# **Inorganic Chemistry**

# Hierarchical CeO<sub>2</sub>@N–C Ultrathin Nanosheets for Efficient Selective Oxidation of Benzylic Alcohols in Water

Juan Hao,<sup>‡</sup> Zhouyang Long,<sup>‡</sup> Liming Sun,<sup>\*</sup> Wenwen Zhan, Xiaojun Wang, and Xiguang Han<sup>\*</sup>

6		Cite This: Inorg.	Chem.	2021,	60, 7732–7737
	~ 4				



Article Recommendations

ACCESS

III Metrics & More

**ABSTRACT:** A monodisperse CeO<sub>2</sub>@N–C ultrathin nanosheet self-assembled hierarchical structure (USHR) has been prepared by metal–organic framework template methods. The uniform coating of nitrogen-doped carbon (N–C) layers could play an important role in the adsorption and activation of benzylic alcohol. The unique 3D hierarchical structure self-assembled by ultrathin nanosheets provided enough active sites for the catalytic reaction. Therefore, the CeO<sub>2</sub>@N–C USHR can afford excellent catalytic performance for selective oxidation of benzylic alcohols in water.



Supporting Information

## INTRODUCTION

In the field of organic synthesis, selective oxidation of aromatic alcohols to relevant carbonyl compounds (e.g., aldehydes and ketones) without overoxidation to carboxylic acids and carbon dioxide remains challenging and fundamentally important.<sup>1,2</sup> Recently, great efforts have been paid to development of high activity, selectivity, and stable catalysts. In order to achieve good catalytic performance, some homogeneous metal complexes of Ru,<sup>3</sup> Pd,<sup>4</sup> and Cu<sup>5</sup> had been used as the co-catalysts; however, they had suffered from the limited reserves and high price, which greatly suppress their practical application. Furthermore, most of the reported catalytic reaction systems require organic solvents, such as toluene,<sup>6,7</sup> ethanol,<sup>8</sup> etc., which are usually toxic and expensive. Therefore, it is urgent to construct a cheap, easily available, green, and high activity catalyst.

CeO<sub>2</sub> has unique oxygen storage capacity, low cost, nontoxicity, and chemical and physical stability, which make it an outstanding support or catalyst for catalytic oxidation.<sup>9–13</sup> In order to achieve the catalytic properties comparable to noble metals, noble metal materials or peroxides as additives or oxidants have been employed to improve the catalytic performance of cerium-based catalysts, which leads to the sharp rise in cost and environmental pollution.<sup>14,15</sup> Recently, lots of research showed that carbon materials as the co-catalysts could enhance the catalytic activity and selectivity due to their low cost and high mobility of charge carriers.<sup>16–22</sup> The density functional theory (DFT) indicated that nitrogen doping can further modulate the spin density, energy bandgap, and charge density,<sup>23</sup> which can result in a material with a higher catalytic performance than pure carbon-based catalysts by reducing the activation energy. Therefore, nitrogen-doped carbon materials may replace noble metals as the co-catalysts with enhanced performance for CeO<sub>2</sub>-based catalysts.

To reduce the activation energy, more active sites of  $CeO_2$  are needed to react with the activated molecules. Therefore, another factor for limiting cerium-based catalytic efficiency is the low proportion of surface active sites. The nanosheets with a twodimensional (2D) structure usually can expose numerous accessible surface active sites in the catalytic process due to the large surface area.<sup>24–27</sup> However, 2D nanosheets with high surface energy are easy to aggregate, which reduces surface active sites and catalytic activity. Three-dimensional (3D) structures inserted by nanosheets with integrated morphology can prevent the aggregation, which can not only avoid the reduction of active sites but also promote mass transfer for the catalytic reaction.<sup>28,29</sup> Therefore, the fabrication of N-doped C layer-coated CeO<sub>2</sub> with a nanosheet-interpreted 3D structure could be beneficial to improve the catalytic activity and selectivity. Nevertheless, the synthesis of such a material is still a big challenge.

Herein, a monodisperse 3D hierarchical architecture selfassembled by ultrathin CeO<sub>2</sub> nanosheets encapsulated by Ndoped carbon layers (CeO<sub>2</sub>@N-C USHR) was synthesized by the thermal treatment of Ce-based metal-organic frameworks (Ce-MOFs). Due to the unique structure of MOFs, the obtained CeO<sub>2</sub>@N-C USHR was uniformly coated by N-doped carbon layers, which had an important influence on the adsorption and activation of benzylic alcohol. The unique 3D hierarchical architecture effectively prevented the agglomeration of ultrathin CeO<sub>2</sub>@N-C nanosheets and provided enough active sites for the catalytic reaction. Based on these two structure characteristics, the CeO<sub>2</sub>@N-C USHR exhibits excellent catalytic activity for selective oxidation of benzylic alcohols in water.

