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Development of visible light response of CeO_{2-x} with a high content of Ce³⁺ and its photocatalytic property

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Abstract: Photocatalysts that are responsive to visible light are necessary to utilize solar. We prepared a reduced CeO_{2-x} with absorption in the visible region by a simple solvothermal method. A new absorption peak appeared around 500 nm (SPR), which is the origin of Ce³⁺. To elucidate the relationship between the Ce³⁺ and activity, decomposition of isopropyl alcohol (IPA) to generate acetone has been carried out under visible light irradiation. CeO_{2-x} showed superior activity than that of pure CeO₂. Ce³⁺ can induce oxygen vacancies in the lattice of CeO_{2-x}, resulting in improvement of activity. In addition, the introduction of Ce³⁺ resulted in improvement of absorption of CeO_{2-x} in the visible light region. Also, the appearance of small tentacles (Confeito-like) on the surface of CeO_{2-x} not only provided more active sites but also prevented aggregation. Owing to its visible light responsiveness and its unique morphology, the performance of the material has been significantly improved.

Solar radiation is an inexhaustible and clean source of energy. Effective harvesting of solar energy by semiconductor materials for photocatalytic applications, such as water splitting,^[1] degradation of pollutants,^[2] and CO₂ fixations,^[3] is an ideal strategy for alleviating the energy crisis.^[4] CeO₂ is one of the promising photocatalysts for solar energy utilization. However, the band gap of CeO₂ is about 3.1 eV, and UV light would be necessary for its photocatalytic reactions to proceed. In order to utilize solar light that includes only 3% UV light and 50% visible light as a light source, the development of visible light-responsive ceria is necessary. Various strategies including morphology control,^[5] ion doping,^[6] combining with other materials,^[7] and noble metal deposition^[8] have been adopted to improve the photocatalytic property of CeO₂. Based on density functional theory calculations, the stabilities of CeO₂ crystal planes are in the order of (111) > (110) > (100).^[9] However, it is well known that the (100) crystal planes often exhibit a significant improvement of catalytic activity compared to the catalytic activities of other two types of low-index planes owing to their high level of chemical activity.^[10] In addition, a high concentration of oxygen vacancies is observed at (110) crystal planes.^[11] So control of morphology would therefore be an effective method for improving performance. Ion doping is another way to enhance activity via providing active sites and inducing the generation of oxygen defects. Very recently, Ce³⁺ self doping method also has been applied to improve their visible light absorption.^[12] With the increase of Ce³⁺, a red shift in the UV-visible spectra could be observed. It could be a good

candidate of photocatalyst. Combining with other materials that own better light absorption is a direct and effective method for improving light absorption. Huang *et al.*^[13] synthesized CeO₂/g-C₃N₄ hetero-structured composites with closely contacted interfaces... by an easy mixing-calcination route. The photocatalytic properties of degradation for methylene blue (MB) and colorless organic pollutant 4-chlorophenol (4-CP) under visible light were improved. Other researchers have also reported that visible light absorption of the photocatalysts was increased by loading Au, Ag, Pt and other noble metals on the CeO₂ surface. The improved photocatalytic performance can be contributed to surface plasmon resonance (SPR) effects. Ana *et al.*^[14] reported that deposition of gold nanoparticles on the surface of photocatalysts with a small amount of loading improved the photocatalytic activity under visible light, which exhibited higher photocatalytic activity than the same material upon irradiation at its band gap. However, the main drawback of this method is that new material must be introduced. We have to bear the cumbersome synthesis steps and additional materials with high prices such as noble metals.

Herein, through a simple solvothermal method, we prepared a reduced CeO_{2-x} with special confeito-like morphology and long range visible light absorption. Here, it is labeled as Confeito-CeO₂. The description of this particular shape comes from the Portuguese candy shown in Figure S1a (Supporting Information). The small tentacles on the surface of cerium oxide particles not only provide more active sites but also inhibit agglomeration. Moreover, the proportion of visible light absorption is significantly improved compared with that of commercial CeO₂ (from HIGH PURITY CHEMICALS Co. Ltd.), labeled as HPC-CeO₂, which could be attributed to the high content of Ce³⁺. Additionally, a new absorption peak is arose around 500 nm, which is extremely similar to Surface Plasmon Resonance (SPR) effect.^[15] This is the first time for visible light absorption to be greatly improved by only regulating the trivalent cerium content without any doping or loading. In virtue of confeito-like morphology and good visible light absorption, its performance for decomposition of isopropyl alcohol (IPA) to generate acetone has been greatly improved.

