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Effects of the Atmosphere in A Hydrothermal Process on the Morphology and Photocatalytic Activity of Cerium Oxide

Sàisài Yuán,[a] Sixiao Liu,[a] Qitao Zhang,[c] Ming Zhang,[a] Bin Xu,*[a] and Teruhisa Ohno*[b]

Abstract: The hydrothermal method is widely applied in nanomaterials synthesis, and most of the influencing factors have already been taken into account. However, the effect of atmosphere in solution on the performance of nanomaterials has been underestimated for a long time. In this article, reaction solvents were saturated with three classical gases (argon, oxygen, and carbon dioxide), and then heated at 180 °C for 24 h to obtain the cerium dioxide (CeO_2) nanoparticles. The properties of the three types of CeO_2 are significantly different from that of the normal CeO_2 (without gas saturation). The morphologies of the prepared CeO_2 particles are different, even appear the hollow structure in CeO_2-CO_2 (synthesized in CO_2 saturated condition). The more absorbing and meaningful thing is that the photocatalytic activity of CeO_2-CO_2 has been greatly improved. The concordance of the CO_2 atmosphere (acid gas) and CeO_2 (owning substantial content of basic sites) is the key point for the excellent photocatalytic performance.

Cerium oxide (CeO_2) is one of the most important earth metal oxides. Due to the unique optical, electrical, magnetic properties and the oxygen storage capacity (OSC) of CeO_2 nanomaterials,[1] they have been used in various applications, in industrial and commercial fields, including solid oxide fuel cells (SOFCs),[2] purification of automobile exhaust,[3] abrasives for chemical mechanical polishing (CMP),[4] and photocatalysis.[5] In order to obtain nanoscale CeO_2 materials, researchers have explored a lot of synthesis strategies, including ball milling, electrochemical, templates assisted, sol-gel, hydrothermal, chemical vapour, and other methods.[1] A hydrothermal method is also suitable for the growth of good-quality crystals because this method over other types of crystal growth is the ability to create crystalline phases which are not stable at the melting point. A hydrothermal reaction is governed by various chemical parameters and thermodynamical, involving chemical composition of the precursor,[6] kind of solvent,[5a] pH value of the reaction medium,[7] reaction temperature, duration of reaction, and pressure. Moreover, other associated technologies, such as microwaves, electrochemistry, external magnetic field, and ultrasound, have been employed However, an important factor in a hydrothermal process, the atmosphere of the solution, may

be ignored by people. For a long time, the effect of the atmosphere on the hydrothermal process has been underestimated due to its extremely little content in the solution. Nevertheless, the solution in a hydrothermal process is boiling or gas phase. The atmosphere will have a significant effect on the final products. If the precursors and solvent are matched with the selected gas (Gas can be strongly absorbed on the precursors or solvent.), the crystal growth process would be altered and further affect their morphologies and performances.

Herein, we selected three typical gases, argon, oxygen and carbon dioxide, to determine the relationship between the atmosphere and properties of CeO_2 nanoparticles. Solutions containing a precursor and a solvent were saturated with various gases, and then heated at 180 °C for 24 h to obtain CeO_2 nanoparticles. The obtained CeO_2 nanoparticles bubbled with different gases were labelled as CeO_2-Ar, CeO_2-O_2, CeO_2-and CO_2, and the sample without bubbling were labelled as CeO_2-normal. The properties of the three types of CeO_2 were significantly different from those of CeO_2 prepared by the normal method (without gas saturation). The morphologies of the prepared CeO_2 particles were also different, and CeO_2-CO_2 even appear the hollow structure. Also, their photocatalytic activities for conversion of isopropyl alcohol (IPA) to acetone were evaluated, and the more absorbing and meaningful thing is that the photocatalytic activity of CeO_2-CO_2 was greatly improved. As mentioned above, matching among the gas, precursors, and solvents is important, the system of CO_2 atmosphere (acid gas), and CeO_2 crystals and ethanol meets the matching requirement. CeO_2 crystals own substantial content of basic sites,[8] and acid gas CO_2 can be absorbed on them. Moreover, the solubility of CO_2 in ethanol is much higher than that in water. This conclusion is very encouraging, which provides a new and facile tactic for controlling hydrothermal process and obtain products with superior performance.

