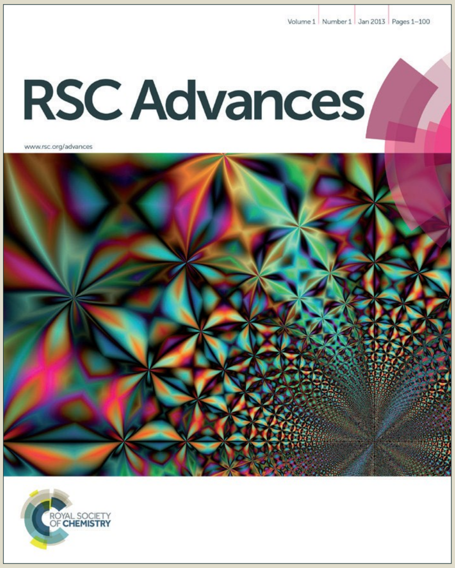
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: L. Xie, K. Wang, G. Du, A. M. Asiri and X. Sun, *RSC Adv.*, 2016, DOI: 10.1039/C6RA17340C.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

View Article Online
DOI: 10.1039/C6RA17340C

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

3D hierarchical CuO/Co_3O_4 core-shell nanowires array on copper foam for on-demand hydrogen generation from alkaline $NaBH_4$ solution

Lisi Xie,[a] Kunyang Wang,[b] Gu Du,[b] Abdullah M. Asiri[c] and Xuping Sun[a]*

In this work, we demonstrate the first use of 3D hierarchical CuO/Co_3O_4 core-shell nanowires array in situ grown on copper foam as a robust and high-active catalyst toward the hydrolytic dehydrogenation of $NaBH_4$ for on-demand hydrogen generation under alkaline solutions. This monolithic catalyst exhibits a maximum hydrogen generation rate of 6162.55 $mL/min/g_{(CuO/Co3O4)}$ at ambient conditions, which is higher than that of most reported Co-based catalysts, with an activation energy of 56.38 KJ/mol. It also shows good durability and reusability and can be used as an on/off switch for on-demand hydrogen generation.

In present days, hydrogen is considered as a promising energy carrier with merits of high energy content, renewability and no emission of greenhouse gas.[1,2] However, one obstacle for hydrogen economy is the issue of hydrogen storage.[3,4] Hydrides are attractive hydrogen-storing materials for portable applications[5-7] and $NaBH_4$ has attracted particularly considerable attention because of its good reducibility of metal precursors and organic compounds,[8-10] high hydrogen storage efficiency (10.8 wt.%),[11] economical cost compared with other chemical hydrides,[12] stability of its solution under high pH value,[13] and potentially safe operation.[14] $NaBH_4$ hydrolysis is a safe exothermic reaction that produces hydrogen according to eq.1:[15]

$$NaBH_4\ (aq) + 2H_2O \rightarrow NaBO_2\ (aq) + 4H_2 \quad (1)$$

Nevertheless, it is usually kept under alkaline conditions to prevent its self-hydrolysis and an active catalyst must be utilized to activate and accelerate its hydrolysis for hydrogen generation. Noble metals like Pt,[16] Rh,[17] Ru,[18] and Pd[19] are the most active such catalysts, but the scarcity and high cost hinder their widespread uses.

In the past decades, Co based materials have been largely investigated as cost-effective catalysts for $NaBH_4$ hydrolysis with favourable activity,[20,21] such as Co nanoparticles,[22] Au@Co core-shell nanoparticles,[23] Co_3O_4 powder,[24] CoO nanocrystals,[25] and $LiCoO_2$,[26] etc. However, the low surface area and difficult separation from fuel solutions limit the application of Co based powder materials in catalysing $NaBH_4$ hydrolysis for hydrogen generation. From the point of technology and operation, self-supported catalyst systems may conquer the above difficulties and have obvious advantages: free of aggregation, easy and rapid recovery from the reaction system for reusability and on-demand hydrogen generation.[27] Though several supported Co based catalysts have been utilized in the hydrolysis of $NaBH_4$, it is still a great challenge to design supported catalysts with larger surface area and more active sites.[1,28.] Hierarchical structure is a promising method to solve the above problem, as the supported core-shell hierarchical structure grown directly on conductive substrate has fascinating synergetic properties and large surface area with some unique physical and chemical properties in catalyst systems. [29,30] Previous report has shown that copper foam can be oxided into nanostructured arrays and applied in catalyst systems.[31]Further, Cu based catalysts have also been used as catalysts for $NaBH_4$ hydrolysis due to its cheap and environmental features.[32] Thus, Cu-Co hierarchical nanostructure may have superior catalytic activity in $NaBH_4$ hydrolysis reaction due to the synergistic effect between Cu and Co and the large surface area of hierarchical nanostructure.[33] What's more, to the best of our knowledge, such Co-Cu hierarchical structure has not been applied in the hydrolysis of alkaline $NaBH_4$ solution.