Received: January 10, 2021 Published: May 25, 2021



#### Inorganic Chemistry

## RESULTS AND DISCUSSION

A facile MOF as a precursor strategy involving the thermal annealing of Ce-MOF precursors under an Ar atmosphere was developed to engineer the monodisperse  $CeO_2@N-C$  ultrathin nanosheet self-assembled hierarchical architecture (USHR). Figure 1a shows the detail synthesis process of USHR. First,



**Figure 1.** (a) Schematic image of the synthetic strategy of monodisperse  $CeO_2@N-C$  ultrathin nanosheet self-assembled hierarchical architecture (USHR). Typical SEM images of (b) Ce-MOF precursor and (c)  $CeO_2@N-C$  USHR, (d) AFM image of the single nanosheet exfoliated from  $CeO_2@N-C$  USHR, and (e) corresponding height profiles of lines in Figure 1d.

based on the introducing regulator strategy, a monodisperse Ce-MOF precursor with nanosheet self-assembled flowers had been obtained by the solvothermal method in an *N*,*N*-dimethylformamide and ethanol mixed solvent (see the experimental details in the Supporting Information). X-ray powder diffraction (XRD) measurement has been used to characterize the crystal structure of Ce-MOFs. The diffraction peaks of the assynthesized Ce-MOFs (Figure S1) matched well with published XRD patterns.<sup>30</sup>

The scanning electron microscopy (SEM) images of the precursors have been shown in Figure 1b, which indicated that these precursor particles possessed high monodisperse and regular hierarchical architecture morphology interpreted by 2D nanosheets. The higher-magnification SEM image showed that these nanosheets possessed smooth surfaces. According to thermogravimetric analysis (TGA) results of Ce-MOFs (Figure S2), there were two major stages of rapid weight loss, indicating that the Ce-MOF precursor decomposes in two steps to produce

CeO<sub>2</sub>@N–C. The second stage starting from 400 °C could be assigned to collapse of the Ce-MOF precursor.<sup>31</sup> Thus, we have chosen the annealing temperature as 550 °C for the carbonization of the Ce-MOF precursor. The product after annealing treatment was characterized by XRD measurements (Figure S3), and the XRD pattern exhibited the diffraction peaks assigned to the cubic CeO<sub>2</sub> phase (PDF No. 00-034-0394), indicating that the Ce-MOF precursors were transformed into  $CeO_2$  during the pyrolysis process. The SEM image (Figure 1c) showed that the product has preserved the overall nanosheet self-assembled flower shape of the Ce-MOF precursors. The magnified observations (inset of Figure 1c) further revealed the 2D ultrathin nanosheets after annealing treatment presented a rough surface. The thickness of the ultrathin nanosheets was further characterized by atomic force microscopy (AFM) analysis (Figure 1d,e), which indicated that the nanosheet had a thickness of about 4-5 nm. By means of the SEM measurement, the thickness statistics of the nanosheet is shown in Figure S4. It could be seen that the thickness of the nanosheet is mainly concentrated at  $4.5 \pm 1.1$  nm, which was consistent with the AFM results.

In order to further understand the inner structural information and components, the  $CeO_2@N-C$  USHR was characterized by transmission electron microscopy (TEM). From Figure 2a, we could further confirm the 2D nanosheet interconnected 3D hierarchical architecture. A high-magnification survey (Figure 2b) detected from a sampling area of the



**Figure 2.** (a) Typical TEM image of a monodisperse  $CeO_2@N-C$ USHR nanoparticle, (b) high-magnification TEM image of  $CeO_2@N-C$ C USHR, (c) high-resolution TEM image, and (d) corresponding SAED pattern of  $CeO_2@N-C$  USHR; (e, f) STEM image and the corresponding elemental line profiles of  $CeO_2@N-C$  USHR nanoparticles, (g-k) STEM image and the corresponding elemental mapping of elements Ce, O, C, and N, and (l) N<sub>2</sub> sorption isotherm and the corresponding BJH pore size distribution curve of  $CeO_2@N-C$ USHR nanoparticles.