The crystallinities of HPC-CeO₂ and Confeito-CeO_{2-x} characterized by X-ray diffraction (XRD) are shown in Figure 1a. All of the main peaks are assigned to the face-centered cubic phase with the space group *Fm3m* of CeO₂ phase (JCPDS No. 34-0394). The intensity and FWHM of Confeito-CeO₂ are stronger and narrower, respectively, than those of HPC-CeO₂, indicating that the crystallinity and grain size of Confeito-CeO₂ are better and larger, respectively. The detail information of grain size is summarized in Table 1, which is according to the calculation by the Debye-Scherrer formula for the strongest peak (111). In addition the lattice parameter of Confeito-CeO₂ has been calculated. The value is 5.4326055 Å (Rwp = 7.56 and Rp = 6.06) and larger than that of pure CeO₂ (5.41001 Å), indicating that there are should be presence of larger radius ions (Ce³⁺). However, it should be noted that there are some unneglectable peaks of sample Confeito-CeO₂. A new peak appeared at ca.18.4°, which could be indexed to the reduced CeO₂, being attributed to the fact that CeO₂ had been partially reduced by the

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ratio of EG (reductant). The partial reductant material (CeO_{2-x}) would have a great impact on the visible light absorption and photocatalytic property.

The unique morphology CeO_2 was prepared via a two-step solvothermal method. We speculated that crystal nuclei formed at a relatively low temperature, and then assembled into large particle at 160°C and growth at 180°C (Scheme 1b). Some simple time-depend experiment has been conducted to give some evidences. With the increase of duration, the tentacles gradually grow up. This could be as a rough evidence for the formation scheme, which will be added to supporting information (Figure S4). We could observe the confeito-like morphology of CeO_{2-x} is shown in Figure S1b and Figure 1c and 1d. Its diameter is ca. 170 nm and there are some small tentacles on the surface. The size of the primary grains composed of large particles is about 10 nm, being in agreement with the XRD results. An HRTEM image and FFT (Fast Fourier Transformation) pattern are collected in Figure 1e and Figure 1f, respectively, corresponding to the selected rectangular area in Figure 1d. There is a well-defined lattice fringe, indicating its better crystallinity. However, there are some oxygen vacancies and defects in the Confeito- CeO_2 lattice structure due to its high content of Ce^{3+} .^[16] The indexing of the FFT pattern shows (111), (110) and (311) lattice planes, which is in good agreement with the DFT results showing that oxygen vacancies preferentially form in the (110) facet.^[11, 17] As for HPC- CeO_2 , it indeed has a large surface area due to its small particle size as shown in SEM and TEM images (Figure S2). However, aggregation, optical property, and band structure restrict its performance. According to the Brunauer-DeMing-DeMing-Teller (BDDT) classification, HPC- CeO_2 and Confeito- CeO_2 are defined as Type-IV (mesoporous) and Type-III (macroporous), respectively (Figure S3). Mesoporous and macroporous are from the gap between particles. HPC- CeO_2 is mesoporous because of the aggregation of particles, and Confeito- CeO_2 is macroporous because the small tentacles on the surface widen the gaps between particles.

Attention! UV-vis spectra are essential to photocatalytic activity. Confeito- CeO_2 possesses stronger absorption than that of HPC- CeO_2 in the wavelength range from 420 nm to 1000 nm in comparison to that of HPC- CeO_2 (Figure 1b). The improvement of visible light absorption has an intimate relationship with the reduced cerium dioxide (CeO_{2-x}). The analogous SPR absorption peak could be attributed to the substantial content of Ce^{3+} (38.8%), which could be confirmed by XPS results (Figure 3). In addition, we can observe a peak at ~ 2 eV in Figure S9, indicating that the presence of Ce^{3+} .^[18] According to plasmonic theory,^[19] to sustain surface plasmons in a semiconductor, the concentration of accumulated free carriers (electrons or holes) must be above the threshold value. In general, this prerequisite in semiconductors is met, through the introduction of aliovalent atoms (Ce^{3+}) or lattice vacancies (oxygen vacancies). It is similar to the doping process, which could enhance the content of carriers and then generate plasmon effect. In our research, we use Ce^{3+} as the dopants. As a consequence, it is reasonable to presume that the upper limit of the carrier concentration in Confeito- CeO_2 is determined by the equilibrium between Ce^{3+} and Ce^{4+} , corresponding to CeO_2 and CeO_{2-x} , thereby leading to their plasmon resonance frequency. Many researchers have obtained similar results in,