Morphologies and surface structures information were characterized by electron microscope technology. Figure. 1a ~ 1d show FE-SEM images of as-prepared samples. Compared with CeO_2-normal, the surface structures of CeO_2-O_2 and CeO_2-CO_2 had different degrees of distortion. A hollow structure was even observed in CeO_2-O_2 and CeO_2-CO_2 samples, which could be contributed to the special properties of O_2 and CO_2. As an acid type of gas, CO_2 could be easily absorbed on the CeO_2 crystals and then influenced its morphology. Although O_2 is a neutral type of gas, it can oxidize ethanol to CO_2 under high temperature and pressure conditions. Therefore, the generated CO_2 could influenced its morphology. Meanwhile, the hollow structure of CeO_2-CO_2 was much more obvious than that of CeO_2-O_2. On the contrary, CeO_2-Ar maintained a complete octahedral structure (even better than that of CeO_2-normal). Due to the bubbling of Ar, little amount of O_2 and CO_2 in the solution were expelled. Thence, the

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obtained more perfect octahedral structure of CeO_2 could be ascribed to a moderate hydrothermal process with the protection of the inert atmosphere. In addition, size distributions of the nanoparticles were examined via a software named "Nano Measurer Tool". As can be seen in Figure. S1, there was a significant difference in particle size. CeO_2-normal, CeO_2-Ar, and CeO_2-CO_2 samples were monodisperse nanoparticles, and their mean sizes were 220 nm, 150 nm, and 350 nm, respectively. Meanwhile, CeO_2-O_2 owned two size distributions, 170 nm (complete octahedron) and 250 nm (partially hollow structure). CeO_2-O_2 could be considered as a "transition state" between $CeO2$-normal and CeO_2-CO_2.
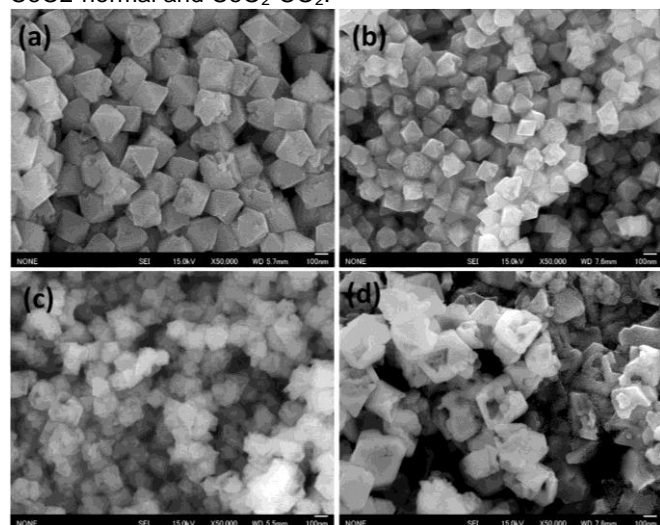

Figure 1. FE-SEM images of all of the samples; (a) CeO_2-normal, (b) CeO_2-Ar, (c) CeO_2-O_2, (d) CeO_2-CO_2.

TEM technology was used to further observe the hollow structure of CeO_2-CO_2. The hollow structure could be confirmed by light and dark contrast in Figure. 2a. Octahedral nanoparticles, distorted and damaged nanoparticles, and hollow structured nanoparticles were observed. The hollow structure might act as a natural barrier for the separation of reactants and products. According to the results of a study by Laurence Vivier, CeO_2 exhibits the highest number of surface basic sites among some selected metal oxides,[9] indicating that CeO_2 is advantageous for capturing acid gas. CO_2 as an acid gas could be quickly absorbed on the surface and inside of CeO_2 crystals, and then it played a crucial role in the hollow structure formation process. Figure. 2b shows a magnified TEM image of the surface information from Figure. 2a. Many small voids appeared on the surface of CeO_2-CO_2. Small voids might be the mass exchange channels for the formation of the hollow structure. Based on the above results, a feasible formation scheme could be speculated (Figure. 2c). First, some CO_2 would absorb on the basic sites of CeO_2 crystals at the beginning of the hydrothermal process. With the crystal growth, the accumulation of CO_2 in basic sites would be fully inside of the particles and absorbed on the surface of the bulk particles. When the amount of CO_2 has approached the critical point under the