pubs.acs.org/IC

nanosheet, which clearly revealed that numerous small CeO<sub>2</sub> particles with uniform size distribution homogeneously laid on the carbon nanosheet walls. Furthermore, the crystallinity of small CeO<sub>2</sub> particles and the carbon nanosheet was determined by using HRTEM and selective area electron diffraction (SAED) patterns. The high-resolution TEM image (Figure 2c) showed interplanar distance assigned to (111) planes of cubic CeO<sub>2</sub> (0.311 nm), revealing that the small particles were CeO<sub>2</sub> nanoparticles. The corresponding SAED pattern showed that polycrystalline rings (Figure 2d) matched well with cubic CeO<sub>2</sub>. Scanning transmission electron microscopy (STEM) elemental profiles and elemental mapping were employed to further study the inter-structure and composition. As shown in Figure 2e,g, the STEM image of the exfoliated ultrathin 2D nanosheets and the corresponding elemental line profiles (Figure 2f) and mapping profiles (Figure 2h-k) showed the uniform distribution of elements Ce, O, C, and N in the nanosheet. Therefore, through the pyrolysis decomposition, the cerium ions in the Ce-MOFs had been converted into CeO<sub>2</sub> nanoparticles, while the organic ligands (1,2,4,5-benzenetetracarboxylic acid) and regulator (1,2-benzisothiazolin-3(2H)-one) could be easily in situ carbonized to form the N-doped carbon layer. Meanwhile, during the annealing process, the produced gas escaped from the inside of the Ce-MOF precursor, which resulted in the formation of a loosely porous structure. The porosity of CeO2@N-C USHR was further investigated by N2 adsorption-desorption isotherms. The N2 sorption isotherms showed that CeO2@N-C USHR had a Brunauer-Emmett-Teller surface area of about 45.6  $m^2/g$ , and the pore distribution was mainly centered at about 4 nm according to the Barrett-Joyner–Halenda method (Figure 21).

The surface chemical composition and valence states of  $CeO_2@N-C$  USHR were further revealed by X-ray photoelectron spectroscopy (XPS). The survey spectrum (Figure S5) showed the existence of Ce, O, C, and N elements in the  $CeO_2@$ N-C USHR sample. Figure 3a shows the high-resolution Ce 3d spectrum with two kinds of splitted peaks (Ce  $3d_{3/2}$  labeled with U and Ce  $3d_{3/2}$  labeled with V). U<sub>1</sub>, U<sub>0</sub>, V<sub>1</sub>, and V<sub>0</sub> reflected the Ce<sup>3+</sup> characteristic peaks, whereas U<sub>3</sub>, U<sub>2</sub>, U, V<sub>3</sub>, V<sub>2</sub>, and V corresponded with Ce<sup>4+</sup> characteristic peaks. In addition, the Ce<sup>3+</sup> and Ce<sup>4+</sup> portions can be calculated to be 28.7 and 71.3%,



Figure 3. High-resolution XPS spectra of the  $CeO_2@N-C$  USHR nanoparticle, (a) Ce 3d, (b) O 1s, (c) C 1s, and (d) N 1s.

respectively.<sup>32,33</sup> The high-resolution O 1 s spectrum (Figure 3b) could be split into three peaks, which could be ascribed to the lattice oxygen ( $O_L$ ) at 529.6 eV, oxygen-deficient regions ( $O_V$ ) at 530.1 eV, and chemisorbed oxygen ( $O_C$ ) at 531.8 eV.<sup>34</sup> The C 1 s spectrum (Figure 3c) indicated the peaks assigned to binding energy at 284.7 eV (C=C/C-C bonds), 285.6 eV (C-N bonds), and 289.3 eV (C-O bonds), respectively.<sup>35</sup> Figure 3d shows a high-resolution N 1s spectrum, which could be split into two Gaussian components centered at 399.8 eV corresponding to N–graphene bonds and 407.2 eV corresponding to N–O bonds. Therefore, the XPS results further indicated that the CeO<sub>2</sub>@N–C USHR nanostructure was composed of CeO<sub>2</sub> nanoparticles coated by N-doped C layers.

