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## Mesoporous Carbon Derived from Vitamin B<sub>12</sub>: A High-Performance Bifunctional Catalyst for Imine Formation

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Mesoporous carbon derived from natural vitamin  $B_{12}$  is first applied in organic synthesis and exhibits exceptionally high dual activity for imine formation via the cross-coupling of alcohols with amines and the self-coupling of primary amines using molecular oxygen or air as the terminal oxidant.

Imine derivatives are common functionality in organic and intermediates. fine chemicals, pharmaceuticals, particularly for the synthesis of anti-cancer and antiinflammatory drugs.<sup>1</sup> In view of the wide applications, considerable efforts have been devoted to the direct formation of imines since the traditional condensation method involves unstable aldehydes and acid catalysts,<sup>2</sup> and the following two approaches have attracted more attention as the starting reagents are readily available and dioxygen or air can serve as the terminal oxidant: (1) the self-coupling of primary amines;<sup>3</sup> (2) the cross-coupling of alcohols with amines.<sup>4</sup> Nevertheless, the main drawback of the former is inefficient to produce hetero-coupled imines due to the intrinsic inevitability of the self-coupling property of amines,<sup>3k</sup> <sup>m</sup> and of the latter often requires excess amounts of alcohols or amines to reach high-productivity levels.<sup>4d-f</sup> Therefore, in order to make the imine formation more effective and optional, designing a catalyst with dual activity is highly desirable. However, only noble metal catalysts such as supported Pt catalyst,<sup>5</sup> and homogeneous TEMPO systems<sup>6</sup> can simultaneously fulfill the two reactions, and heterogeneous non-noble metal catalyst has not yet been reported to date.

Mesoporous carbon materials, benefiting from their dual roles as supports<sup>7</sup> and as 'carbocatalysts' in their own right,<sup>8</sup> have been widely applied in various organic transformations.<sup>9</sup>

Besides, the introduction of heteroatoms (B, N, P, S, etc.) and non-noble transition metals (Fe, Co, etc.) can further improve the catalytic efficiency of the materials by tuning the electronic properties and generating active sites.<sup>10</sup> Generally, functional carbons are prepared by direct pyrolysis of the precursors containing carbon support, heteroatomic ligand and metal salt.<sup>11</sup> However, the strong interaction between these three components is difficult to construct, which may result in the agglomeration of metal species during the heat treatment,<sup>10c</sup> and affect the final stability and activity of the catalysts. A good solution is to synthesize metal complex precursors at molecular level containing these elements,<sup>12</sup> and more available strategy is to utilize natural products endowing with carbon, heteroatom and metal,13 which will make the fabrication of carbon materials greener and more sustainable, and also promote the catalytic reactions more practical.

Recently, we have found the carbon materials derived from macrocyclic compounds show high activity toward the self-coupling of primary amines.<sup>3n</sup> However, the precursors are not readily available, and the catalysts are also failed to produce hetero-coupled imines. In this work, we select natural vitamin  $B_{12}$  as the precursor to fabricate mesoporous carbon catalysts, which not only inherit the high activity of the catalysts derived from macrocyclic compounds for the self-coupling of primary amines, but also present exceptional capability for the cross-coupling of alcohols with amines. To the best of our knowledge, the mesoporous carbons derived from natural vitamin  $B_{12}$ , for the first time, are applied in organic synthesis and work as heterogeneous non-noble metal catalysts presenting dual activity for imine formation.

The catalyst preparation is quite simple:  $VB_{12}$  and colloidal silica are well mixed followed by removing the solvent and pyrolysis at different temperatures (400-900 °C) for 2 h under N<sub>2</sub> atmosphere. Then, the obtained powders are treated with hydrofluoric acid to remove the silica template, and the final catalysts are labeled as m-VB<sub>12</sub>-X (m represents the mesoporous structure; VB<sub>12</sub> is the abbreviation of vitamin B<sub>12</sub>; X refers to the carbonization temperature).

