

Article

Nanoreactor of MOF-Derived Yolk-Shell Co@C-N: Precisely Controllable Structure and Enhanced Catalytic Activity

Huirong Chen, Kui Shen, Qing Mao, Junying Chen, and Yingwei Li

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b03270 • Publication Date (Web): 09 Jan 2018

Downloaded from http://pubs.acs.org on January 10, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Nanoreactor of MOF-Derived Yolk-Shell Co@C-N: Precisely Controllable Structure and Enhanced Catalytic Activity

Huirong Chen, Kui Shen,* Qing Mao, Junying Chen, and Yingwei Li*

State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

ABSTRACT: Hollow yolk-shell nanoreactors are of great interest in heterogeneous catalysis owing to their improved mass transfer ability and stability. Here, we report a facile and straight route to synthesize a highly efficient and recyclable yolk-shell Co@C-N nanoreactor with controllable properties by the direct thermolysis of a hollow Zn/Co-ZIF precursor. Based on systematical optimization of the pyrolysis temperature and the shell-thickness of Zn/Co-ZIFs, we could completely anchor and stabilize uniform Co nanoparticles (NPs) in the hollow yolk, accommodated by the Co-ZIF derived Ndoped carbon nanosheets. This nanosheet-assembled yolk was further confined by a permeable and robust N-doped carbon (C-N) shell to protect the Co NPs against leaching and also enabled the reaction to take place in the hollow void. Consequently, the optimal yolk-shell Co@C-N nanoreactor showed a significantly enhanced catalytic activity for the aqueous oxidation of alcohols, yielding >99% conversion under atmospheric air and base-free conditions, which was much higher than that of the solid counterparts derived from pure ZIF-67 and solid core-shell ZIF-67@ZIF-8 precursors (with 14% and 59% conversion under the same reaction condition, respectively). The enhanced catalytic activity should be attributed to the yolk-shell structure that could facilitate the transport of reactant/product, and the strong interaction between the Co NPs and N-doped carbon nanosheet to afford positive synergistic effects. Moreover, this catalyst also showed good recyclability, magnetically reusability and general applicability for a broad substrate scope, further highlighting the structure superiority of our yolk-shell nanoreactor. This strategy might open an avenue to synthesize various hollow yolk-shell nanoreactors with controllable structures and enhanced catalytic performances.

KEYWORDS: nanoreactor, hollow yolk-shell nanostructure, metal-organic frameworks, Co-based catalysts, oxidation of alcohols

INTRODUCTION

In recent years, hollow yolk-shell nanostructures have received increasing attention as they can be used as the most ideal framework in nanoreactor for the catalytic transformation of organic molecules.¹ As compared to their solid core-shell counterparts, the void space between the shell and core in the hollow system provides a unique room for confined catalysis.² Moreover, the permeable shell enables facile mass transportation for the reactive species and protects the catalytically active sites against leaching even under harsh reaction conditions, leading to enhanced activity and stability for hollow yolkshell materials.³

For the synthesis of hollow nanoreactors, the most important and challenging part would be selective functionalization of the interior space in the hollow nanoshell, which allows chemical reactions to take place within the protected cavity.⁴ A few strategies have been developed for the preparation of yolk-shell architectures during the past few years. In these approaches, hard/soft-templating, the Kirkendall effect, the Ostward ripening, ship-in-abottle, post-impregnation, and selective etching are widely employed as the core technologies.⁵ However, most of these approaches yielded yolk@shell nanostructures

composed of a single-core nanocrystal and a porous nanoshell.⁶ For the catalytic applicability of a nanoreactor, it is more desirable for the cavity to possess large numbers of tiny cores rather than a single core in large size. Nevertheless, efficient synthetic methods for multiyolk@shell nanostructures have hardly been explored so far.⁷ The reason is that the tiny nanocrystals, if left moveable within the cavity, will undergo an inevitable sintering process to form a single large particle in order to lower their surface energies.⁸ As it is well known, the particle size is critical for the use of nanoparticles (NPs) in heterogeneous catalysis. A reduction in particle size usually leads to a significant increase in reactivity due to the higher surface-to-volume ratio of the active species.^{1a} Therefore, to obtain a highly efficient and stable hollow yolk-shell nanostructure the key point lies in a balance between the following two factors, i.e., embedding tiny multi-core particles in the hollow cavity as much as possible and simultaneously protecting the small particles from serious aggregation during the preparation and reaction processes. Given these premises, we proposed that introduction of nitrogen-doped carbon nanosheets into the hollow cavity of the nanostructure would be a promising strategy to tackle this issue, because they cannot only stabilize the tiny metal NPs in a highly dispersed fashion

ACS Paragon Plus Environment



Figure 1. (a) Schematic illustration of the synthesis of hollow yolk-shell Co@C-N nanoreactors. (b) Schematic illustration of the synthesis of solid Co-based nanocomposites by direct pyrolysis of ZIF-67 nanocrystals. (c) Schematic illustration of the synthesis of solid core-shell Co-based nanocomposites by pyrolysis of core-shell ZIF-67@ZIF-8 precursors.

but also enhance the catalytic activity by providing a synergistic effect to the metal active sites.

Metal-organic frameworks (MOFs) built with metal ions and organic ligands have attracted continuously increasing interest due to their high surface area, porosity, and chemical tunability.9 More recently, a great deal of research has been focused on preparation of new metalcarbon composites for advanced applications including heterogeneous catalysis, electrochemistry, and gas adsorption, by using MOFs as sacrificial templates.¹⁰ For example, thermolysis of ZIF-67 has been frequently employed as a facile approach to synthesize novel nitrogendoped carbon supported Co materials." However, this strategy would inevitably result in serious aggregation of Co NPs at high pyrolysis temperatures (Figure 1b). Therefore, we attempted to employ a core-shell structure ZIF-67@ZIF-8 as sacrifice template (Figure 1c). Although this method could effectively address the issue of Co aggregation, achieving highly dispersed Co NPs on N-doped carbon as the multi-core, the resultant core-shell material also had a low surface area and solid structure together with an unsatisfactory ability of mass transfer, which are certainly unfavorable for heterogeneous catalytic reactions. In these regards, it would be a more reasonable choice if we used MOFs with more sophisticated structures as precursors to fabricate a hollow core-shell nanocomposite.