The uniformly N-doped C-coated CeO<sub>2</sub> nanoparticles with hierarchical architecture provided highly approachable adsorption and active catalytic sites, leading to the promising performance of CeO<sub>2</sub>@N-C USHR as the catalyst. The ability of CeO<sub>2</sub>@N-C USHR to catalyze the oxidation reaction of benzyl alcohol to benzaldehyde in water had been investigated. The influences of the catalyst amount on the reaction yields toward oxidation of benzyl alcohol to benzaldehyde had been studied, and the data are shown in Figure S6. It can be seen that when the catalyst amount increased from 10 to 50 mg, the conversion of benzyl alcohol increased from 25.1 to 99.9%. Thus, the catalyst amount was set at 50 mg in the following catalytic tests. The blank experiments indicated that no oxidation occurs in the absence of heating or catalysts, indicating that the usage of an appropriate catalyst and heating were the two key elements for this reaction (Table S1). Therefore, the catalytic oxidation of benzyl alcohol was performed in glass pressure bottles in the water at different temperatures (Figure 4a). To thoroughly investigate the catalytic performance of CeO<sub>2</sub>@N-C USHR (CeO<sub>2</sub> nanoparticles coated by N-doped C), CeO<sub>2</sub>@C USHR (CeO<sub>2</sub> nanoparticles coated by C, Figure S7), pure CeO<sub>2</sub> USHR (CeO<sub>2</sub> nanoparticles, Figure S8), and commercial CeO<sub>2</sub> (Figure S9) are used as reference samples. The <sup>13</sup>C NMR spectra of benzyl alcohol and benzaldehyde are shown in Figure S10. As shown in Figure 4b, CeO<sub>2</sub>@N-C USHR exhibited production yield reaching above 99.9% after 48 h, which was the highest catalytic activity.<sup>7,36-38</sup> The catalytic activity of four samples followed the trend CeO2@N-C USHR >  $CeO_2 \otimes C$  USHR >  $CeO_2$  USHR > commercial  $CeO_2$ . The above catalytic experiments indicated that both the morphology (hierarchical architecture assembled by ultrathin nanosheets) and the composite (N-doped C layer) have important effects on their catalytic activity. The nanosheet self-assembled hierarchical architecture increased the specific surface area of the catalyst and exposed more active sites. The N-doped C layer might act as the medium to strengthen the adsorption of reactants (benzyl alcohol) on CeO<sub>2</sub> catalysts and reduced the activation energy of the catalytic reaction. To investigate the origin and reveal the activity of CeO2@N-C USHR for the oxidation of benzyl alcohol to benzaldehyde, the kinetic analysis for catalytic oxidation was performed. Figure 4c shows the curves of benzyl alcohol conversion versus reaction time at different reaction temperatures. It appeared that the conversion of benzyl alcohol increased when the reaction temperature increased from 353 to 423 K. The trend of yields for different catalysts at various temperatures matched well with the yield at 150 °C (Figure S11 and Figure S12). Accordingly, we plotted  $\ln k$  versus 1/T (Figure 4d), where k is the rate constant obtained by the linearly fitting relationship between the yield of benzyl alcohol and the reaction time according to the integral rate equation. As shown in Figure



**Figure 4.** (a) Catalytic equation and reaction conditions for selective oxidation of benzyl alcohol; (b) reaction yields of benzaldehyde from the oxidation of benzyl alcohol using  $CeO_2@N-C$  USHR,  $CeO_2@C$  USHR,  $CeO_2$  USHR, and commercial  $CeO_2$  as catalysts at 150 °C for 48 h in water; (c) benzyl alcohol conversion profiles obtained at the indicated reaction temperature using the  $CeO_2@N-C$  USHR catalyst; (d) Arrhenius plot of the oxidation of benzyl alcohol with molecular oxygen; (e) catalytic durability of  $CeO_2@N,S-C$  USHR; (f) catalyzed oxidation of various types of alcohols using  $CeO_2@N-C$  USHR.

4d, all the plots of ln k versus 1/T were satisfactorily linear. For the CeO<sub>2</sub>@N-C USHR catalyst, the slope and intercept were -4819 and 8.28, respectively. According to the slope and intercept values and the Arrhenius equation, i.e., ln  $k = \ln A - E_a/RT$ , the apparent activation energy ( $E_a$ ) for the CeO<sub>2</sub>@N-C USHR catalyst calculated by the Arrhenius equation was 40.0 ± 1.6 kJ·mol<sup>-1</sup>, which was the lowest among these catalysts (CeO<sub>2</sub>@C USHR (47.0 ± 3.5 kJ·mol<sup>-1</sup>); CeO<sub>2</sub> USHR (56.8 ± 1.9 kJ·mol<sup>-1</sup>)) (Table 1). The results indicated that the external

Table 1. Apparent Activation Energy  $(E_a)$  and Pre-Exponential Factor (a) of Catalyzed Oxidation of Benzyl Alcohol to Benzaldehyde Using Various Catalysts

catalysts	E <sub>a</sub> (kJ/mol)	pre-exponential factor (A/mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )
CeO <sub>2</sub> @N–C USHR	$40.0 \pm 1.6$	21,162
CeO <sub>2</sub> @C USHR	$47.0\pm3.5$	18,769
CeO <sub>2</sub> USHR	$56.8 \pm 1.9$	3944

C layer could reduce the  $E_a$  of oxidation of benzyl alcohol to benzaldehyde, and N-doped C can further strengthen this effect. Impressively, CeO<sub>2</sub>@N-C USHR nanoparticles could also exhibit good stability with no obvious decrease in activity during 5 catalytic cycles (Figure 4e), and their original morphology and crystal structure had been well maintained (Figure S13).<sup>39-44</sup> To demonstrate the universality of this catalytic system, the oxidation of a variety of alcohol substrates was investigated over the CeO<sub>2</sub>@N-C USHR catalysts (Figure 4f, Table S2, and Figure S14). The oxidation of 4-hydroxybenzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, 2-aminobenzyl alcohol, cinnamyl alcohol, and indole-3-carbinol proceeds efficiently over the target catalyst CeO<sub>2</sub>@N-C USHR with high yields of their corresponding products; however, the attachment of electron-withdrawing groups (like -F, -Cl, and -Br) to the para-position of the phenyl ring largely decreased the efficiency of the oxidation reaction. The corresponding 1H NMR spectra of products and reactants are shown in Figure S14.