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Initially, we focused on the cross-coupling of benzyl alcohol (1a) with equimolar amounts of aniline (2a) at 100  $^{\circ}$ C under O<sub>2</sub> atmosphere, since no carbon-based catalyst has been disclosed for this coupling reaction. Blank experiment confirmed that the reaction hardly proceeded in the absence of catalyst, and commercially available VB12 only gave the desired imine (3a) in 26% yield (Table 1, entries 1, 2). To our delight, the utilization of mesoporous carbon m-VB<sub>12</sub>-6 led to 94% conversion with 91% selectivity (Table 1, entry 3). Moreover, the selectivity can be further improved with m-VB<sub>12</sub>-8 providing 3a in 96% yield, and no loss of activity was observed even using air as the oxidant (Table 1, entries 4, 5). Nevertheless, the temperature greatly affected the catalytic efficiency as the conversion of 1a was gradually decreased to 74% performing the reaction at 80 °C (Table 1, entry 6). For comparison, m-CoPc-8 employing cobalt phthalocyanine (CoPc) as the precursor also showed moderate activity toward the reaction, but m-Pc-8 prepared from metal-free phthalocyanine (Pc) was inefficient (Table 1, entries 7, 8). Taking the components of these catalysts into account, we can deduce that the cobalt species surviving from the acid treatment may play pivotal roles in this transformation. To verify this hypothesis, mesoporous carbons derived from copper phthalocyanine and iron phthalocyanine were also prepared, but only afforded 3a in 48% and 37% yields respectively (Table 1 entries 9, 10), further revealing the indispensability and superiority of cobalt to other non-noble metals for this coupling reaction.

Table 1 Cross-coupling of benzyl alcohol (1a) wit	th aniline (2a) over various catalysts "
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	DECON + Ph-NHa	Catalyst, O2 balloon	Ph	
	1a 2a	K <sub>2</sub> CO <sub>3</sub> , Heptane, 100 °C, 12 h	Ph <sup>-</sup> N 3a	
Entry	Catalyst	Conv. <sup>b</sup> (%)	Yield <sup>b</sup> (%)	
1	-	4	4	
2	VB <sub>12</sub>	30	26	
3	m-VB <sub>12</sub> -6	94	86	
4	m-VB <sub>12</sub> -8	99	96	
5 <sup>°</sup>	m-VB <sub>12</sub> -8	99	97	
6 <sup><i>d</i></sup>	m-VB <sub>12</sub> -8	74	67	
7	m-CoPc-8	75	65	
8	m-Pc-8	16	12	
9	m-FePc-8	52	48	
10	m-CuPc-8	43	37	

<sup>*a*</sup> Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (10 mol%), heptane (1 mL), catalyst (10 mg), O<sub>2</sub> balloon, 100 °C, 12 h. <sup>*b*</sup> Determined by GC using diphenyl as the internal standard and confirmed by GC-MS. <sup>*c*</sup> Air balloon. <sup>*d*</sup> 80 °C.

The microstructure of m-VB12-8 was first analyzed by the  $N_2$  sorption. And the corresponding Brunauer-Emmett-Teller (BET) surface area and the average pore size were 637 m<sup>2</sup>/g and 12.3 nm, respectively (Figure S4). The porous structure was also observed from the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 1a, b). Whereas, we did not find any cobalt-containing nanoparticles on the catalyst, since the etching agent may dissolve the silica template and cobalt/cobalt oxide particles at the same time.<sup>14</sup> Nevertheless, the energy-dispersive X-ray (EDX) spectrum showed the presence of C, N, O, P and Co