Herein, we developed a facile strategy to prepare multi-yolk@shell nanostructures by direct thermolysis of a single hollow Zn/Co-ZIF precursor (Figure 1a). The obtained hollow Co@C-N materials feature a high surface area, which consists of an N-doped carbon (C-N) nanosheet anchored Co core and a porous C-N shell with controllable structures. Accordingly, the porous C-N shell would enable facile mass transfer and the C-N nanosheets in the void space could play important roles in stabilizing the tiny Co NPs and also providing electronic synergistic effects between them. These characters endow this unique hollow yolk-shell Co@C-N nanoreactor with superior catalytic activities in aerobic oxidation of alcohols under neat water and base-free conditions using air as a green oxidant, as compared to the Co-based materials prepared by using ZIF-67 and ZIF-67@ZIF-8 as precursors (Figure 1b and 1c). Furthermore, these highly efficient hollow nanoreactors are easily separated and recovered by a magnet due to the presence of magnetic Co NPs and show no significant loss of catalytic activities after reuses.

59

60

EXPERIMENTAL SECTION

Chemicals. All chemicals were of analytic grade and purchased from commercial suppliers.

Preparation of hollow Zn/Co-ZIF. In a typical synthesis, Co(NO3)2•6H2O (1.098 g), Zn(NO3)2•6H2O (1.116 g) and 2-methylimidazole (1.232 g) were dissolved in 15 mL methanol, 15 mL methanol, and 30 mL methanol, respectively, to obtain three methanolic solutions. After stirring for 10 min at room temperature, the methanolic solution of Co(NO₃)₂ was slowly injected into the solution of 2-methylimidazole at room temperature. After reacting for a certain time t, the methanolic solution of Zn(NO₃)₂ was added into the above mixed solution. After stirring for another 5 min, the resulting suspension was transferred to a Teflon-lined stainless-steel autoclave and hydrothermally treated at 120 °C for 4 h. The formed powder was collected by centrifugation, washed thoroughly with methanol, and dried overnight at 110 °C. By adjusting the value of t (0.5, 1 and 5 min), we were able to controllably synthesize three kinds of hollow Zn/Co-ZIF with different shell thicknesses (denoted as Zn/Co-ZIF(0.5), Zn/Co-ZIF(1) and Zn/Co-ZIF(5), respectively).

Preparation of ZIF-67@ZIF-8. The procedure was the same as that for the synthesis of hollow Zn/Co-ZIF but without the hydrothermal treatment.

Preparation of ZIF-67. ZIF-67 was prepared according to the previous reports¹² but with some modifications. In a typical synthesis, $Co(NO_3)_2 \cdot 6H_2O$ (1.091 g) was dissolved into methanol (30 mL) to form a solution. 2-Methylimidazole (0.616 g) was dissolved in methanol (20 mL) to generate another clear solution. Then the two methanolic solutions were mixed together under stirring for 5 min. The mixture was kept on reacting at room temperature for 12 h. The resulting bright purple powders were collected by centrifugation, washed thoroughly with methanol, and dried overnight at 110 °C.

Preparation of hollow yolk-shell Co@C-N nanoreactor. In a typical synthesis, o.5 g of hollow Zn/Co-ZIF was placed in a tubular furnace and then heated at 800 °C for 3 h with a heating rate of 1 °C/min from room temperature under argon atmosphere. For comparison purposes, another two control samples were also prepared by using pure ZIF-67@ZIF-8 or ZIF-67 with similar crystal sizes as single precursor under the same thermal conditions, which were denoted as ZIF-67@ZIF-8-800 and ZIF-67-800, respectively.

Procedures for the aerobic oxidation of alcohols. For a typical catalytic test, alcohol (0.1 mmol), H_2O and a certain amount of catalyst (10 mol% Co) were added in a Schlenk tube. The reaction mixture was stirred at 110 °C under atmosphere air condition. After a given reaction time, 100 µL of n-hexadecane as the internal standard was added. Then the product was extracted with ethyl acetate from the liquid mixture, and subsequently subjected to GC-MS (Agilent, 7890B GC/5977A MS) equipped with a HP-5 MS capillary column (0.25 mm × 30 m).

Characterization. Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku diffractometer (D/MAX/IIIA, 3 kW) using Cu Ka radiation (40 kV, 30 mA, λ =0.1543 nm). BET surface areas and pore structure were measured with N2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before the measurements, the samples were degassed at 150 °C for 4 h. X-ray photoelectron spectroscopy (XPS) was performed by using Kroatos Axis Ultra DLD system with a base pressure of 10⁻⁹ Torr. The cobalt contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument. The surface morphology of the materials was investigated by a high-resolution scanning electron microscopy (SEM, MERLIN of ZEISS). The structure and the element mapping were determined by a high resolution transmission electron microscope (TEM, JEOL, JEM-2100F) with EDX analysis (Bruker Xflash 5030T) operated at 200 kV.

RESULTS AND DISCUSSION

The preparation strategy for the hollow Co@C-N yolkshell nanoreactor is briefly illustrated in Figure 1a. The synthesis started with the formation of a single ZIF-67 nanocrystal which was then coated with a ZIF-8 layer to obtain a core-shell ZIF-67@ZIF-8 structure (Figure S1). The as-prepared ZIF-67@ZIF-8 was then treated with Co²⁴ in methanol at 120 °C for 4 h to generate a hollow Zn/Co-ZIF material (Figure S₂).¹³ As shown in Figure S₂ and S₃, both of pure ZIF-67 and ZIF-67 phase in ZIF-67@ZIF-8 core-shell structure can be transformed into a new Co-ZIF phase by solvothermal reaction in a methanol solution containing cobalt ions.14 Typically, in order to prepare Zn/Co-ZIF with a relatively thin, medium or thick shell, we choose three crystallization times of 0.5, 1, and 5 minutes, respectively, to regulate the growth process of ZIF-67 (Figure S4). As a result, three samples with different mean shell thicknesses of 138.8±16.5, 85.5±15.6 and 34.7±8.6 nm (Figure S5) (denoted as Zn/Co-ZIF(0.5), Zn/Co-ZIF(1) and Zn/Co-ZIF(5), respectively) were successfully prepared. The PXRD patterns of all the obtained Zn/Co-ZIF materials matched well with the pristine ZIF-8 and ZIF-67, confirming their isostructural nature and high crystallinity (Figure S6). From the TEM images (Figure S₅), we confirmed that all the resultant particles possessed a dodecahedron-shaped hollow interior, together with some Co-ZIF nanosheets confined by the ZIF-8 shell.

