$ eV) is larger than that of undoped CeO_2, and the energy band moves toward the direction of low energy compared with the pure system. It can be found that the partial density of states of N 2p orbital has one peak near the Fermi level and hybridizes with O 2p orbital, which generates impurity energy levels at the bottom of the forbidden band.

From Fig. 2(c), it can be seen that the forbidden band width of C-doped CeO_2 is larger than that of pure CeO_2. The hybridization of C-2p and Ce-4f forms the impurity band in the forbidden band of CeO_2.

Figure 2(d) shows the band structure and partial density of states of N/C co-doped CeO_2. The forbidden band width of N/C co-doped CeO_2 is 2.037 eV, which is larger than that of the pure system, and the energy band of N/C-CeO_2 moves downward to the low energy directly. It can be seen that the impurity energy level is introduced by the N-2p near the Fermi level and C-2p at the top of the valence band. The results above show that the electrons can be easily excited from the valence band to the conduction band, which indicates that the doping is beneficial to the improvement of the photo-catalytic activity.

Above all, the doping introduces new impurity energy levels, resulting in the energy band moving downward to the low energy directly and contributing to the improvement of the photo-catalytic activity in all kinds of the doped CeO_2.

3.4. Optical properties

CeO_2 has better optical property than the other materials,[19,20] which has been investigated by analyzing the UV–vis absorption coefficient. The absorption coefficient can be calculated from the relation using k

$$\alpha = \frac{4\pi k}{\lambda}, \tag{1}$$

where α is the absorption coefficient and λ is the wavelength of light.[21] All the systems exhibit a strong absorption band in the visible light region due to the charge-transfer transition between the full O-2p and the empty Ce-4f electron orbitals, as shown in Fig. 3. Because there is an underestimation of the band gap in the calculation of pure CeO_2, we use a 1.239 eV "scissor operation" to move up the absorption edge to the experimental value.

From Fig. 3, it can be seen that the absorption edges of the doped CeO_2 show different red-shifts compared to that of pure CeO_2. A band-edge absorption around 380 nm appears in pure CeO_2. The band-edge absorptions of N, C, and N/C doped CeO_2 systems are around 420 nm, 440 nm, and 500 nm, respectively. Compared with pure CeO_2, additional absorptions up to 800 nm can be observed for the N, C, and N/C doped CeO_2 systems. Among all the doped systems, the optical properties of N/C co-doped CeO_2 are modified farthest.

These results are similar to the report that N and C co-doping is an effective route for the improvement of the photo-catalytic activity of CeO_2.[22]

From the above results, we can explain the transition process of electrons in the doped CeO_2 systems. The N-2p and C-2p orbitals form impurity levels in the forbidden band of CeO_2. During the photo-catalytic process, these impurity levels can accept some electrons transiting from the valence band under suitable photon irradiation. It is a supplemental transition, the electrons can still directly transit from the valance band to the conduction band. Due to N-2p orbital hybridized with O-2p, the band gap of N-doped CeO_2 decreases, the visible light absorption broadens and more photons can be utilized. So the photo-catalytic activity can be improved by doping with N. Similar reasons hold for C-doped CeO_2; C-2p orbital hybridizing with Ce-4f results in more electrons transited from the valence band to the conduction band, and higher photo-catalytic activity is obtained in C-doped CeO_2. As for N/C co-doped CeO_2, the enhanced photo-catalytic activity is the result of co-operation of N and C impurities. N-2p orbital hybridized with O-2p in the forbidden band and C-2p orbital hybridized with Ce-4f at the top of the valence band are the determinant for broadening the utilization of the visible light range.

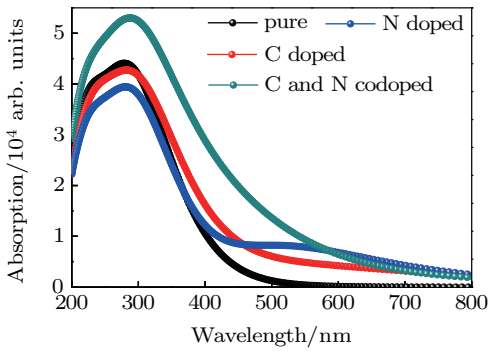


Fig. 3. (color online) Absorption spectra of pure CeO_2, N-doped CeO_2, C-doped CeO_2, N/C co-doped CeO_2.

4. Conclusion

The N- and C-doping effects on the structure, electronic density of states, and optical properties of CeO_2 have been studied by using the first-principles method based on the density functional theory. The results indicate that the lattice is distorted by the dopant. The doping introduces an impurity energy band in the forbidden band of CeO_2 and widens the forbidden band in different systems. Nevertheless, the impurity levels improve the ability of visible light absorption and prevent the band gap from widening. N/C co-doping is the most beneficial to the photo-catalytic activity of CeO_2 compared with the pure and mono-doped CeO_2 systems. The theoretical calculated results explain the photo-catalytic activity improvement of N/C doped CeO_2 in experiment.

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