high temperature, the generated CO_2 bubbles would explode and form the void channels. These void channels could connect the interior and exterior of the particles for the mass exchange. Meanwhile, these void channels make the bulk CeO_2 form the density difference and become the driving force of Ostwald ripening.[10] Continuously, Ostwald ripening process starts. As the reaction is prolonged, the hollow structure is formed.
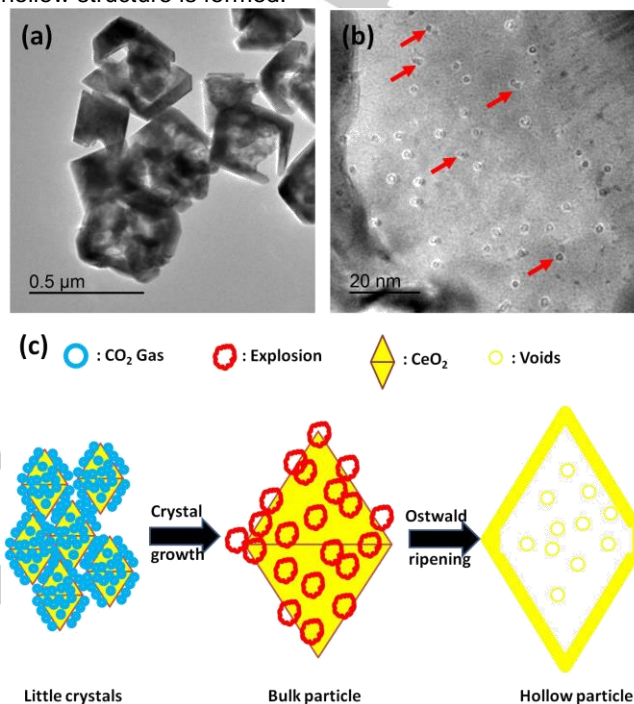

Figure 2. (a) and (b) TEM images of CeO_2-CO_2; (c) feasible scheme of the hollow structure formation process.

Although the atmosphere had a significant effect on the morphologies of all of the samples, it did not change the composition or phase of CeO_2. As shown in Figure. 3a, all of the characteristic peaks were indexed to the face-centered cubic phase with space group $Fm\bar{3}m$ of ceria (JCPDS card no. 34-0394). No other peaks were detected, and the sharp peaks indicated the high purity and a highly crystalline nature of all of the samples. Figure. 3b shows UV-vis diffuse reflectance spectra of all the samples. There is a strong absorption band from 200 nm to 400 nm in the spectra, which is assigned to the charge transfer from O^{2-} in O 2p to Ce^{4+} in Ce 4f. As a result, a LED 365 lamp was chosen as the light source for photocatalytic evaluation. The plots (Figure. S2) with steep edges of the transformed Kubelka–Munk function versus light energy showed the band gaps of all of the samples. The values of band gaps (CeO_2-normal: 3.1 eV, CeO_2-Ar: 3.15 eV, CeO_2-O_2: 3.1 eV, CeO_2-CO_2: 3.17 eV) are pretty approaching, enabling that all of the sample can be excited by the ultraviolet light source and conduct the photocatalytic process.

Photocatalytic activity was evaluated by the conversion of isopropanol to acetone under LED 365 nm irradiation. Figure. 4a shows photocatalytic activities of all of the samples, and they are consistent with our anticipation that

CeO_2-CO_2 possesses the highest activity. CeO_2-CO_2 not only showed the highest conversion rate but also exhibited the fastest reaction speed. Conversions for conversion of isopropanol to acetone of other three samples were ignited at the third hour, but CeO_2-CO_2 started for the first time. This excellent activity could be ascribed to the hollow structure that enabled CeO_2-CO_2 to absorb more reactants before irradiation (Figure. S3) and provide more active sites in the process. Sample of CeO_2-CO_2 with ten hours irradiation, the amount of generated acetone gradually decreased. It could be contributed to saturation of acetone, and then it was decomposed to CO_2. This further indicated that CeO_2-CO_2 owned higher oxidation capacity. The photocatalytic activity curve of CeO_2-O_2 gradually approached a plateau after 22 h of reaction, indicating that the amount of acetone was reaching a critical value. However, the photocatalytic processes of CeO_2-normal and CeO_2-Ar were almost stagnated after 22 h of reaction, indicating that the photocatalysts were deactivated. All of the results reveal that the atmosphere in the hydrothermal process has a great effect on the photocatalytic activity of CeO_2.
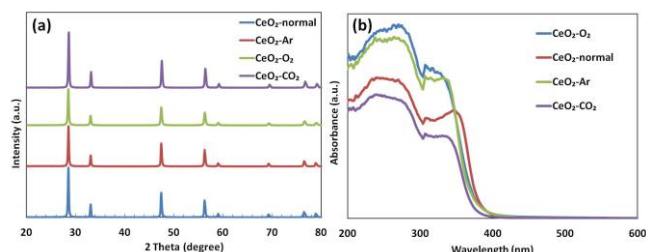

Figure 3. Crystal phase and optical information of all of the samples. (a) XRD patterns, (b) UV-vis spectra.