(Figure S5), and the elemental mapping analysis confirmed that the elements were homogeneously distributed throughout the whole mesoporous structure (Figure S6). Moreover, the X-ray photoelectron spectroscopy (XPS) revealed that approximately 1.0 at% of cobalt species were survived from the acid treatment (Figure S7). Subsequently, we investigated the electronic states of the catalyst by X-ray absorption fine-structure (XAFS) and high resolution XPS spectra. The near-edge spectrum of Co in m-VB12-8 was different to that of Co foil, CoO, or Co<sub>3</sub>O<sub>4</sub> reference, further revealing the absence of cobalt/cobalt oxide particles in our catalyst (Figure S8). The high resolution XPS spectrum of Co  $2p_3/_2$  can be deconvoluted into two peaks centered at 799.9 eV and 781.5 eV, assigned to Co-O and Co-N, respectively (Figure 1c).<sup>15</sup> And the N 1s spectrum can be fitted with three peaks, including pyridinic N (398.6 eV), pyrrolic N(399.9 eV), and oxidized N (402.6 eV) (Figure 1d).<sup>16</sup> Notably, the peak at 398.6 eV should also contain the contribution of Co-N, as its binding energies was close to pyridinic N.<sup>17</sup> Previous studies revealed that the cobalt ions stabilized by nitrogen were of vital importance for the generating catalysts with reasonable activity in oxidation reactions,<sup>10c, 18</sup> and the nitrogen-doped carbons can also serve as coordination sites to stabilize the active species.<sup>19</sup> Given the cobalt ions were well coordinated at the central of  $VB_{12}$  precursor, the agglomeration of cobalt species could be greatly hindered during the subsequent heat treatment. In addition, the self-supporting feature of the catalyst preparation enormously increased the density of active sites. Therefore, the surviving cobalt species may homogeneously distribute on the carbon matrix at subnanoscale level, and with the advantage of the porous structure, high activity for this cross-coupling reaction was easily achieved.



Figure 1 (a) SEM image, (b) TEM image, and (c) high-resolution Co  $2p_{3/2}$  and (d) N 1s XPS spectra of m-VB\_{12}-8.

With the optimized conditions in hand, we then examined the scope of present catalytic system for various alcohols and amines. As depicted in Table 2, benzylic alcohols can smoothly react with **2a** to afford the desired imines in excellent yields Published on 26 October 2015. Downloaded by Simon Fraser University on 27/10/2015 14:25:10.

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regardless of the presence of electron-donating or electronwithdrawing groups (Table 2, entries 1-3). Besides, unsaturated alcohol such as cinnamyl alcohol can also be readily transformed into the corresponding imine without loss of the C=C bond (Table 2, entry 4). When more challenging aliphatic alcohol was tested, a relatively low yield was observed (Table 2, entry 5). As for amine part, substituted anilines, cyclical and aliphatic amines all reacted efficiently with **1a** to produce the imine products in excellent yields (Table 2, entries 6-9).

### Table 2 Cross-coupling of alcohols with amines to imines catalyzed by m-VB\_{12}-8 $^{\rm a}$



<sup>*a*</sup> Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (10 mol%), heptane (1 mL), catalyst (10 mg), air balloon, 100 °C, 12 h. <sup>*b*</sup> Determined by GC and confirmed by GC-MS. Numbers in parentheses referred to yields of isolated products

To further extend the applications, we examined the activity of the prepared materials for the self-coupling of benzylamine (4a) under neat conditions, which was an effective strategy to homo-coupled imines. The precursor VB<sub>12</sub>, similar to the literature report of cobalt complex, was inefficient under mild reaction conditions,<sup>30</sup> and only gave the corresponding imine (5a) in 14% yield after 8 h (Table 3, entry 1). Besides, direct pyrolysis of VB<sub>12</sub> without any template under N<sub>2</sub> atmosphere would result in an inactive material (Table 3, entry 2). In contrast, mesoporous carbon m-VB<sub>12</sub>-X (X=4, 5, 6, 7, 8, and 9) were high active toward the reaction (Table S2, entries 1-7), and m-VB<sub>12</sub>-6 has sufficient catalytic activity to give 5a in 92% yield (Table 3, entry 3). Notably, compared to m-CoPc-6, metal-free m-Pc-6 presented higher activity for this transformation, which strongly demonstrated that the surviving cobalt species were not necessary to this self-coupling reaction(Table 3, entries 4, 5). Besides, mesoporous graphitic carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>) only afforded 5a in 23% yield (Table 3, entry 6), implying the structure of the precursor also affected the final activity of the catalyst. Based on the above results and previous reports,<sup>3n</sup> we proposed that the defect sites on the carbon matrix rather than the metal species catalyzed the self-coupling of primary amines, and the accessible mesoporous structure can greatly promote the mass transfer and the active site's exposure (Scheme S2).