Finally, the Zn/Co-ZIF was subjected to hightemperature pyrolysis at 800 °C under Ar atmosphere to yield the desired hollow Co@C-N nanoreactors. The assynthesized nanocomposites were denoted as Co@C-N(0.5)-800, Co@C-N(1)-800 and Co@C-N(5)-800, respectively, corresponding to the different Zn/Co-ZIF precursors with various shell-thicknesses (i.e., Zn/Co-ZIF(0.5), Zn/Co-ZIF(1) and Zn/Co-ZIF(5)).

The morphologies and structures of the Zn/Co-ZIF derived nanocomposites can be revealed by SEM and TEM images. As shown in Figure 2, both of Co@C-N(0.5)



Figure 2. SEM (a, e, i), TEM (b, c, f, g, j, k) and EDS mapping (d, h, l) images of Co-based materials with different shell-thickness: (a-d) Co@C-N(0.5)-800, (e-h) Co@C-N(1)-800, (i-l) Co@C-N(5)-800.

-800 and Co@C-N(1)-800 basically retained the original rhombic dodecahedron shape with an average size of around 400 nm, while Co@C-N(5)-800 showed a sphere morphology with its surface very smooth and less angularly distinct (Figure S7). Obviously, the relative thin shell of Zn/Co-ZIF(5) lacked enough carbon source to keep its dodecahedron morphology during the calcination process at high temperature (Figure S5). The TEM images (Figure 2 and Figure S8) revealed that the as-obtained nanocomposites were of a hollow yolk-shell structure, in which the Co doped C-N nanosheet was the "core" and the porous N-doped graphite carbon was the "shell". The HRTEM (Figure S8c) and corresponding FFT (Figure S8d) images clearly showed that the interplanar spacing of the selected nanoparticle in the hollow void was ca. 0.21 nm, which could be assigned to the (111) plane of Co NPs.¹⁵ This result indicated that Co(II) in the Co-ZIF had been reduced into metallic Co which was uniformly distributed in the C-N nanosheet (also derived from the Co-ZIF). The STEM and corresponding EDS mapping images of an individual Co@C-N particle (Figure 2d, h and l) revealed that the C and N elements were homogeneously distributed in the shell layer while the Co NPs were mainly dispersed in the core section of the nanocomposites. For the Co@C-N(5)-800 sample, a small amount of Co NPs could be observed in the C-N shell area, probably due to the relative large

quantity of Co(II) ions in the precursor that were more easily induced by the ZIF-8 derived N-doped graphitic carbon and thus moved to the shell layer. It was noteworthy that there were also some C and N elements distributed in the core section, exactly in the place where the Co NPs existed, further demonstrating the Co-C-N nanosheet structure confined within the hollow cavity. The strong interaction between the Co NPs and C-N nanosheets could be helpful in stabilizing the tiny Co NPs under harsh reaction conditions and also offer an excellent synergistic effect to improve the catalytic performances.

The crystal structures of the Co@C-N(0.5)-800, Co@C-N(1)-800 and Co@C-N(5)-800 were identified by XRD analysis (Figure S9). All these Co@C-N materials exhibited similar characteristic diffraction with two peaks at 44.4 and 51.6°, which could be attributed to the metallic Co (JCPDS no. 15-0806).¹⁶ More intensive diffraction was observed as the cavity size increased (from Co@C-N(0.5)-800 to Co@C-N(5)-800), implying an increase in Co contents of the particles. The surface areas and pore structure of the Co@C-N materials were measured by nitrogen adsorption/desorption isotherms at 77 K (Figure S9b). All the samples exhibited a high surface area (Table S1) ranging from 600 to 1000 m² g⁻¹, suggesting highly porous structures. Hysteresis loops between adsorption and desorption branches could be clearly observed at *P*/*P*₀ of 0.5-

3

4

5 6

7 8

9

10

15

16 17

18

19

20 21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60



Figure 3. SEM (a1, b1, c1), TEM (a2-3, b2-3, c2-3), EDS mapping (a4, b4, c4) images and the Co NPs size-distribution profiles (a5, b5, c5) of Co-based materials obtained by pyrolyzing the hollow Zn/Co-ZIF(1) precursors at different temperature ranging from 700 to 1000 °C: (a1-5) Co@C-N(1)-700, (b1-5) Co@C-N(1)-900, (c1-5) Co@C-N(1)-1000.

1 for all three materials, demonstrating the presence of mesopores.¹⁷ Typically, the Co@C-N(1)-800 achieved the highest Brunauer-Emmett-Teller (BET) surface area of 965 $m^2 g^{-1}$, far exceeding that of Co@C-N(0.5)-800 (733 m^2 g^{-1}) and Co@C-N(5)-800 (617 m² g⁻¹). In addition, to determine the magnetic property of the samples, roomtemperature VSM magnetization curves were measured and shown in Figure S9. The saturation magnetization intensity of Co@C-N(0.5)-800, Co@C-N(1)-800 and Co@C-N(5)-800 was 2, 9, and 22 emu g⁻¹, respectively, which agreed well with the AAS results, i.e., the higher Co contents the stronger saturation magnetization (Table S₁). Neither obvious remanence nor coercivity was observed in the magnetization curves, indicating the superparamagnetic character of the materials,¹⁸ which was beneficial to an easy separation of catalysts from the reaction solution with a magnet.

In order to understand the effect of calcination temperature on properties of the final products, a series of control experiments were carried out by varying the annealing temperature from 700 to 1000 °C, using the same hollow Zn/Co-ZIF(1) as precursor. The resultant material was denoted as Co@C-N(1)-700, Co@C-N(1)-800, Co@C-N(1)-900, and Co@C-N(1)-1000, respectively. SEM images (Figure 3) showed that at relatively low temperatures (700 and 800 °C), the obtained particles basically maintained their original rhombic dodecahedron shape; while at higher temperatures (900 and 1000 °C) some of the hollow structures had already been broken. These findings could be further confirmed by the TEM and EDS elemental images (Figure 3). Only Co@C-N(1)-700 and Co@C-N(1)-800 exhibited a well-defined hollow yolk-shell structure. It can also be seen that, for Co@C-N(1)-700 and

Co@C-N(1)-800, Co NPs were accommodated by the C-N nanosheet and highly dispersed in the confined hollow cavity with a small and uniform particle size of 12.1 \pm 2.4 nm and 19.4 \pm 3.9 nm, respectively. However, Co in the Co@C-N(1)-900 was seriously aggregated into much bigger particles (around 100 nm) and some of them had migrated to the outside C-N shell layer. The Co NPs in Co@C-N(1)-1000 were even bigger with a mean size of > 150 nm (Figure 3). These results suggested that the thermolysis temperature played important roles in determining the Co particle sizes, and the final structures and morphologies of the Co@C-N nanocomposites.