Herein, we demonstrate the development of hierarchical CuO/Co_3O_4 core-shell nanowires array on copper foam (CuO/Co_3O_4 core-shell NA/CF) as a robust and cost-effective catalyst for on-demand hydrogen generation via the hydrolytic dehydrogenation of $NaBH_4$ in alkaline media, with an activation energy (E_a) of 56.38 KJ/mol. This 3D monolithic catalyst offers a maximum hydrogen generation rate (HGR) of

---

[a] *Chemical Synthesis and Pollution Control, Key Laboratory of Sichuan Province, School of Chemistry and Chemical engineering, China West Normal University, Nanchong 637002, Sichuan, China. E-mail: sunxp@cwnu.edu.cn*

[b] *Chengdu institute of Geology and Mineral Resources, Chengdu 610081, Sichuan, China*

[c] *Chemistry Department, King Abdulaziz University, Jeddah 21589, Saudi Arabia*

† *Electronic Supplementary Information (ESI) available: Experimental section and supplementary figures. See DOI:*

View Article Online
DOI: 10.1039/C6RA17340C

6162.55 mL/min/g$_{(CuO/Co3O4)}$ at ambient conditions. It also exhibits good stability and reusability and behaves as an on/off switch for on-demand hydrogen generation. These attractive features promise its use as an earth-abundant catalyst material toward large-scale production of hydrogen fuels for applications.

CuO/Co_3O_4 core-shell NA/CF was fabricated by the following three steps in Fig. 1a (see ESI for preparation details): (1) $Cu(OH)_2$ nanowires array was grown on commercially available CF by a wet-chemical route at room temperature; (2) $CoCO_3(OH)_2 \cdot nH_2O$ core-shell NA/CF was subsequently grown on the $Cu(OH)_2$ backbones via chemical bath deposition (CBD) (Fig. S2),[34] (3) the resulting $Cu(OH)_2/CoCO_3(OH)_2 \cdot nH_2O$ core-shell NA/CF as precursor was converted to CuO/Co_3O_4 core-shell NA/CF by air annealing. Scanning electron microscopy (SEM) analysis suggests that macroporous copper foam (Fig. 1b) is completely covered with $Cu(OH)_2$ nanowires array after ammonium persulfate treatment, as shown in Fig. 1c and 1d . Fig. 1e and 1f show the SEM images of CuO/Co_3O_4 core-shell NA/CF, providing one piece of clear evidence to support the formation of hierarchical core-shell nanowires array on CF. Its energy-dispersive X-ray (EDX) spectrum confirms the existence of Cu, Co and O elements (Fig. S3). The SEM and corresponding EDX elemental mapping images for such nanoarray demonstrate the uniform distribution of Cu, Co and O elements (Fig. 1g). The much stronger signals for Co and O also imply the shell nature for Co_3O_4 species.

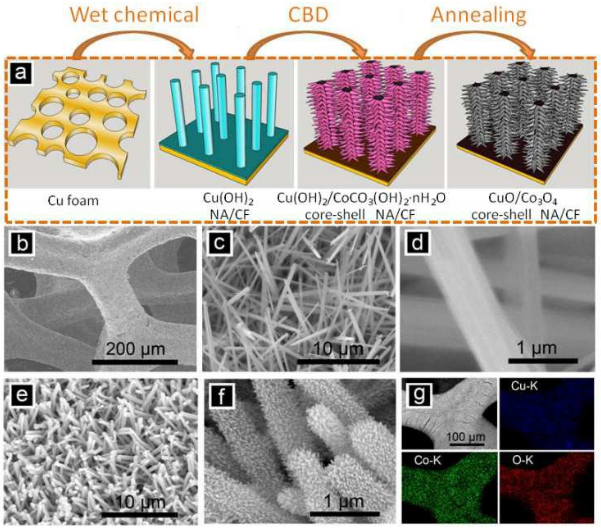


Fig. 1. (a) A schematic diagram for illustrating the fabrication procedure of CuO/Co_3O_4 core-shell NA/CF. SEM images of (b) bare CF, (c, d) $Cu(OH)_2$ NA/CF and (e, f) CuO/Co_3O_4 core-shell NA/CF. (g) SEM and EDX elemental mapping images of Cu, Co, and O elements for CuO/Co_3O_4 core-shell NA/CF.