Table 3 Self-coupling of benzylamine (4a) over different catalysts <sup>a</sup>



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Entry	Catalyst	Conv. <sup>b</sup> (%)	Yield <sup>b</sup> (%)
1	VB <sub>12</sub>	15	14
2	VB <sub>12</sub> -6	7	7
3	m-VB <sub>12</sub> -6	97	92
4	m-CoPc-6	69	67
5	m-Pc-6	85	82
6	mpg-C <sub>3</sub> N₄	36	23

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 $^a$  Reaction conditions: **4a** (5 mmol), catalyst (20 mg), O<sub>2</sub> balloon, 8 h, 100 °C.  $^b$  Determined by GC using diphenyl as the internal standard and confirmed by GC-MS.

Subsequently, we investigated various amines for this coupling reaction. As summarized in Table 4, excellent yields were observed for the self-coupling of both electron-rich (OCH<sub>3</sub> and CH<sub>3</sub>) and electron-deficient (F, Br, and CF<sub>3</sub>) benzylamines (Table 4, entries 2-6). Moreover, heteroatom-containing amines were also well tolerated, providing the corresponding imines in good yields (Table 4, entries 7-9). Whereas, the self-coupling of *n*-hexylamine was difficult to proceed owing to the inactive  $\alpha$ -hydrogen (Table 4, entry 10). Besides, secondary amine and cyclic amine were suitable for this reaction leading to the desired imines in moderate to good yields (Table 4, entries 11-12).

Table 4 m-VB12-6-catalyzed the self-coupling of amines to give homo-coupled imin	nes <sup>a</sup>
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<sup>*a*</sup> Reaction conditions: **4** (5 mmol), catalyst (20 mg), O<sub>2</sub> balloon, 8 h, 100 °C. <sup>*b*</sup> Determined by GC and confirmed by GC-MS. Numbers in parentheses referred to yields of isolated products. <sup>*c*</sup> *N*-benzylaniline as the substrate <sup>*d*</sup> 18 hours.

To identify the effectiveness and reusability of m-VB<sub>12</sub>-6, a 100 mmol scale self-coupling of **4a** was performed, and the reaction proceeded smoothly to provide the desired **5a** in 95% yield (Table 5). Notably, the catalyst/substrate ratio was just 0.47 wt% and was one magnitude lower than that of reported carbon-based catalytic systems,<sup>3g, 3l</sup> and the recovered catalyst can also be used at least five times without any appreciable loss of activity on this 100 mmol scale. In addition, the hotfiltration test showed that no further consumption of **1a** took place after the catalysti was filtered at the conversion of 36%, suggesting the catalysis was truly heterogeneous (Figure S10).

Table 5 Recycling of m-VB<sub>12</sub>-6 for the self-coupling of benzylamine (4a) <sup>a</sup>

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Run	0	1	2	3	4	5
Yield <sup>b</sup> (%)	95	92	94	95	95	93
9	14.00		C (50			420.00

<sup>a</sup> Reaction conditions: 4a (100 mmol), m-VB<sub>12</sub>-6 (50 mg), O<sub>2</sub> balloon, 48 h, 120 °C.
<sup>b</sup> Determined by GC and confirmed by GC-MS.

In summary, we have developed an efficient, bifunctional and reusable mesoporous carbon catalyst for imine formation. The m-VB<sub>12</sub>-X catalyst is prepared by simple thermolysis of natural vitamin  $B_{12}$  with silica template. The high catalytic efficiency of the catalysts is not only manifested at the selfcoupling of primary amines, affording the corresponding homo-coupled imines, but also reflected at the cross-coupling of alcohols with amines, providing more diverse types of imines. Control experiments combined with the characterizations reveal that the defect sites on the carbon matrix catalyze the self-coupling of primary amines, while the surviving cobalt species play important roles in the crosscoupling of alcohols with amines. This work may provide a new strategy to design bifunctional catalysts for imine formation and make the synthesis of imines more effective and flexible as well.