To gain more structure and composition information about the Co@C-N materials obtained at different temperatures, XRD, Raman and nitrogen adsorption/desorption experiments were also performed. The XRD patterns (Figure S10) of all these composites confirmed the formation of metallic Co.¹⁶ Higher calcination temperatures facilitated the production of a Co phase with higher crystallization degree. In the Raman spectra of these MOFs-derived materials, the D band could be observed at 1315 cm⁻¹ due to the disordered features caused by lattice defects.¹⁹ The G band at 1590 cm⁻¹ could be assigned to the first-order scattering of the E_{2g} vibrational mode within aromatic carbon rings.¹⁹ The relative intensity ratio of D to G band (I_D/I_G) in the Raman spectra was 2.51, 2.42, 2.01 and 1.91 for Co@C-N(1)-700, Co@C-N(1)-800, Co@C-N(1)-900, and Co@C-N(1)-1000, respectively, implying that the crystallization degree of graphitic carbon was increased as the ratio declined. In the nitrogen adsorption isotherms, all the samples showed a similar type I plus type IV adsorption profile (Figure S10), indicating their micro/mesopore structures.¹⁷ The BET sur-



Figure 4. High-resolution Co 2p (a) and N Is (b) XPS spectra of Co@C-N(1)-700, Co@C-N(1)-800, Co@C-N(1)-900, and Co@C-N(1)-1000. (c) The contents of pyridinic-N, Co-N_X, pyrrolic-N, and graphitic-N in the Co@C-N(1)-T obtained at different temperatures. (d) Schematic illustration of the possible N bonding configurations.

face area of Co@C-N(1)-700, Co@C-N(1)-800, Co@C-N(1)-900, and Co@C-N(1)-1000 was 549, 965, 1241, and 1688 m² g⁻¹, respectively. The BET surface area increased with the thermolysis temperature, which may be attributed to the high graphitic degree of the carbon under high thermolysis temperature, in agreement with the Raman results.

X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical states and coordination environment of elements in the samples. In the cobalt region (Figure 4a), only peaks characteristic of metallic Co were observed with typical binding energies (BE) of 793.5 and 778.7 eV, assigned to Co 2p1/2 and Co 2p3/2 electrons of Co metal, respectively.²⁰ Deconvolution analysis revealed that the Co region at ca 778.7 eV consisted of three peaks at 778.7, 780.1, 782.7 eV and 785.4, respectively (Figure S11). The binding energy at 780.1 eV and 785.4 eV (satellite peak) were matched well with the character of Co-O bonding structure.²¹ These results indicated there also existed a small amount of cobalt oxide in all samples, probably due to the partial oxidation of Co nanoparticle surface by air during synthesis and storage processes. This observation also suggested that part of the Co atoms could have some interaction with the nitrogen or carbon atoms surrounding the Co NPs. Four peaks in the N 1s spectra at 398.4, 399.1, 400.2 and 401.3 eV (Figure 4b) were attributed to pyridinic-N, Co-N_x, pyrrolic-N and graphitic-N, respectivly.²² As shown in Figure 4d, pyridinc-N substituted a carbon atom in C6 ring and bonded with two sp² carbon atoms. Graphitic-N bonded to three sp² carbon atoms within the graphitic carbon plane. Pyrrolic-N was in a five-membered ring, donating two electrons to the π system. The N atom of Co-N_x was referred to the one that bonded with Co NPs. The total N contents decreased with an increase in pyrolysis temperature (Figure 4c). However, the percentage of graphitic-N in the total N atoms (graphitic-N: total-N) increased when the thermolysis temperature was enhanced, suggesting the



Figure 5. (a, b) TEM and (c) STEM and EDS mapping images of ZIF-67@ZIF-8-800; (d, e) TEM and (f) STEM and EDS mapping images of ZIF-67-800.

higher the temperature, the higher the graphitation degree. It was noteworthy that the contents of Co-N_x in the Co@C-N(1)-800 was higher than that of the other three materials. It is believed that such a coordination interaction between the nitrogen and cobalt was propitious to improve the catalytic activity and prevent Co against serious aggregation in the reaction process.

In order to demonstrate the advantages of hollow yolk-shell nanostructures, we further prepared two other Co-based materials by direct pyrolysis of a solid core-shell ZIF-67@ZIF-8 or a pure ZIF-67 precursor under the same calcination condition. The obtained materials were denoted as ZIF-67@ZIF-8-800 and ZIF-67-800, respectively. XRD patterns (Figure S12) showed similar diffraction peaks as the hollow Co@C-N nanoreactor, indicating the presence of metallic Co. However, the structure, morphology and Co NPs environment were quite different from each other. As revealed by the TEM and EDS images (Figure 5), Co NPs in the ZIF-67@ZIF-8-800 were mostly dispersed in the solid core where the ZIF-67 precursor located, which were tightly encapsulated by a ZIF-8 derived C-N shell layer. For ZIF-67-800, Co NPs seriously agglomerated and randomly distributed in the whole C-N support. Nitrogen adsorption/desorption tests (Figure S13) showed micropore structure for both ZIF-67@ZIF-8-800 and ZIF-67-8, with a much lower BET surface area (356 m² g^{-1} for ZIF-67-800 and 570 m² g⁻¹ for ZIF-67@ZIF-8-800) as compared to that of the hollow Co@C-N(1)-800. All these results indicated that the unique hollow Zn/Co-ZIF precursor led to the formation of hollow yolk-shell Co@C-N nanoreactor possessing comprehensively excellent properties for potential catalytic applications.

The as-prepared Co-based materials were employed as catalysts for the aerobic oxidation of alcohols. The reactions were performed under base-free conditions using atmospheric pressure of air as the green oxidant. Oxidation of 1-phenylethanol in toluene at 100 °C gave relatively low conversions with >99% acetophenone selectivities within 1 h over the Co@C-N composites (Table S2, entries 1-4). Among the four Co@C-N materials, Co@C-N(1)-800 was the most active one for 1-phenylethanol oxidation

3 4 5

Table 1. Aqueous oxidation of 1-phenylethanol catalyzed by various catalysts^{*a*} ОН ^

	Catalyst		
Entry	Catalyst	$\operatorname{Con.}(\%)^b$	Sel.(%) ^b
1	Co@C-N(0.5)-800	33	>99
2	Co@C-N(1)-800	>99	>99
3	Co@C-N(5)-800	56	>99
4	ZIF-67-800	14	>99
5	ZIF-67@ZIF-8-800	59	>99
6	ZIF-8-800	5	>99
7	Activated carbon	<1	>99
8 ^c	C-N(1)-800	9	>99
9^d	Co/C	29	>99
10	Co(NO3)2	<1	>99

^a Reaction conditions: 1-phenylethanol (0.1 mmol), catalyst (10 mol% Co), water (2 mL), air (1 bar), 110 °C, 1 h. Conversion and selectivity were determined by GC. ^c The as-synthesized Co@C-N(1)-800 was immersed in aqua regia to remove Co.^d Co/C was prepared by an impregnation method.