In order to illuminate the mechanism of  $CeO_2 @N-C USHR$ for oxidation of benzyl alcohol to benzaldehyde with enhanced catalytic activity, the adsorption and activation effects of  $(111)_{CeO2}$  (i.e.,  $CeO_2$  (111) surfaces) and  $(001)_{N-graphite}$  (i.e., N-doped graphite (001) surfaces) on benzyl alcohol were investigated, respectively. We have used the DFT to research the adsorptions of benzyl alcohol on  $(111)_{CeO2}$  and  $(001)_{N-graphite}$ , and the corresponding calculated adsorption energies were 0.15 and -3.40 eV, respectively. The optimized configurations for the adsorption of benzyl alcohol on  $(111)_{CeO2}$  and  $(001)_{N-graphite}$  are shown in Figure S15, which indicated that the coating of the Ndoped carbon layer on the CeO<sub>2</sub> surface was beneficial to the adsorption of benzyl alcohol, attributing to the  $\pi-\pi$  stacking interaction between the graphite ring and the benzene ring of benzyl alcohol. Activation of benzyl alcohol by the N-doped carbon layer was studied by electron density difference maps (Figure 5) and Mulliken population (Table S3). From Figure 5a,b, it can be found that the charge exchange between O and H<sub>O</sub> atoms of benzyl alcohol became weaker after adsorption on the  $(001)_{N-\text{graphite}}$ . A similar situation also occurred between C and H<sub>1</sub> atoms; that is, the charge exchange between C and H<sub>1</sub>



**Figure 5.** Electron density difference maps of benzyl alcohol from different angles: (a, c) before adsorption and (b, d) after adsorption on the N-doped graphite (001) surface.

atoms after adsorption (Figure 5c) was weaker than that before adsorption (Figure 5d). After benzyl alcohol adsorbed on the  $\left(001\right)_{N\text{-graphite}}$  the calculated Mulliken charge on O and C increased from -0.78 and -0.36 e to -0.74 and -0.34 e, respectively; meanwhile, the Mulliken charge on  $H_0$  and  $H_1$ decreased from 0.55 and 0.31 e to 0.53 and 0.28 e, respectively (Table S3). The bond lengths of corresponding  $O-H_0$  and C-H<sub>1</sub> stretched from 0.976 and 1.112 Å to 0.983 and 1.114 Å, respectively. Based on the charge redistribution and the elongated bond length, it could be inferred that the  $O-H_O$ and C-H<sub>1</sub> bonds of benzyl alcohol became weak and easy to break after adsorption on the  $(001)_{N-graphite}$ . In other words, the N-doped carbon layer could activate  $O-H_0$  and  $C-H_1$  bonds in benzyl alcohol, which was conducive to the oxidation of benzyl alcohol to benzaldehyde. The above calculation data exhibited that coating N-doped carbon layers on CeO<sub>2</sub> not only effectively enhanced the adsorption of benzyl alcohol but also had an important influence on the activation of benzyl alcohol.

## CONCLUSIONS

In summary, N-doped porous carbon-coated CeO<sub>2</sub> with hierarchical architecture has been engineered via a Ce-MOF as the hard template. Experimental results about the catalytic activities toward selective oxidation of benzyl alcohol to benzaldehyde and the corresponding theoretical calculation indicated that the N-doped C layer can act as the medium to strengthen the adsorption of benzyl alcohol reactants on CeO<sub>2</sub> catalysts and reduced the activation energy of the catalytic reaction. The 3D hierarchical architecture can provide lots of active sites to react with activator molecules. Therefore,  $CeO_2(a)$ N-C USHR exhibits excellent catalytic performance, including the activity, selectivity, and cycle stability, due to the synergetic effect of 3D hierarchical architecture and N-doped C layers. The obtained CeO<sub>2</sub>@N-C USHR product in this study is promising for other catalytic systems and may inspire further studies to develop green synthesis.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00076.

Experiment details, XRD and TGA results of the Ce-MOF precursor (Figures S1, S2), XRD and XPS of the CeO<sub>2</sub>@ N–C USHR (Figures S3, S4), and characteristics and catalytic activity of compared samples and recycled CeO<sub>2</sub>@N,S-C HN (Figures S5–S10) (PDF)

## AUTHOR INFORMATION

#### **Corresponding Authors**

- Liming Sun Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China; Email: limingsun1226@jsnu.edu.cn
- Xiguang Han Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China; Ocrid.org/0000-0003-2469-4572; Email: xghan@jsnu.edu.cn

## Authors

Juan Hao – Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China

- Zhouyang Long Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China
- Wenwen Zhan Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China; orcid.org/0000-0002-7004-9155
- Xiaojun Wang Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, P. R. China; @ orcid.org/0000-0002-1461-4922

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c00076

#### **Author Contributions**

<sup>‡</sup>These authors contributed equally.