for instance ITO,^[20] TiO_{2-x} ,^[21] and MoO_{3-x} .^[15] It is known that noble metals have been widely employed as SERS-active substrates due to their intense LSPR absorption in the visible region, which can improve the electromagnetic field and produce high Raman intensity. The strong absorption of Confeito- CeO_2 around visible light regions allows us to explore the potential application of SERS detection. Herein, we obtained its SERS activity that based on plasmonics are shown in Figure 2a. It is apparent that the Raman signals of MB significantly enhance on the surface of Confeito- CeO_2 . It can be as indirect evidence of the SPR effect. This SPR effect is originated to the free carriers by tuning the content of Ce^{3+} .^[15, 21-22] This result is extremely abnormal but interesting compared to noble metals. In addition, the band gap values of the samples were determined by plotting $[\text{F}(\text{R})/h\nu]^{1/n}$ vs. $h\nu$ ($n = 2$ for indirect band gap) as shown in Figure S5. The narrowing of the band gap of Confeito- CeO_2 (Table 1) is associated with oxygen vacancies and formation of Ce^{3+} .^[16]

To obtain the band structure, Mott-Schottky analyses were carried out by using an Impedance Potential method at 0.5 kHz, 0.75 kHz and 1 kHz in Na_2SO_4 solution (pH = 6). Mott-Schottky plots of both samples are shown in Figure S6. Positive slopes at both frequencies were obtained, indicating that both samples behave as n-type semiconductors. In the case of n-type semiconductors, E_{fb} is generally located near the C.B., and it can be estimated from the intersection of a plot of $1/C^2$ against E by the following equation:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0N} \left(E - E_{fb} - \frac{kT}{e} \right),$$

where C is capacitance, e is the electron charge, ϵ is the dielectric constant, ϵ_0 is permittivity of vacuum, N is acceptor density, E is the electrode potential, E_{fb} is the flat band potential, k is the Boltzmann constant, and T is temperature. As shown in Figure S6, the x-axis intersections of the two samples are -0.9 V (Confeito- CeO_2), and -1.26 (HPC- CeO_2) vs. Ag/AgCl (pH = 6) for all frequencies (0.5 kHz, 0.75 kHz, and 1 kHz) and can be used to determine E_{fb} from the above equation $E_{fb} = E - kT/e$. The calculations showed that E_{fb} values were approximately -0.44 V (Confeito- CeO_2), and -0.72 (HPC- CeO_2) v.s. NHE (pH = 0) by correcting the solution pH. According to the band gap values, we can calculate the position of V.B. and then roughly give the band positions of the two samples (Scheme 1a). The oxidation potential of acetone/isopropanol was calculated by the Nernst equation, indicating that the V.B. level of both samples is sufficient for this reaction in theory.

Based on the above results, we utilized CeO_{2-x} as a photocatalyst for the decomposition of isopropyl alcohol (IPA) to generate acetone. The time courses of acetone formation in photocatalytic oxidation of 2-propanol under Xe lamp (cutoff = 420 nm) irradiation are presented in Figure 2b. With irradiation for 24 h, the generated amount under Confeito- CeO_2 is approaching to 100 ppm. It is about ten-times greater than that of HPC- CeO_2 . The recycle experiment is exhibited in Figure S8. The paramount factor for such excellent activity is the substantial content of Ce^{3+} in Confeito- CeO_2 . With the high content of Ce^{3+} in Confeito- CeO_2 , the visible light absorption was improved. In the first place, Ce^{3+} will narrow the band gap,^[16] and then more visible light can be utilized for the photocatalytic

Table 1. Textural properties and band structure of HPC- CeO_2 and Confeito- CeO_2 .

Samples	$G_s^{[a]}$ (Å)	$S_{BET}^{[b]}$ (m^2/g)	$P_s^{[c]}$ (nm)	$P_v^{[d]}$ (cc/g)	$E_g^{[e]}$ (eV)	V.B. (V) ^[f]	Ce ³⁺ %
HPC-CeO ₂	83.6	119.31	1.640	0.059	3.10	2.38	17.8
Confeito-CeO ₂	144.1	26.22	2.727	0.021	2.95	2.51	38.8

[a] Grain size. [b] Brunauer–Emmett–Teller specific surface area. [c] Pore size. [d] Pore volume. [e] Band gap. [f] Valence band.