(Table S2, entry 2). Using the Co@C-N(1)-800 catalyst, different solvents were screened, and water was shown to be the best one (Table S2, entry 7). When the temperature was increased to 110 °C, acetophenone was obtained in almost quantitative yield (Table S2, entry 13). The reaction also proceeded when the Co dosage was significantly decreased (Table S2, entry 14), and the conversion should be able to be enhanced by simply prolonging the reaction time. It was evident that the oxidant (i.e., air) was inevitable for this oxidation transformation (Table S2, entry 15). In the absence of any catalyst, the reaction hardly occurred under the investigated condition (Table S2, entry 16). A series of carbon- or Co- based materials were prepared and also tested as reference catalysts in the aqueous oxidation of 1-phenylethanol under the optimized condition. It can be seen that among the three hollow Co@C-N nanocomposites with different shell thicknesses, the Co@C-N(1)-800 with medium shell thickness exhibited much better catalytic performance than Co@C-N(0.5)-800 and Co@C-N(5)-800 (Table 1, entries 1-3). The declined activity over Co@C-N(0.5)-800 was probably due to the thick C-N shell that was not favorable for efficient mass transfer. For the Co@C-N(5)-800, the lack of adequate C-N support would be insufficient to provide an excellent synergistic effect.

For comparison, the catalytic activities of other MOFderived materials were also examined. ZIF-67-800, which also had a C-N support but the Co NPs were seriously

 Table 2. Aqueous oxidation of various alcohols catalyzed
 by Co@C-N-800^a

$R_1 \xrightarrow{OH} R_2 \xrightarrow{Co@C-N(1)-800} R_1 \xrightarrow{O} R_2$					
Entry	Substrate	Product	Conv. (%) ^b	Sel. (%) ^b	
1	OH C		>99	>99	
2	F OH	F	>99	>99	
3	Br	Вг	>99	>99	
4	CI CI CI	CI	>99	>99	
5 [°]	OH		>96	>99	
6 ^c	OH		69	>99	
7	ОН		95	88	
8^{d}	он	ů.	78	95	
9 ^c	ОН		93	82	
10 ^c	ОСТОН		81	88	
11 ^c	О2N	O ₂ N O	94	85	
12 ^c	ОН		99	91	
13 ^c	СІ	CIO	96	90	
14 ^c	Вг	Br	99	92	
15 ^d	ОН		75	81	
16 ^d	ОН		99	90	
17 ^d	но	0	99	81	
18 ^d	И ОН	N O	93	75	
19 ^e	Отон		75	88	
20 ^e	осорон	o~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	82	95	

ACS Paragon Plus Environment

55 56

57

58

59

60

^{*a*} Reaction conditions: alcohol (0.1 mmol), catalyst (10 mol% Co), water (2 mL), air (1 bar), 110 °C, 1 h. ^{*b*} Conversion and selectivity were determined by GC. ^{*c*} 4 h. ^{*d*} 6 h. ^{*e*} 10 h.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51 52

53

54

55

56

57

58 59

60

aggregated, showed a very low conversion of 1phenylethanol (Table 1, entry 4). This result indicated that small and highly dispersed Co NPs were critical for achieving a high catalytic efficiency. ZIF-67@ZIF-8-800, which had a similar composition as Co@C-N(1)-800 but did not have a hollow cavity, afforded only a medium conversion under identical conditions (Table 1, entry 5), suggesting the importance of hollow structure in the composite for alcohol oxidation. It is worth noting that the complete transformation of 1-phenylethanol takes only one hour at 383 K over Co@C-N(1)-800, corresponding to a TOF value of 9.97 h^{-1} , which is higher than that of ZIF-67@ZIF-8-800 and ZIF-67-800, respectively (Table S3). In fact, Co@C-N(1)-800 was also much more efficient than most of the previously-reported non-noble catalysts even under a more moderate and/or green reaction condition (Table S₃). Furthermore, the heterogeneous nature of the catalyst was proved by a hot filtration experiment. As shown in Figure S14, the oxidation reaction of alcohol almost no longer proceeded after the filtration of catalyst when the conversion reached about 24.1%. AAS analysis of the reaction solution revealed that the Co content in the solution was below the detection limit, implying no significant leaching of the Co sites occurred during the oxidation process.

Only traces of conversions were obtained when using ZIF-8-800 and activated carbon as the catalyst (Table 1, entries 6, 7), demonstrating Co was the active site for the oxidation under the investigated conditions. Therefore, when the highly active Co@C-N(1)-800 was immersed in aqua regia to remove Co, it lost most of its activity in the oxidation of 1-phenyl-ethnanol (Table 1, entry 8). In addition, a Co/C catalyst, which was prepared by using a traditional impregnation method, showed only 29% conversion (Table 1, entry 9). Finally, the use of homogeneous $Co(NO_3)_2$ catalyst gave essentially no conversion (Table 1, entry 10), suggesting the reactions were mostly proceeded on the heterogeneous catalyst surface.

The substrate scope of the selective alcohol oxidation over Co@C-N(1)-800 was investigated under atmospheric air and base-free conditions. Various secondary benzylic alcohols bearing electron-donating or withdrawing groups gave the corresponding ketones in almost quantitative yields (Table 2, entries 1-5). 1-(Naphthalen-2-yl)ethanol also underwent oxidation smoothly and afforded 69% yield (entry 6). It was worth noting that the catalyst also displayed a high activity in the oxidation of cinnamyl alcohol (entry 7). It is well-known that aliphatic alcohols are more reluctant to aerobic oxidation,²³ but the Co@C-N(1)-800 material was also capable of selectively catalyzing these alcohols into the corresponding oxidation products in good yield (entry 8). Notably, excellent selectivities to the target products were obtained for most of the investigated substrates. The present catalytic system was also highly efficient for the oxidation of primary alcohols,

affording the corresponding aldehydes in good to excellent yields (entries 9-16). Moreover, polyhydric alcohol and alcohols containing heteroatoms such as nitrogen could also be oxidized smoothly to the corresponding carbonyl compounds in high yields (entries 17-19). To our delights, the biomass-derived 5-hydroxymethylfurfural (HMF) could also be selectively oxidized into 2,5diformylfuran (DFF) in good yield (entry 20). All these results demonstrated the wide substrate tolerance of the Co@C-N(1)-800 material for selective oxidation of alcohols.