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 22005126), the Natural Science Foundation of Jiangsu Province (BK20191466) and Xuzhou City (KC20061), and the Postgraduate Research and Practical Innovation Program of Jiangsu Province (KYCX20\_2247).

## REFERENCES

(1) Sheldon, R. A.; Arends, I. W. C. E.; Brink, G. J. T.; Dijksman, A. Green, Catalytic Oxidations of Alcohols. *Acc. Chem. Res.* 2002, 35, 774–781.

(2) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. New developments in catalytic alcohol oxidations for fine chemicals synthesis. *Catal. Today* **2000**, *57*, 157–166.

(3) Johnson, J. B.; Bäckvall, J. E. Mechanism of Ruthenium-Catalyzed Hydrogen Transfer Reactions. Concerted Transfer of OH and CH Hydrogens from an Alcohol to a (Cyclopentadienone)ruthenium Complex. J. Org. Chem. 2003, 68, 7681–7684.

(4) Brink, G. J. T.; Arends, I. W. C. E.; Sheldon, R. A. Green, Catalytic Oxidation of Alcohols in Water. *Science* **2000**, *287*, 1636–1639.

(5) Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. Copper(II)-catalysed aerobic oxidation of primary alcohols to aldehydes. *Chem. Commun.* **2003**, 2414–2415.

(6) Geng, L. L.; Zhang, X. Y.; Zhang, W. X.; Jia, M. J.; Liu, G. Highly dispersed iron oxides on mesoporous carbon for selective oxidation of benzyl alcohol with molecular oxygen. *Chem. Commun.* **2014**, *50*, 2965–2967.

(7) Geng, L. L.; Zheng, B.; Wang, X.; Zhang, W. X.; Wu, S. J.; Jia, M. J.; Yan, W. F.; Liu, G. Fe<sub>3</sub>O<sub>4</sub> Nanoparticles Anchored on Carbon Serve the Dual Role of Catalyst and Magnetically Recoverable Entity in the Aerobic Oxidation of Alcohols. *ChemCatChem* **2016**, *8*, 805–811.

(8) Watanabe, H.; Asano, S.; Fujita, S.; Yoshida, H.; Arai, M. Nitrogen-Doped, Metal-Free Activated Carbon Catalysts for Aerobic Oxidation of Alcohols. *ACS Catal.* **2015**, *5*, 2886–2894.

(9) Hu, F. Y.; Chen, J. J.; Peng, Y.; Song, H.; Li, K. Z.; Li, J. H. Novel nanowire self-assembled hierarchical  $CeO_2$  microspheres for low temperature toluene catalytic combustion. *Chem. Eng. J.* **2018**, 331, 425–434.

(10) Peng, R. S.; Li, S. J.; Sun, X. B.; Ren, Q. M.; Chen, L. M.; Fu, M. L.; Wu, J. L.; Ye, D. Q. Size effect of Pt nanoparticles on the catalytic oxidation of toluene over  $Pt/CeO_2$  catalysts. *Appl. Catal. B-Environ.* **2018**, 220, 462–470.

(12) Lykaki, M.; Pachatouridou, E.; Carabineiro, S. A. C.; Lliopoulou, E.; Andriopoulou, C.; Kallithrakas-Kontos, N.; Boghosian, S.; Konsolakis, M. Ceria nanoparticles shape effects on the structural defects and surface chemistry: Implications in CO oxidation by Cu/CeO<sub>2</sub> catalysts. *Appl. Catal. B-Environ.* **2018**, *230*, 18–28.

(13) Spezzati, G.; Benavidez, A. D.; Delariva, A. T.; Su, Y. Q.; Hofmann, J. P.; Asahina, S.; Olivier, E. J.; Neethling, J. H.; Miller, J. T.; Datye, A. K.; Hensen, E. J. M. CO oxidation by Pd supported on  $CeO_2(100)$  and  $CeO_2(111)$  facets. *Appl. Catal. B-Environ.* **2019**, 243, 36–46.

(14) Chen, A.; Yu, Y.; Wang, R.; Yu, Y.; Zang, W.; Tang, P.; Ma, D. Nitrogen-doped dual mesoporous carbon for the selective oxidation of ethylbenzene. *Nanoscale* **2015**, *7*, 14684–14690.

(15) Yang, S.; Peng, L.; Huang, P.; Wang, X.; Sun, Y.; Cao, C.; Song, W. Nitrogen, Phosphorus, and Sulfur Co-Doped Hollow Carbon Shell as Superior Metal-Free Catalyst for Selective Oxidation of Aromatic Alkanes. *Angew. Chem., Int. Ed.* **2016**, *128*, 4084–4088.

(16) Sun, X. M.; Li, Y. D. Colloidal Carbon Spheres and Their Core/ Shell Structures with Noble-Metal Nanoparticles. *Angew. Chem., Int. Ed.* **2004**, 43, 597–601.