In order to determine whether the morphology played a key role in the outstanding photocatalytic activity of CeO_2-CO_2, BET characterization was conducted and then photocatalytic activities of all of the samples would be normalized with specific surface areas. The specific surface areas of CeO_2-Ar, CeO_2-normal, CeO_2-O_2, and CeO_2-CO_2 samples were 12.431 m^2/g, 10.515 m^2/g, 14.235 m^2/g and 12.485 m^2/g, respectively, as calculated by the multi points Brunauer–Emmett–Teller (BET) equation from N_2 adsorption-desorption isotherms (Figure. S4a). Moreover, the pore volumes of all of the samples could be obtained by the highest points of the isothermal curves, CeO_2-Ar (11.7 cc/g), CeO_2-normal (12.2 cc/g), CeO_2-O_2 (14.7 cc/g) and CeO_2-CO_2 (15.7 cc/g), which were in agreement with the morphologies of all of the samples. The larger pore volumes were from the hollow structure and the gaps among the particles. The pore size distribution of all samples is concentrated in 2 nm (Figure S4b). CeO_2-CO_2 has an additional particle size range around 7 nm, which could be contributed to its hollow structure. However, the specific surface area values of CeO_2-O_2 and CeO_2-CO_2 were much smaller than we expected, which could be understandable that the particle sizes of CeO_2-O_2 and CeO_2-CO_2 greatly increased. While the specific surface area is inversely proportional to the size of the particles.

Normalization of photocatalytic activity versus specific surface area, reaction time and mass indicated that morphology was not the key point for excellent photocatalytic activity of CeO_2-CO_2. There must be other factors, such as the content of Ce^{3+} and oxidation capacity, that dominate the photocatalytic activity.

Consequently, XPS analysis was carried out to obtain the more detailed information of the surface composition and chemical state (content of Ce^{3+}), and the results were shown in Figure. 5a. The CeO_2 spectrum is composed of two multiplets (v and u), which correspond to the spin-orbit split 3d5/2 and 3d3/2 core holes.[11] Here, the Ce^{3+} content of each sample could be briefly estimated based on peak fitting,[12] and the values were 19.1 % (CeO_2-normal), 20.2 % (CeO_2-Ar), 18.1 % (CeO_2-O_2) and 24.6 % (CeO_2-CO_2), respectively. Ce^{3+} is generated from the reducing of CeO_2 by ethanol in the hydrothermal process. However, oxygen would transfer Ce^{4+} to Ce^{3+}, which led the lowest content of Ce^{3+} in sample of CeO_2-O_2. CeO_2-normal also owned low content of Ce^{3+}, which could be contributed to the presence of oxygen in air. A moderate amount of Ce^{3+} will improve the photocatalytic activity because Ce^{3+} can generate oxygen vacancies and provide active sites for reactants. However, more Ce^{3+} will generate excessive oxygen vacancies and become the recombination centre of photogenerated electron-hole pairs and then depress the activity.[13] An appropriate content of Ce^{3+} is a reason for the superior photocatalytic activity of CeO_2-CO_2.
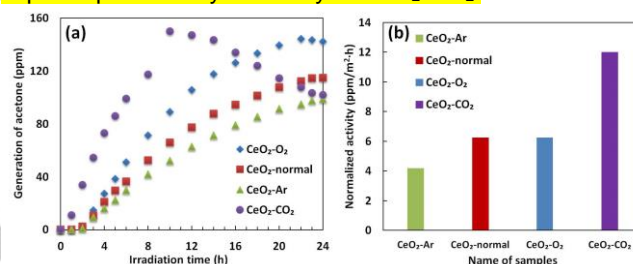

Figure 4. (a) Photocatalytic activities for decomposing 2-propanol to acetone, (b) normalized photocatalytic activities, the meaning of y axis is $Amount_{acetone}$/Time x S_{BET} x Mass, the amount of acetone irradiated for 10 hours is used to normalize.