The effect of reaction temperature on the conversion of 1-phenylethanol was studied over the Co@C-N(1)-800, ZIF-67@ZIF-8-800, and ZIF-67-800 catalysts. The results were shown in Figure 6. It can be seen that with an increase in reaction temperature from 343 to 403 K the reaction rates were remarkably accelerated for all the catalysts. It was also found that under identical reaction condition, the reaction rate obtained on the Co@C-N(1)-800 catalyst were much faster than that of ZIF-67@ZIF-8-800 and ZIF-67-800. Apparent activation energy (Ea) and preexponential coefficients (A) in the Arrhenius equation (lnk=lnA-Ea/RT) were determined by plotting natural log of rate constant (k) against temperature (K). The calculated Ea values for the Co@C-N(1)-800, ZIF-67@ZIF-8-800 and ZIF-67-800 were 25.8, 45.5 and 70.8 kJ/mol, respectively (Figure 6d-f). The much lower activation energy of the Co@C-N(1)-800 should be related to the unique hollow yolk-shell nanoreactor which made it a more suitable candidate for the oxidation of alcohols. The effect of 1phenylethanol concentration on the reaction rate was investigated by using various initial 1-phenylethanol concentrations with other conditions constant. The plots in Figure S15a showed that the initial 1-phenylethanol concentration had no obvious influence on the reaction rate. The plot of the reaction rate versus 1-phenylethanol concentration in logarithmic scale was shown in the inset of Figure S15a, which gave a straight line with a slope of -0.1 (closed to zero), indicating that the oxidation reaction catalyzed by Co@C-N(1)-800 was zero-order in respect to the substrate concentration. Figure S15b exhibited the time courses of alcohol conversion in the presence of different Co concentrations. The results demonstrated that the reaction rates were strongly depended on the amount of catalyst and the oxidation reaction was first-order in respect to the Co concentration (inset of Figure S15b). For comparison, we also conducted another similar set of experiments by varying the 1-phenylethanol concentrations, but using the solid core-shell ZIF-67@ZIF-8-800 as catalyst (Figure S16). The reaction over ZIF-67@ZIF-8-800 was also proved to be zero-order in respect to substrate concentration. However, the reaction rate of ZIF-67@ZIF-8-800 was obviously much lower as compared to Co@C-N(1)-800 catalyst. Given the similarities between ZIF-67@ZIF-8-800 and Co@C-N(1)-800 in the aspect of compositions, it was reasonably suggested that the improved catalytic activity of Co@C-N(1)-800 could be attributed to its hollow yolk-shell structure that endowed it much better mass transfer ability when compared with the solid one.

2

3

4

5

6 7

8

9

10

11

12

13

14 15

16

17

18

19

24

31

32 33

34 35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

ACS Catalysis



Figure 6. Effects of reaction temperature on the oxidation of 1-phenylethanol over Co@C-N(1)-800 (a), ZIF-67@ZIF-8-800 (b) and ZIF-67-800 (c). The corresponding Arrhenius plots for Co@C-N(1)-800 (d), ZIF-67@ZIF-8-800 (e), and ZIF-67-800 (f). Reaction condition: 1-phenylethanol (0.1 mmol), catalyst (10 mol% Co), water (2 mL), air (1 bar).



Figure 7. Proposed mechanism for the oxidation of alcohols over the hollow yolk-shell Co@C-N(1)-800 nanoreactor. (a) Alcohol molecules pass through the porous C-N shell and are subsequently oxidized into the target products over the Co-C-N nanosheet in the confined hollow cavity. (b) Simplified mechanism model for oxidation of alcohols at the surface of Co NPs in the Co-C-N nanosheet.

On the basis of the experimental results and literature reports,²⁴ we proposed a possible reaction mechanism for catalytic oxidation of alcohols over the Co@C-N(1)-800 nanoreactor (Figure 7). In the nanocomposite, the Co NPs were confined in the hollow void stabilized by the N-doped carbon nanosheets. It was reported that the Co@C-N can be served as a Mott-Schottky type nanocatalyst for a specific reaction, in which the metal-N-carbon heterojunction could enhance the electron transfer and thus improve its catalytic performance.²⁵ The inserting of nitrogen atoms into carbon framework may adjust the position of valence band or conducting band of the doped carbon phase. Nitrogen-rich carbon with a relatively higher flat band potential than that of metallic Co, will accept electrons from Co nanoparticles until their Fermi level reaches equilibrium. Such a Schottky barrier will obviously result in an electron redistribution at the interface of cobalt and nitrogen-doped carbon and enrich the positive charges on the side of metallic cobalt. The more oxidative area thus forms on the side of the Co nanoparticles accordingly. In this case, the electron-poor Co nanoparticles are sufficiently strong to attract and activate O₂ for the further oxidation reaction of alcohol. Therefore, the oxygen molecules might be adsorbed onto the anionic Co site, probably in a superoxo-like form.²⁴ On the other hand, the alcohol molecules could pass through the porous C-N shell and also adsorbed on the surfaces of Co NPs. Subsequently, the cooperative action of O_2^{δ} with a neighbouring Co atom facilitated the break of the O-H bond of alcohol to form the Co-alcoholate and hydroperoxy intermediates (OOH). Finally, the Co-alcoholate species underwent a β -hydride elimination to produce the corresponding carbonyl compounds, along with recovery of the initial metallic Co site.

In a final set of experiments, we investigated the reusability of the highly active Co@C-N(1)-800 catalyst for the aerobic oxidation of 1-phenylethnol in aqueous medium. After reaction, the catalyst was easily separated with the assistance of an external magnet (Figure S17). As shown in Figure S17, the recovered catalyst could be reused at least 6 times without any remarkable loss of efficiency for the aerobic oxidation of 1-phenylethanol under the investigated conditions. The XRD patterns of the used Co@C-N(1)-800 (Figure S17c) indicated the diffraction peaks of the Co phase were almost identical to the fresh one, consistent with the TEM image, where no apparent Co aggregation could be observed on the recycled catalyst (Figure S17d).