process. Moreover, some CeO_{2-x} materials form due to Ce³⁺, which further expands its absorption ranging from 420 nm to 1000 nm. There is one more point that should be noted: charge separation will also promote activity. The more Ce³⁺ generated, the more formation of oxygen vacancies. Oxygen vacancies could trap the photogenerated electrons, and then promote charge separation. The photoelectrochemical properties of the two types of CeO₂ were characterized by measuring the photocurrent under a 500 W Xe lamp equipped with a cutoff filter ($\lambda = 420$ nm). As anticipated, Confeito-CeO₂ exhibited an excellent photocurrent response, about 5-times higher than that of HPC-CeO₂ (Figure 2c). This result is evidence for better charge separation and light harvest. The last but not the least, the confeito unique shape also plays a role in the reaction. Moreover, Figure S7 shows that 90% of IPA had been consumed via adsorption and conversion one hour later. However, the consumptions of IPA in the two samples are approaching, indicating that surface area is a negligible factor. Dominant factors are oxygen vacancies (due to Ce³⁺ and the (110) facet) and monodispersity.

Finally, we raise a question. Why is the rate of this photocatalytic process slow? How can we speed up the reaction? It is easy to think that there is a transition state between IPA and acetone. We therefore calculated transition state (TS) information with Gaussian software and verified its reliability by calculating the frequency (only one imaginary frequency). Figure 2d shows the thermodynamic and kinetic process of the reaction. Although the full reaction is an uphill process, the energy is less than that of the ground state to transition state. According to this, we can speculate that the V.B. position of Confeito-CeO₂ satisfies the oxidation potential of TS, while the potential difference is not sufficient. In the future, we will adjust the content of Ce³⁺ to lower the V.B. position and speed up the reaction.

