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Experimental and first-principles DFT study on oxygen vacancies on cerium dioxide and its effect on enhanced photocatalytic hydrogen production

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ABSTRACT

Experimental and computational (DFT) approaches were carried out to investigate oxygen vacancies on cerium dioxide. Computational result indicates oxygen vacancies can shorten the band gap of CeO₂ and enhance the absorption for visible light because Ce (III) created by generation of oxygen vacancies is easier for excitation than Ce (IV) under same irradiation. The order of calculated band gap for Ce₁₆O₃₁, (111) < (113) < (133), and the absorption data suggests that (111) plane may be the most ideal position for oxygen vacancies to enhance photocatalytic activity. The result has been tested and verified by experimental study, including UV–Vis spectra, XPS, XRD and PL. The enhanced hydrogen productions of CeO₂ samples, from 34.8 μmol to 63.0 μmol, are 2.0–3.5 times as high as that of commercial CeO₂ (17.8 μmol).

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Introduction

Converting solar energy into fuel via photocatalytic water splitting to generate hydrogen is an attractive scientific and technological goal to solve the energy crisis [1]. Single semiconductor only absorbs a narrow range of solar light. In order to enhance the solar light absorption, at least two catalysts are combined to a Z-scheme [2] or p–n conjugation [3] photocatalyst system. In this case, selection of catalysts is the key to achieve this goal. Among all reported semiconductor support, cerium dioxide is a stable, nontoxic and multifunctional catalyst [4–7]. Due to the special f and d electron orbital

structure of cerium atoms, visible light absorption and quantum efficiency of cerium dioxide can be distinctly enhanced by doping some non-noble semiconductors like TiO₂ [4,5], Bi₂O₃ [6] and Cu₂O [7], even though its wide band gap, low quantum efficiency and high recombination hinder its further application in photocatalysis. In this case, cerium dioxide can be utilized as a potential catalyst for solar energy conversion.

Experimental research on CeO₂ indicate that defects such as oxygen vacancies and step edges are the most reactive sites on the surfaces of metal oxides [8], especially for cerium dioxide. Oxygen vacancy defects on CeO₂ can be rapidly formed and eliminated, giving it a high “oxygen storage capacity”, and

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these defects also start up $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycles [9] to enhance the activities of redox reactions. It has been proved that the generation of Ce^{3+} caused by oxygen vacancy is the main active oxygen species for oxidation [10]. Many experimental studies have been reported that electrons can be easily trapped in the oxygen vacancy sites during light excitation [11–15] and each missing oxygen atom may leave two extra electrons at the site of the vacancy which leads to creation of surface electron centers for the formation of the negatively charged species [11,16]. It is one of the factors for enhancement of photocatalytic activities. However, how oxygen vacancies on CeO_2 enhance photocatalytic activity is still unclear.

DFT calculation can obtain deeper insight into the catalytic properties of catalysts. It has been reported that existence of oxygen vacancies on (110) or (111) planes has higher oxidation reactivity than other planes because of the better geometric, energetic and electronic effects [17]. Multiple oxygen vacancy on the 2×1 reconstructed surface leads to dramatically improve the activity for catalytic oxidation by significantly migrating the lattice oxygen atoms and oxygen vacancies [18]. The negative U behavior of oxygen vacancies on CeO_2 also leads to excellent photocatalytic behavior [19].

In this paper, density of states (DOS), band structure and optical properties of $\text{Ce}_{16}\text{O}_{32}$ and $\text{Ce}_{16}\text{O}_{31}$ models were calculated by Materials Studio software in order to analyze the correlation between enhanced electron transfer and oxygen vacancies on cerium dioxide. Calculation was performed by the CASTEP program within the Perdew-Wang 1991 PW91 generalized gradient approximation (GGA). In order to demonstrate the accuracy of computational data, cerium dioxide synthesized by glycine-nitrate combustion method was characterized by UV–Vis spectra, XPS, XRD, and PL. The result indicates that oxygen vacancies exist on the surface of particles which leads to enhancement of the visible light absorption and reduction of electron–hole recombination, thus enhance the photocatalytic activity of water splitting for hydrogen production.