CONCLUSION

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

60

In summary, we have developed a novel, highly efficient, and reusable Co-based nanoreactor system. The hollow multi-core yolk-shell Co@C-N nanocomposites were synthesized by direct thermolysis of designed hollow Zn/Co-ZIF precursors under inert atmosphere. The C-N shell thickness and the mean size of Co NPs could be controllably regulated by simply adjusting the preparation conditions (such as crystallization time and calcination temperature). It was found that the C-N nanosheets in the hollow cavity could effectively stabilize the Co NPs, and also provide excellent electronical synergistic effects. Moreover, the hollow confined cavity and porous C-N shell were helpful to facilitate the mass transportation and prevent the Co NPs against leaching. Owing to these unique properties, the hollow Co@C-N nanoreactors were highly efficient in aerobic oxidation of alcohols in neat water under atmospheric pressure of air and base-free conditions. Besides achieving high activity and selectivity to the target products, the developed catalytic system also featured a broad substrate scope for various alcohols. Furthermore, the catalysts could be easily recycled and reused without any significant loss of efficiency. The present reaction system might provide a simple, cost effective, and environmentally friend procedure for the preparation of carbonyl compounds from selective alcohols oxidation.

ASSOCIATED CONTENT

Supporting Information

Additional TEM and SEM images, XRD patterns, XPS and Raman spectra, magnetization curves, and reaction results This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail for K.S.: cekshen@scut.edu.cn. *E-mail for Y.L.: liyw@scut.edu.cn.

Notes

The authors declare no competing financial interest

ACKNOWLEDGMENT

This work was supported by the National Natural Science
Foundation of China (21436005, 21576095, 21606087), the
Fundamental Research Funds for the Central Universities
(2017PY004, 2017MS069), the State Key Laboratory of Pulp
and Paper Engineering (2017ZD04), and the Natural Science
Foundation of Guangdong Province (2016A050502004,
2017A030312005).

REFERENCES

(1) (a) Liu, A.; Traulsen, C. H. H.; Cornelissen, J. J. L. M. *ACS Catal.* **2016**, *6*, 3084-3091; (b) Zeng, T.; Zhang, X.; Wang, S.; Ma, Y.; Niu, H.; Cai, Y. *Chem. Eur. J.* **2014**, *20*, 6474-6481.

(2) (a) Wei, F.; Cao, C.; Sun, Y.; Yang, S.; Huang, P.; Song, W. *ChemCatChem* **2015**, *7*, 2475-2479; (b) Fodor, D.; Ishikawa, T.; Krumeich, F.; Bokhoven, J. A. V. *Adv. Mater.* **2015**, *27*, 1919-1923; (c) Dai, C.; Zhang, A.; Liu, M.; Gu, L.; Guo, X.; Song, C. *ACS Nano* **2016**, *10*, 7401-7408.

(3) (a) Huo, J.; Aguilera-Sigalat, J.; El-Hankari, S.; Bradshaw, D. *Chem. Sci.* **2015**, *6*, 1938-1943; (b) Cui, Z.; Chen, Z.; Cao, C.; Jiang, L.; Song, W. *Chem. Commun.* **2013**, *49*, 2332-2334.

(4) (a) Kim, S. M.; Jeon, M.; Kim, K. W.; Park J.; Lee, I. S. *J. Am. Chem. Soc.* **2013**, 135, 15714–15717; (b) Lee, J.; Kim, S. M.; Lee, I. S. *Nano Today* **2014**, *9*, 631-667; (c) Wong, Y. J.; Zhu, L.; Teo, W. S.; Tan, Y. W.; Yang, Y.; Wang, C.; Chen, H. *J. Am. Chem. Soc.* **2011**, 133, 11422–11425.

(5) (a) Zhang, L.; Roling, L. T.; Wang, X.; Vara, M.; Chi, M.; Liu, J.; Choi, S.; Park, J.; Herron, J. A.; Xie, Z.; Mavrikakis M.; Xia, Y. *Science* **2015**, *349*, 412-416; (b) Liu, H.; Joo, J. B.; Dahl, M.; Fu, L.; Zeng, Z.; Yin, Y. *Energy Environ. Sci.* **2015**, *8*, 286-296; (c) Dong, A. G.; Wang, Y.; Tang, Y.; Ren, N.; Zhang, Y.; Gao, Z. *Chem. Mater.* **2002**, *14*, 3217-3219; (d) Dai, C.; Zhang, A.; Li, J.; Hou, K.; Liu, M.; Song, C.; Guo, X. *Chem. Commun.* **2014**, 50, 4846-4848; (e) Lou, X.; Wang, Y.; Yuan, C.; Lee, J. Y.; Archer, L. A. *Adv. Mater.* **2006**, *18*, 2325-2329; (f) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711-714.

(6) (a) Lee, J.; Park, J. C.; Song, H. *Adv. Mater.* **2008**, *20*, 1523-1528; (b) Kim, J. G.; Kim, S. M.; Lee, I. S. *Small* **2015**, *11*, 1930-1938; (c) Yang, Y.; Liu, X.; Li, X.; Zhao, J.; Bai, S.; Liu, J.; Yang, Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 9164-9168.

(7) (a) Li, G.; Tang, Z. *Nanoscale* **2014**, 6, 3995-4011; (b) Liu, J.; Qiao, S.; Chen, J.; Lou, X.; Xing, X.; Lu, G. *Chem. Commun.* **2011**, 47, 12578–12591.

(8) (a) Sun, Q.; Ren, Z.; Wang, R.; Chen, W.; Chen, C. *J. Nanopart. Res.* **2011**, 13, 213–220; (b) Lou, X.; Yuan, C.; Rhoades, E.; Zhang, Q.; Archer, L. A. *Adv. Funct. Mater.* **2006**, *16*, 1679-1684.

(9) (a) Furukawa, H., Cordova, K. E., O'Keeffe M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444; (b) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. *Nat. Commun.* **2012**, *3*, 954; (c) Zhang, T.; Lin, W. *Chem. Soc. Rev.* **2014**, *43*, 5982-5993; (d) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, *112*, 836-868.