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### Notes and references

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- (a) S.-I. Murahashi, Angew. Chem. Int. Ed. Engl. 1995, 34, 2443-2465; (b) S. Kobayashi, H. Ishitani, Chem. Rev. 1999, 99, 1069-1094; (c) Z.-Y. Liu, Y.-M. Wang, Z.-R. Li, J.-D. Jiang, D. W. Boykin, Bioorg. Med. Chem. Lett. 2009, 19, 5661-5664.
- (a) R. D. Patil, S. Adimurthy, Asian J. Org. Chem. 2013, 2, 726-744; (b) M. Largeron, Eur. J. Org. Chem. 2013, 2013, 5225-5235.
- 3 (a) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, Angew. Chem. Int. Ed. 2011, 50, 657-660; (b) X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, Angew. Chem. Int. Ed. 2011, 50, 3934-3937; (c) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, ACS Catal. 2011, 1, 1150-1153; (d) M. Largeron, M. B. Fleury, Angew. Chem. Int. Ed. 2012, 51, 5409-5412; (e) H. Yuan, W.-J. Yoo, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 2012, 134, 13970-13973; (f) S.-i. Naya, K. Kimura, H. Tada, ACS Catal. 2012, 3, 10-13; (g) C. Su, M. Acik, K. Takai, J. Lu, S.-j. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki, Y. J. Chabal, K. Ping Loh, Nat. Commun. 2012, 3, 1298; (h) M. Largeron, M. B. Fleury, Science 2013, 339, 43-44; (i) X. Qiu, C. Len, R. Luque, Y. Li, ChemSusChem 2014, 7, 1684-1688; (j) M. Largeron, M. B. Fleury, Chem. Eur. J. 2015, 21, 3815-3820; (k) R. D. Patil, S. Adimurthy, Adv. Synth. Catal. 2011, 353, 1695-1700; (I) H. Huang, J. Huang, Y.-M. Liu, H.-Y. He, Y. Cao, K.-N. Fan, Green Chem. 2012, 14, 930-934; (m) A. Monopoli, P. Cotugno, F. Iannone, F. Ciminale, M. M. Dell'Anna, P. Mastrorilli, A. Nacci, Eur. J. Org. Chem. 2014, 2014, 5925-5931; (n) B. Chen, L. Wang, W. Dai, S. Shang, Y. Lv, S. Gao, ACS Catal. 2015, 2788-2794; (o) S. Zhao, C. Liu, Y. Guo, J.-C. Xiao, Q.-Y. Chen, J. Org. Chem. 2014, 79, 8926-8931; (p) S. Biswas, B. Dutta, K. Mullick, C.-H. Kuo, A. S. Poyraz, S. L. Suib, ACS Catal. 2015, 5, 4394-4403.
- 4 (a) H. Sun, F.-Z. Su, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, Angew. Chem. Int. Ed. 2009, 48, 4390-4393; (b) B. Gnanaprakasam, J.

Zhang, D. Milstein, *Angew. Chem. Int. Ed.* **2010**, *49*, 1468-1471; (c) B. Chen, J. Li, W. Dai, L. Wang, S. Gao, *Green Chem.* **2014**, *16*, 3328-3334; (d) L. Zhang, W. Wang, A.-Q. Wang, Y.-T. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J.-Y. Son, H. Oji, T. Zhang, *Green Chem.* **2013**, *15*, 2680-2684; (e) E. L. Zhang, H. W. Tian, S. D. Xu, X. C. Yu, Q. Xu, *Org. Lett.* **2013**, *15*, 2704-2707; (f) M. Tamura, K. Tomishige, *Angew. Chem. Int. Ed.* **2015**, *54*, 864-867.