Methods

Computational details

First-principles calculations in this paper were performed by the CASTEP program within the Perdew-Wang 1991 (PW91) [20] generalized gradient approximation (GGA) in materials studio software. Cutoff energy was set as 410 eV. A series of models were built based on a $2 \times 2 \times 1$ cerium dioxide supercell, and k-points [21] was set as $1 \times 1 \times 3$. All lattices of CeO_2 with single vacancy were built according to the XPS quantitative analysis. The cerium 4f, 5d, 6s and oxygen 2s, 2p electrons were treated as valence electrons. Besides, ultrasoft pseudopotentials were used and the relevant representations were carried out in reciprocal space. The set SCF tolerance was 5.0×10^{-7} .

Experimental

CeO_2 catalyst was prepared by glycine-nitrate combustion method as our preview work [22,23]. The powder was

characterized after calcined at 300 °C, 400 °C, 500 °C, 600 °C, respectively. X-ray diffraction (XRD) analysis was performed with the PANalytical X'Pert diffractometer (X'Pert PRO MPD, PW3040/60) within the $2-\theta$ ranged from 5° to 80° by a speed of 6° per minute with Cu-K α ($\lambda = 0.154060$ nm) radiation (40 kV, 40 mA). The crystallite size was calculated by the Scherrer equation from the XRD spectra. UV–vis spectroscopy in the 300 nm–1000 nm was measured with a Lambda 750 Diffuse Reflectance Spectroscopy. X-Ray photoelectron spectroscopy (XPS) analysis was conducted through a thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) equipped with an Al K radiation source. Fluorescence spectra were obtained using a photoluminescence (PL) spectrometer (Perkin Elmer, LS-55). Photocatalytic reactions for overall water splitting were carried out in a 15 mL quartz cell with a 25 mm \times 25 mm window for light transmission at room temperature under visible light irradiation ($\lambda > 400$ nm, ≈ 0.18 W/cm²). The catalyst powder (30 mg) was suspended in 10 vol. % methanol aqueous solution (15 mL) by magnetic stirring. In this paper, methanol plays a role as the sacrifice agent to scavenge photogenerated holes. The evolved gases were determined with a gas chromatograph equipped with a TCD detector.

Results and discussion

Computational study

The models of $\text{Ce}_{16}\text{O}_{31}$ lattice with single oxygen vacancy was built according to atomic compositions (%) measured by XPS. There are three possible sites for oxygen vacancy in this $2 \times 2 \times 1$ cerium dioxide supercell. Two layers of oxygen atoms can be seen in the right side of Fig. 1, and three sites for oxygen vacancy lie in the second oxygen layer (layer 2). Site A, B and C lie in (111) plane, (331) plane and (133) plane of supercell lattice, respectively. And each of these three sites missing an oxygen atom creates a model with single oxygen vacancy.

It is known that electron–hole generation under light irradiation depends on the band structure and the electronic density of states (DOS), so calculated partial DOS (Fig. 2) and the band structures (Table 2) were considered. PDOS of cerium atoms in $\text{Ce}_{16}\text{O}_{31}$ lattices also have a little shift towards negative potential than $\text{Ce}_{16}\text{O}_{32}$ lattice, which leads to the negative shift of valence band potential of. And the band gaps of $\text{Ce}_{16}\text{O}_{31}$ are all shortened compare to those of $\text{Ce}_{16}\text{O}_{32}$. It provide a favorable condition for catalysts with oxygen vacancies to be excited by visible light.

Schematic diagram of electron transfer and partial DOS of Ce (III), O and Ce (IV) are showed in Fig. 3. For cerium atoms, generation of oxygen vacancy created Ce^{3+} [11] leads to the empty valence orbits being occupied by extra electrons obtained from removed oxygen ions [8], thus the energy of these orbits shift toward negative potential, especially for 4f orbit and then shorten the band gaps. The DOS energy ranges of Ce 4f and O 2p are overlapped which leads to electron transfer between them during excitation. However, DOS of Ce 4f for Ce (III) is larger than that of Ce (IV) in positive energy range, which indicates Ce (III) is easier for excitation than Ce (IV) under same irradiation. The light absorption of $\text{Ce}_{16}\text{O}_{32}$ and

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