(10) (a) Shen, K.; Chen, X.; Chen, J.; Li, Y. ACS Catal. 2016, 6, 5887-5903; (b) Dong, Z.; Le, X.; Liu, Y.; Dong, C.; Ma, J. J. Mater. Chem. A 2014, 2, 18775-18785; (c) Chen, Y.; Cai, G.; Wang, Y.; Xu, Q.; Yu, S.; Jiang, H. Green Chem. 2016, 18, 1212-1217. (d) Wang, C. H.; Wang, H. Y.; Luo, R.; Liu, C.; Li, J. S.; Sun, X. Y.; Shen, J. Y.; Han, W. Q.; Wang, L. J. Chem. Eng. J. 2017, 330, 262-271; (e) Liu, C.; Wang, J.; Li, J. S.; Liu, J. Z.; Wang, C. H.; Sun, X. Y.; Shen, J. Y.; Han, W. Q.; Wang, L. J. J. Mater. Chem. A 2017, 5, 1211-1220; (f) Wang, C. H.; Liu, C.; Li, J. S.; Sun, X. Y.; Shen, J. Y.; Han, W. Q.; Wang, L. J. Chem. Commun. 2017, 53, 1751-1754.

(11) (a) Xia, Y.; Yan, Y.; Li, N.; Wu, H. B.; Lou, X.; Wang, X. *Nat. Energy* **2016**, *1*, 15006; (b) Sun, N.; Zhang, X.; Deng, C. *Nanoscale* **2015**, *7*, 6487-6491; (c) Zhong, W.; Liu, H.; Bai, C.; Liao, S.; Li, Y. *ACS Catal.* **2015**, *5*, 1850-1856.

(12) (a) Tang, J.; Salunkhe, R. R.; Liu, J.; Torad, N. L.; Imura, M.; Furukawa, S.; Yamauchi, Y. *J. Am. Chem. Soc.* **2015**, *137*, 1572-1580; (b) Avci, C.; Arinez-Soriano, J.; Carne-Sanchez, A.;

	Guillerm, V.; Carbonell, C.; Imaz, I.; Maspoch, D. Angew.
1	Chem. Int. Ed. 2016 , 54, 14417-14421.
2	(13) Chen, H.; Shen, K.; Chen, J.; Chen, X.; Li, Y. J. Mater.
3	Chem. A 2017, 5, 9937-9945.
4	(14) Tally, J., Zhally, F., Lu, H., Holly, A., Jially, H., Wu, T., Li Y Angew Chem Int Ed 2015 54 10880-10802
5	(15) Shen, K.; Chen, L.; Long, I.; Zhong, W.; Li, Y. ACS Catal.
6	2015 , 5, 5264-5271.
/	(16) Nam, K. M.; Shim, J. H.; Ki, H.; Choi, S. I.; Lee, G.; Jang,
8	J. K.; Jo, Y.; Jung, M. H.; Song, H.; Park, J. T. Angew. Chem. Int.
9	<i>Ed.</i> 2008 , <i>47</i> , 9504-9508.
10	(17) Shen, K.; Qian, W.; Wang, N.; Su, C.; Wei, F. J. Am.
11	Chem. Soc. 2013, 135, 15322-15325; (b) Zhao, J.; Hua, Z.; Liu, Z.;
12	Li, Y.; Guo, L.; Bu, W.; Cui, X.; Ruan, M.; Cnen, H.; Sni, J.
17	(18) Yamauraa M · Camiloa R L · Sampaioh L C · Macedo
14	M. A., Nakamurad, M.: Toma, H. E. I. Maan, Maan, Mater
15	2004 , 279, 210-217.
10	(19) Negri, F.; Castiglioni, C.; Tommasini, M.; Zerbi, G. J.
17	Phys. Chem. A 2002, 106, 3306-3317.
19	(20) (a) Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau,
20	L. W. M.; Gerson, A. R.; Smart, R. S. C. Appl. Surf. Sci. 2011,
20	257, 2717-2730; (b) Yan, J.; Zhang, X.; Shioyama, H.; Xu, Q. J.
27	Power Sour. 2010, 195, 1091-1904. (a) Wang 7 : Pong $S : Hu V : Li I : Van T : Vang G : Li$
23	$D \cdot Srinivasan M \cdot Pan Z \cdot Ramakrishna S I Mater Chem A$
24	2017 , 5, 4949-4961; (b) Su, Y.; Zhu, Y.; Jiang, H.; Shen, J.;
25	Yang, X.; Zou, W.; Chen, J.; Li, C. <i>Nanoscale</i> 2014 , 6, 15080-
26	15089; (c) Jiang, N.; You, B.; Sheng, M.; Sun, Y. Angew. Chem.
27	2015, 127, 6349-6352.
28	(22) (a) Song, X.; Guo, L.; Liao, X.; Liu, J.; Sun, J.; Li, X. Small
29	2017 , <i>13</i> , 1700238; (b) Wang, Q.; Shang, L.; Shi, R.; Zhang, X.;
30	Zhao, Y.; Waterhouse, G. I. N.; Wu, L. Z.; Tung, C. H.; Zhang,
31	1. Auv. Energy Matter. 2017, 7, 1700407.
32	Nuel D: Giordano I. ChemCatChem 2017 o 728-722: (b)
33	Liu, H.; Chang, L.; Chen, L.; Li, Y. J. Mater. Chem. A 2015, 3,
34	8028-8033; (c) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. J. Am.
35	Chem. Soc. 2013, 135, 2357-2367.
36	(24) (a) Davis, S. E.; Ide, M. S.; Davis, R. J. Green Chem. 2013,
37	15, 17-45; (b) Besson, M.; Gallezot, P. Catal. Today 2000, 57,
38	127-141; (c) Ragupathia, C.; Vijayaa J. J.; Narayanana, S.; Jesu-
39	dossa S. K.; Kennedy, L. J. Ceram. Int. 2015, 41, 2069-2080; (d)
40	Adad, A.; Corma, A.; Garcia, H. Chem. Eur. J. 2008, 14, 212-
41	(25) (a) Su H · 7hang K X · 7hang B · Wang H H · Yu O
42	Y.: Li, X. H.: Antonietti, M.: Chen, I. S. <i>J. Am. Chem. Soc.</i> 2017 .
43	139, 811-818; (b) Wang, Z. L.; Hao, X. F.; Jiang, Z.; Sun, X. P.;
44	Xu, D.; Wang, J.; Zhong, H. X.; Meng, F. L.; Zhang, X. B. J.
45	Am. Chem. Soc. 2015, 137, 15070-15073; (c) Li, X. H.; Antoniet-
46	ti, M. Chem. Soc. Rev. 2013, 42, 6593-6604; (d) Fan, X.; Zhang,
47	L.; Cheng, R.; Wang, M.; Li, M.; Zhou, Y.; Shi, J. ACS Catal.
48	2015 , 5, 5008-5015.
49	
50	
51	
52	

Insert Table of Contents artwork here