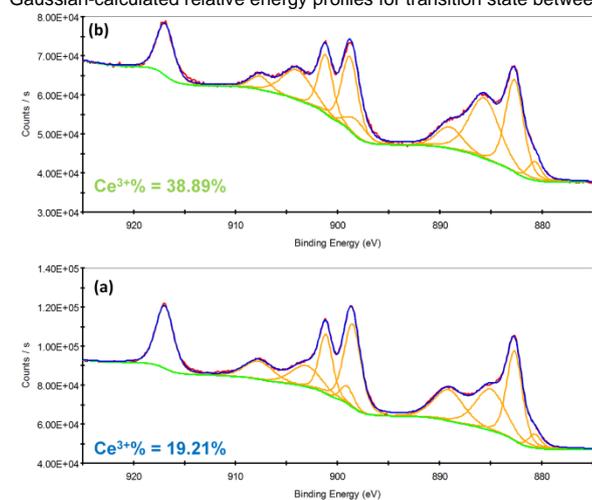
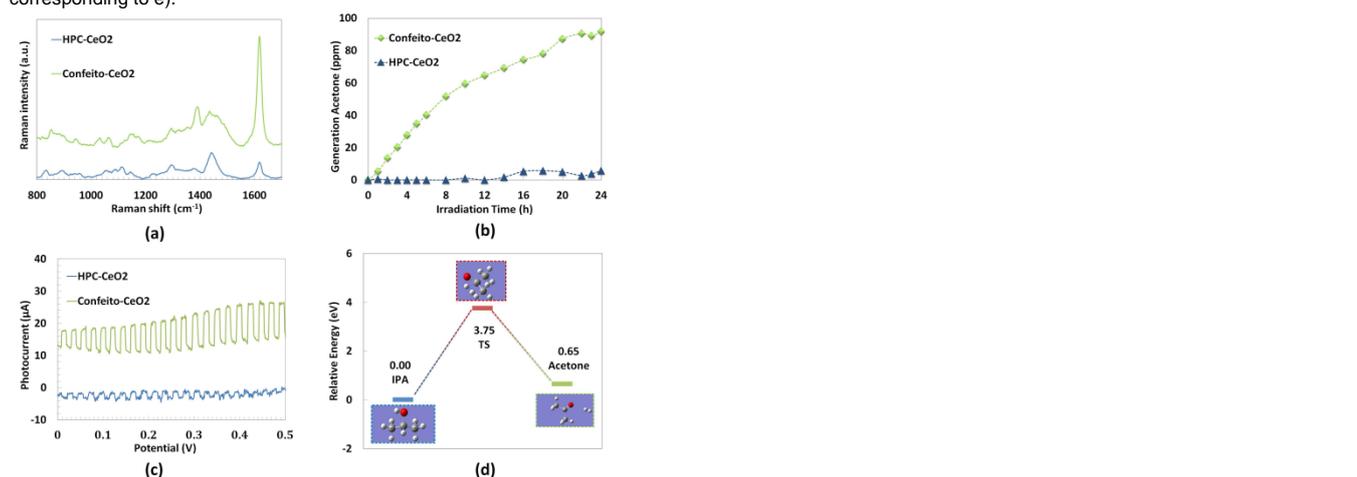
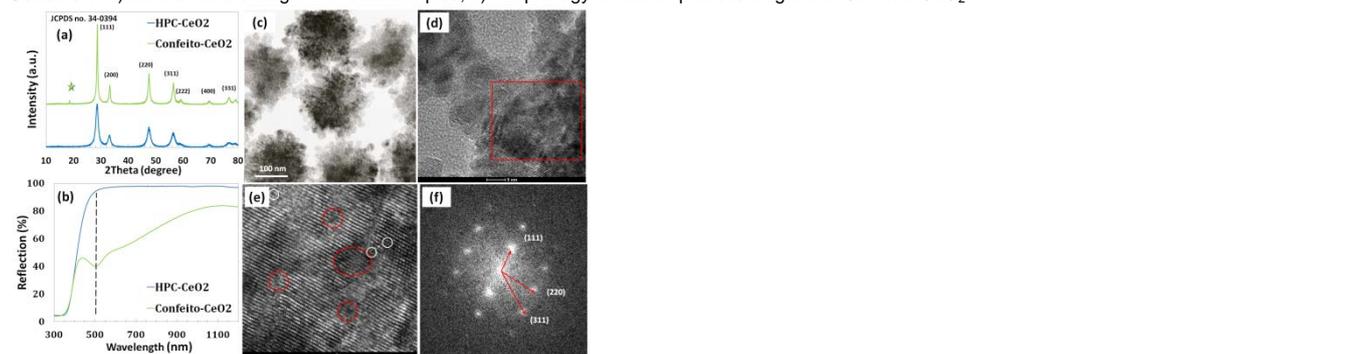
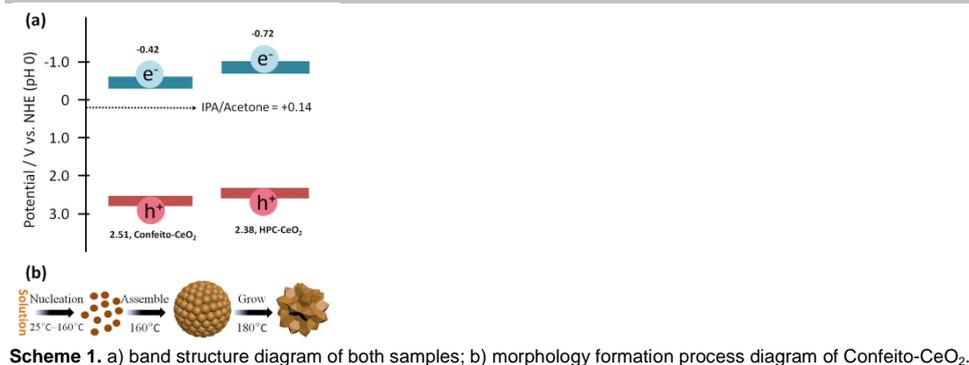
In summary, a reduced CeO_{2-x} material was successfully prepared via a simple hydrothermal method. The unique confeito-like particles possess a long range of visible light absorption due to the substantial content of Ce³⁺. The special absorbed peak at ca. 500 nm even leads a SERS activity, indicating the generation of SPR effect. This SPR effect is originated to the free carriers by tuning the content of Ce³⁺. Meanwhile, the valence band is modified to be more positive, which is beneficial for photocatalysis. Summed up the results, the Confeito-CeO₂ exhibits an excellent performance for decomposition of isopropyl alcohol to acetone. This work shows new opportunities for photocatalytic preparation with long range visible light absorption and more positive V.B. by controlling the content of Ce³⁺.

Acknowledgements

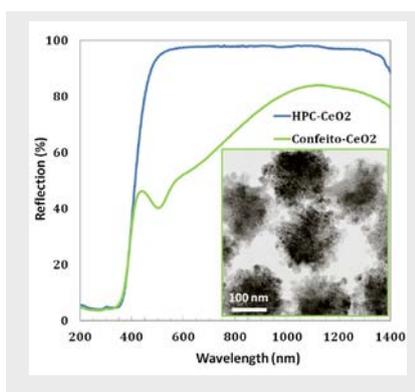
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Keywords: visible light response • CeO_{2-x} • SPR • Ce³⁺ • Confeito-like

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A unique confeito-like reduced CeO_{2-x} material was successfully prepared via a simple hydrothermal method. The particles possess a long range visible light absorption and a new absorption peak arises at 500 nm due to SPR effect, which should be attributed to its substantial content of Ce^{3+} . The photocatalytic activity of Confeito- CeO_2 is superior in decomposition of isopropyl alcohol to acetone.



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