Fig. S4 shows the X-ray diffraction (XRD) pattern for CuO/Co_3O_4 core-shell NA/CF in the diffraction angle range of 30-80°. The three strong peaks at 43.30°, 50.43°, and 74.13° can be assigned to the (111), (200), and (220) planes of metallic Cu substrate (JCPDS No. 04-0836), respectively. Other peaks at 35.50°, 36.84°, 38.73°, 59.35° and 65.22° arise from CuO and Co_3O_4. The absence of additional diffraction peaks suggests the complete conversion of $CoCO_3(OH)_2 \cdot nH_2O$ into CuO/Co_3O_4 after annealing. Fig. 2a shows the XPS survey spectrum, confirming the presence of only Cu, Co and O. The C 1s signals arise from exposure to atmosphere.[35] As shown in Fig. 2b, the CuO exhibits a Cu $2p_{3/2}$ peak and Cu $2p_{1/2}$ peak at binding energies (BEs) of 933.8 and 953.8 eV, respectively,[36,37] together with two high-intensity shake-up satellites (those located at 942.4, and 963.3 eV).[38] Fig. 2c shows the XPS spectra of Co. Two prominent peaks at BEs of 795.2 and 779.6 eV correspond to Co^{2+} $2p_{1/2}$ and $2p_{3/2}$, respectively.[39] Two small peaks at 803.5 and 788.9 eV can be attributed to $2p_{3/2}$ and $2p_{1/2}$ of Co^{3+}, respectively, confirming the existence of Co_3O_4.[40,41] As shown in Fig. 2d, the O 1s core-level spectrum is broad, and two peaks are marked as I and II. Peak I, the lower energy of 529.7 eV, is in agreement with lattice O.[42,43] The high BE of 531.5 eV (peak II), is attributed to the low coordinated oxygen ions at the surface.[40,44]

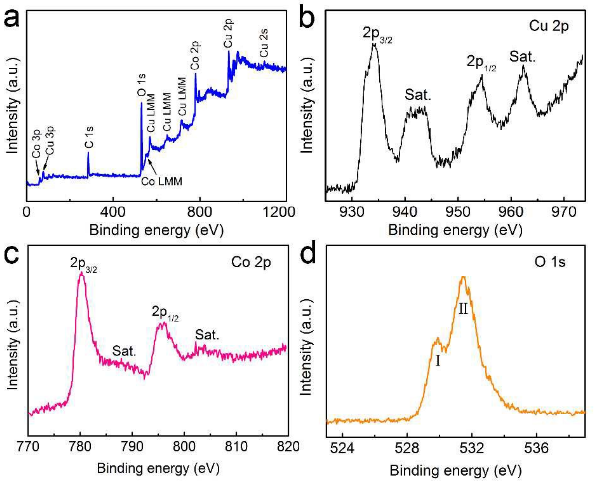


Fig. 2. XPS spectra of CuO/Co_3O_4 core-shell NA/CF. (a) XPS survey spectrum. XPS spectrum in the (b) Cu 2p, (c) Co 2p, and (d) O 1s regions.

We examined the catalytic activity of the monolithic CuO/Co_3O_4 core-shell NA/CF toward $NaBH_4$ hydrolysis by putting them in alkaline $NaBH_4$ solution. Co_3O_4 NA/CF and CuO NA/CF were also tested for comparison. As observed, slow hydrogen release occurs for CuO NA/CF and Co_3O_4 NA/CF (Fig. S5a and b) while a large amount hydrogen gas appears vigorously on CuO/Co_3O_4 core-shell NA/CF (Fig. S5c and Movie S1). Fig. S5d compares the catalytic activities for the $NaBH_4$ hydrolysis on CuO NA/CF, Co_3O_4 NA/CF and CuO/Co_3O_4 core-shell NA/CF. Obviously, CuO/Co_3O_4 core-shell NA/CF shows the highest catalytic activity as compared to the same amount of others. This excellent performance may be attributed to the following factors: (1) this nanostructured branched metal oxide has large reactive sites and facilitates the diffusion of materials; (2) CuO plays the role of substrate and synergistic effect to the hydrolysis reaction of $NaBH_4$.[45,46]