(17) Holst, J. R.; Gillan, E. G. From Triazines to Heptazines: Deciphering the Local Structure of Amorphous Nitrogen-Rich Carbon Nitride Materials. *J. Am. Chem. Soc.* **2008**, *130*, 7373–7379.

(18) Zhang, L. L.; Zhao, X. S. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520–2531.

(19) Lee, W. J.; Maiti, U. N.; Lee, J. M.; Lim, J.; Han, T. H.; Kim, S. O. Nitrogen-doped carbon nanotubes and graphene composite structures for energy and catalytic applications. *Chem. Commun.* **2014**, *50*, 6818–6830.

(20) Zhong, W.; Liu, H.; Bai, C.; Liao, S.; Li, Y. Base-Free Oxidation of Alcohols to Esters at Room Temperature and Atmospheric Conditions using Nanoscale Co-Based Catalysts. *ACS Catal.* **2015**, *5*, 1850–1856.

(21) Gu, D.; Li, W.; Wang, F.; Bongard, H.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao, D.; Schüth, F. Controllable Synthesis of Mesoporous Peapod-like  $Co_3O_4$ @Carbon Nanotube Arrays for High-Performance Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2015**, *54*, 7060–7064.

(22) Wang, S. Y.; Zhang, L. P.; Xia, Z. H.; Roy, A.; Chang, D. W.; Baek, J. B.; Dai, L. M. BCN Graphene as Efficient Metal-Free Electrocatalyst for the Oxygen Reduction Reaction. *Angew. Chem., Int. Ed.* **2012**, *51*, 4209–4212.

(23) Tong, Y.; Chen, P. Z.; Zhang, M. X.; Zhou, T. P.; Zhang, L. D.; Chu, W. S.; Wu, C. Z.; Xie, Y. Oxygen Vacancies Confined in Nickel Molybdenum Oxide Porous Nanosheets for Promoted Electrocatalytic Urea Oxidation. *ACS Catal.* **2018**, *8*, 1–7.

(24) Lei, W.; Zhang, T.; Gu, L.; Liu, P.; Rodriguez, J. A.; Liu, G.; Liu, M. Surface-Structure Sensitivity of CeO<sub>2</sub> Nanocrystals in Photocatalysis and Enhancing the Reactivity with Nanogold. *ACS Catal.* **2015**, *5*, 4385–4393.

(25) Fang, Z. W.; Peng, L. L.; Qian, Y. M.; Zhang, X.; Xie, Y. J.; Cha, J. J.; Yu, G. H. Dual Tuning of Ni–Co–A (A = P, Se, O) Nanosheets by Anion Substitution and Holey Engineering for Efficient Hydrogen Evolution. *J. Am. Chem. Soc.* **2018**, *140*, 5241–5247.

(26) Rui, K.; Zhao, G. Q.; Chen, Y. P.; Lin, Y.; Zhou, Q.; Chen, J. Y.; Zhu, J. X.; Sun, W. P.; Huang, W.; Dou, S. X. Hybrid 2D Dual-Metal-Organic Frameworks for Enhanced Water Oxidation Catalysis. *Adv. Funct. Mater.* **2018**, *28*, No. 1801554.

(27) Wang, P. P.; Sun, H.; Ji, Y.; Li, W.; Wang, X. Three-Dimensional Assembly of Single-Layered MoS<sub>2</sub>. *Adv. Mater.* **2014**, *26*, 964–969.

(28) Zhu, J.; Yin, Z.; Yang, D.; Sun, T.; Yu, H.; Hoster, H. E.; Hng, H. H.; Zhang, H.; Yan, Q. Hierarchical hollow spheres composed of ultrathin Fe<sub>2</sub>O<sub>3</sub> nanosheets for lithium storage and photocatalytic water oxidation. *Energy Environ. Sci.* **2013**, *6*, 987–993.

(29) Luo, Y.; Bernot, K.; Calvez, G.; Freslon, S.; Daiguebonne, C.; Guillou, O.; Kerbellec, N.; Roisnel, T. 1,2,4,5-Benzene-tetra-carboxylic

acid: a versatile ligand for high dimensional lanthanide-based coordination polymers. *CrystEngComm* **1882-1896**, 2013, 15.

(30) Mullins, D. R.; Overbury, S. H.; Huntley, D. R. Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces. *Surf. Sci.* **1998**, *409*, 307–319.

(31) Maiti, S.; Pramanik, A.; Mahanty, S. Extraordinarily High Pseudocapacitance of Metal Organic Framework Derived Nanostructured Cerium Oxide. *Chem. Commun.* **2014**, *50*, 11717–11720.