- 5 W. He, L. Wang, C. Sun, K. Wu, S. He, J. Chen, P. Wu, Z. Yu, *Chem. Eur. J.* **2011**, *17*, 13308-13317.
- 6 E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.* **2013**, *15*, 2704-2707.
- 7 (a) X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li, Y. Wang, J. Am. Chem. Soc. 2012, 134, 16987-16990; (b) P. Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, Nat. Commun. 2013, 4, 1593; (c) L. Geng, X. Zhang, W. Zhang, M. Jia, G. Liu, Chem. Commun. 2014, 50, 2965-2967.
- 8 H. Yang, X. Cui, X. Dai, Y. Deng, F. Shi, *Nat. Commun.* **2015**, *6*, 6478.
- (a) D. R. Dreyer, C. W. Bielawski, Chem. Sci. 2011, 2, 1233-1240; (b) D. S. Su, S. Perathoner, G. Centi, Chem. Rev. 2013, 113, 5782-5816; (c) G.-P. Hao, M. Oschatz, W. Nickel, M. Adam, S. Kaskel, Curr. Org. Chem. 2014, 18, 1262-1279; (d) Y. Kuang, N. M. Islam, Y. Nabae, T. Hayakawa, M.-a. Kakimoto, Angew. Chem. Int. Ed. 2010, 49, 436-440; (e) D. R. Dreyer, H. P. Jia, C. W. Bielawski, Angew. Chem. Int. Ed. 2010, 49, 6813-6816; (f) J. Long, X. Xie, J. Xu, Q. Gu, L. Chen, X. Wang, ACS Catal. 2012, 2, 622-631; (g) H. Watanabe, S. Asano, S.-i. Fujita, H. Yoshida, M. Arai, ACS Catal. 2015, 5, 2886-2894; (h) X.-H. Li, M. Antonietti, Angew. Chem. Int. Ed. 2013, 52, 4572-4576; (i) H. Wang, X. Zheng, H. Chen, K. Yan, Z. Zhu, S. Yang, Chem. Commun. 2014, 50, 7517-7520; (j) J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, D. S. Su, Science 2008, 322, 73-77; (k) Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao, D. Ma, Angew. Chem. Int. Ed. 2013, 52, 2109-2113; (I) J.-H. Yang, G. Sun, Y. Gao, H. Zhao, P. Tang, J. Tan, A.-H. Lu, D. Ma, Energy Environ. Sci. 2013, 6, 793-798.
- 10 (a) J. P. Paraknowitsch, A. Thomas, *Energy Environ. Sci.* 2013, 6, 2839-2855; (b) R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science* 2013, *342*, 1073-1076; (c) R. V. Jagadeesh, H. Junge, M.-M. Pohl, J. r. Radnik, A. Brückner, M. Beller, *J. Am. Chem. Soc.* 2013, *135*, 10776-10782; (d) D. Banerjee, R. V. Jagadeesh, K. Junge, M. M. Pohl, J. Radnik, A. Brückner, M. Beller, *Angew. Chem. Int. Ed.* 2014, *53*, 4359-4363.
- 11 M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* 2009, 324, 71-74.
- 12 (a) L. Lin, Q. Zhu, A.-W. Xu, J. Am. Chem. Soc. 2014, 136, 11027-11033; (b) Z. Li, G. Li, L. Jiang, J. Li, G. Sun, C. Xia, F. Li, Angew. Chem. Int. Ed. 2014, 53, 1-6.
- 13 M.-M. Titirici, R. J. White, N. Brun, V. L. Budarin, D. S. Su, F. del Monte, J. H. Clark, M. J. MacLachlan, *Chem. Soc. Rev.* 2015, 44, 250-290.
- 14 K. T. Lee, X. Ji, M. Rault, L. F. Nazar, *Angew. Chem. Int. Ed.* **2009**, *48*, 5661-5665.
- 15 G. Wu, Z. Chen, K. Artyushkova, F. H. Garzon, P. Zelenay, ECS Trans. 2008, 16, 159-170.
- 16 U. Koslowski, I. Herrmann, P. Bogdanoff, C. Barkschat, S. Fiechter, N. Iwata, H. Takahashi, H. Nishikori, *ECS Trans.* **2008**, *13*, 125-141.
- 17 L. Zhang, A. Wang, W. Wang, Y. Huang, X. Liu, S. Miao, J. Liu, T. Zhang, *ACS Catal.* **2015**. *5*, 6563-6572.
- (a) J. Deng, H. J. Song, M. S. Cui, Y. P. Du, Y. Fu, *ChemSusChem* 2014, 7, 3334-3340; (b) W. Zhong, H. Liu, C. Bai, S. Liao, Y. Li, *ACS Catal.* 2015, 5, 1850-1856.
- 19 R. Nie, J. Shi, W. Du, W. Ning, Z. Hou, F.-S. Xiao, *J. Mater. Chem. A* **2013**, *1*, 9037-9045.

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