However, oxidation capacity is a dominant factor under the premise of all the samples can be excited by the light source. We therefore determined the position of the Valence Band Maximum (VBM) by an anodic scan in the dark.[14] For an n-type semiconductor under a dark condition, the reverse biasing induces more band bending. An increase in the biasing to a certain potential leads to extreme depletion or carrier inversion once the Fermi level energy is positive with respect to the valence band energy.[15] At that moment, the current flowing across the interface is irreproducible and likely to be dominated by the tunnelling process through the Helmholtz layer.[16] The onset of that process yields the VBM. Figure. 5b shows linear sweep voltammetry (LSV) curves of the samples under a dark condition. The relative VBM values were in the order of CeO_2-CO_2 > CeO_2-O_2 > CeO_2-Ar > CeO_2-normal, indicating that the oxidation capacity of CeO_2-CO_2 was

highest. Although there was no obvious disparity among all of the samples in their VBM values, VMB determine their reaction feasibility and velocity. As a result, a moderate amount of Ce^{3+} and the highest VBM level were key points for the superior photocatalytic activity.

In summary, we have presented a facile hydrothermal approach to adjust the morphologies and photocatalytic performances of CeO_2 through a gas bubbling method. We investigated the effect of the atmosphere on the hydrothermal process, and we showed that CO_2 and O_2 atmospheres were in favour of hollow structure formation and improve the activity. In addition, it was found that a moderate content of Ce^{3+} and the highest VBM level played key roles in the improvement of photocatalytic activity. Since CeO_2 materials have substantial basic sites, acid gas can be strongly absorbed with it and then excellent performance can be obtained. A most important of all is that we should choose the matching system between atmosphere and target product. Only in this way can a product with excellent properties be obtained. Herein, we have elucidated the relationship between the solution atmosphere and the hydrothermal process, and we have revealed a new factor in the hydrothermal process that has been ignored by people.
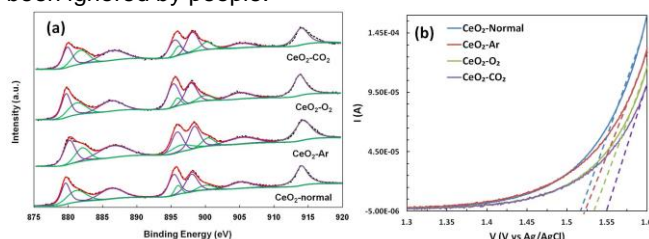

Figure 5. (a) XPS spectra of all of the samples. (b) relative VBM levels of all of the samples from LSV curves.

Experimental Section

All chemicals used in the experimental section were analytical grade and used as received without further purification. Various CeO_2 particles with different morphologies were synthesized by a simple gas-saturation hydrothermal method. Typically, 1.0 g of Cerium(III) nitrate hexahydrate and 0.10 g of PVP were dissolved in a mixture solution of ethanol (40 mL) and deionized water (40 mL) with magnetic stirring for 30 min. Consecutively, fully mixed solution was bubbled with Ar, O_2, and CO_2 for 30 min. Then the suspension was transferred to a 100-mL Teflon-lined autoclave and heated at 180 °C for 24 h. After cooling to room temperature, the product was collected by centrifugation, washed with ethyl alcohol and water until the ionic strength was less than 10 μS/cm, and dried at 70 °C overnight. Finally, we obtained various CeO_2, and reserved them under black-UV illumination.

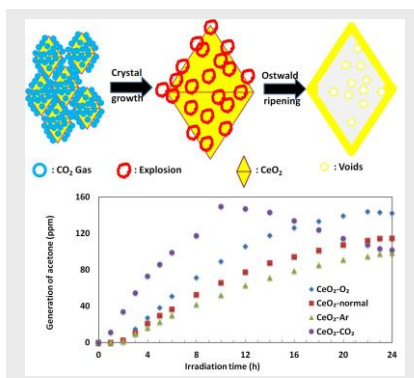## Conflicts of interest

The authors declare no conflict of interest.

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Layout 1:

COMMUNICATION

The effect of the atmosphere in solution was investigated in a hydrothermal process. Solutions with precursors were bubbled with Ar, O_2, and CO_2, resulting in changes on the morphologies of prepared CeO_2 particles. Importantly, it was shown that the atmosphere has a great effect on photocatalytic activity.

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