(32) Hierso, J.; Sel, O.; Ringuede, A.; Laberty-Robert, C.; Bianchi, L.; Grosso, D.; Sanchez, C. Design, Synthesis, Structural and Textural Characterization, and Electrical Properties of Mesoporous Thin Films Made of Rare Earth Oxide Binaries. *Chem. Mater.* **2009**, *21*, 2184– 2192.

(33) Cai, M. Q.; Li, R.; Wang, F.; Guo, X.; Bai, Q.; Sun, L. M.; Han, X. G. Architecture of designed hollow indium oxide microspheres assembled by porous nanosheets with high gas sensing capacity. *J. Alloys Compd.* **2017**, *729*, 222–230.

(34) Wang, F.; Zhuo, H. Y.; Han, X. G.; Chen, W. M.; Sun, D. Foamlike CoO@N,S-codoped carbon composites derived from a welldesigned N,S-rich Co-MOF for lithium-ion batteries. *J. Mater. Chem. A* **2017**, *5*, 22964–22969.

(35) Dhavale, V. M.; Gaikwad, S. S.; Kurungot, S. Activated nitrogen doped graphene shell towards electrochemical oxygen reduction reaction by its encapsulation on Au nanoparticle (Au@N-Gr) in water-in-oil "nanoreactors". J. Mater. Chem. A **2014**, *2*, 1383–1390.

(36) Zhao, G. F.; Yang, F.; Chen, Z. J.; Liu, Q. F.; Ji, Y. J.; Zhang, Y.; Niu, Z. Q.; Mao, J. J.; Bao, X. H.; Hu, P. J.; Li, Y. D. Metal/oxide interfacial effects on the selective oxidation of primary alcohols. *Nat. Commun.* **2017**, *8*, No. 14039.

(37) Wang, Q.; Cai, X. C.; Liu, Y. Q.; Xie, J. Y.; Zhou, Y.; Wang, J. Pd nanoparticles encapsulated into mesoporous ionic copolymer: Efficient and recyclable catalyst for the oxidation of benzyl alcohol with O<sub>2</sub> balloon in water. *Appl. Catal. Environ.* **2016**, *189*, 242–251.

(38) Iraqui, S.; Kashyap, S. S.; Rashid, M. H. NiFe<sub>2</sub>O<sub>4</sub> nanoparticles: an efficient and reusable catalyst for the selective oxidation of benzyl alcohol to benzaldehyde under mild conditions. *Nanoscale Adv.* **2020**, *2*, 5790–5802.

(39) Jing, K. Q.; Ma, W.; Ren, Y. H.; Xiong, J. H.; Guo, B. B.; Song, Y. J.; Liang, S. J.; Wu, L. Hierarchical Bi<sub>2</sub>MoO<sub>6</sub> spheres in situ assembled by monolayer nanosheets toward photocatalytic selective oxidation of benzyl alcohol. *Appl. Catal. Environ.* **2019**, *243*, 10–18.

(40) Fu, Y. H.; Sun, L.; Yang, H.; Xu, L.; Zhang, F. M.; Zhu, W. D. Visible-light-induced aerobic photocatalytic oxidation of aromatic alcohols to aldehydes over Ni-doped NH<sub>2</sub>-MIL-125(Ti). *Appl. Catal. Environ.* **2016**, *187*, 212–217.

(41) Japa, M.; Tantraviwat, D.; Phasayavan, W.; Nattestad, A.; Chen, J.; Inceesungvorn, B. Simple preparation of nitrogen-doped  $TiO_2$  and its performance in selective oxidation of benzyl alcohol and benzylamine under visible light. *Colloids Surf. A Physicochem. Eng. Aspects* **2021**, *610*, No. 125743.

(42) Unsworth, C. A.; Coulson, B.; Chechik, V.; Douthwaite, R. E. Aerobic oxidation of benzyl alcohols to benzaldehydes using monoclinic bismuth vanadate nanoparticles under visible light irradiation: Photocatalysis selectivity and inhibition. *J. Catal.* **2017**, 354, 152–159.

(43) Cui, Z. Q.; Wang, W. K.; Zhao, C. J.; Chen, C.; Han, M. M.; Wang, G. Z.; Zhang, Y. X.; Zhang, H. M.; Zhao, H. J. Spontaneous Redox Approach to the Self-Assembly Synthesis of  $Au/CeO_2$ Plasmonic Photocatalysts with Rich Oxygen Vacancies for Selective Photocatalytic Conversion of Alcohols. *ACS Appl. Mater. Interfaces* **2018**, *10*, 31394–31403.

(44) Zhang, J. H.; Meng, S. G.; Ye, X. J.; Ling, C. C.; Zhang, S. J.; Fu, X. L.; Chen, S. F. Synergistic effect of photocatalysis and thermocatalysis for selective oxidation of aromatic alcohols to aromatic aldehydes using  $Zn_3In_2S_6@ZnO$  composite. *Appl. Catal. Environ.* **2017**, *218*, 420–429.