The catalytic activity of CuO/Co_3O_4 core-shell NA/CF was further investigated by hydrolyzing alkaline $NaBH_4$ solutions under different conditions. Fig. 3a presents the effect of $NaBH_4$ concentration on hydrogen generation. The HGR maintains almost constant with increasing $NaBH_4$ concentration from 0.2 wt% to 2.0 wt%, suggesting that the catalytic hydrolysis reaction over CuO/Co_3O_4 core-shell NA/CF catalyst follows

View Article Online
DOI: 10.1039/C6RA17340C

zeroth order kinetics in this concentration range.[47] The reaction rate equation based on zero-order kinetics can be described as follow:[48]

$$-4 \times d[NaBH_4] / dt = d[H_2] / dt = r_{H2} \quad (2)$$

where r_{H2} is the hydrogen release rate (mL/min).

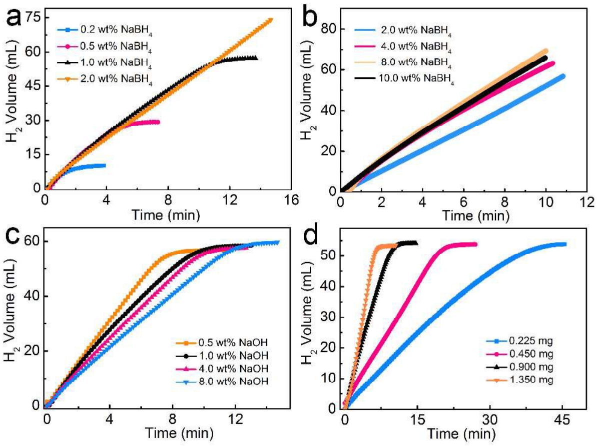


Fig. 3. Effect of concentrations of $NaBH_4$ and NaOH as well as catalyst loading on the HGR: (a) and (b) [NaOH] = 1 wt%, CuO/Co_3O_4 loading = 0.9 mg. (c) $[NaBH_4]$ = 1 wt%, CuO/Co_3O_4 loading = 0.9 mg. (d) [NaOH] = 1 wt%, $[NaBH_4]$ = 1 wt%. All hydrolysis experiments were done at 298 K and ambient pressure.

It has been well understood that the reaction order with respect to $NaBH_4$ concentration changes with $NaBH_4$ concentration.[49,50] From Fig. 3b, it can be shown that the HGR increases with further rising $NaBH_4$ concentration, but this enhancement is limited to $NaBH_4$ concentration of 8 wt%. The HGR decreases when $NaBH_4$ concentration is further increased to 10 wt.%. Similar results were also reported by other researchers.[51,52] It can be explained as follows: (1) increased $NaBH_4$ concentration could increase the viscosity of the fuel solution; (2) the $NaBO_2$, as a hydrolysate, has lower solubility than $NaBH_4$ and thus could decrease mass transfer rate.[53,54] Fig. 3c shows the effect of different NaOH concentrations on the release rate of hydrogen, suggesting an increase in NaOH concentration causes decreased HGR. It can be explained as follows. NaOH is an inhibitor to slow down the self-hydrolysis of $NaBH_4$ in solution and thus more NaOH gives less H_2 via $NaBH_4$ decomposition. Increased NaOH concentration also increases the solution viscosity and reduces the available free H_2O to react with $NaBH_4$.[15] The hydrogen release rate may be expressed using eq.3:[48,55]

$$r_{H2} = k / (1 + k_1 [NaOH]^{0.3}) \quad (3)$$

where k is rate constant and k_1 the coefficient for the effect of NaOH concentration. It was also found that the catalyst loading has great influence on hydrogen generation performance. As shown in Fig. 3d, an increase of catalyst loading leads to a higher r_{H2}. Fig. S6 depicts the correlation of catalyst loading on r_{H2}. The value of r_{H2} was calculated from the slope of the linear part of each plot shown in Fig. 3d. The logarithmic plot of the calculated initial reaction rate vs. $m_{CuO/Co3O4}$ has a slope of 1.03 ≈ 1.0 indicating that the hydrolysis is first order with respect to the catalyst loading.[56]

To obtain the E_a for the hydrolysis of $NaBH_4$ catalyzed by CuO/Co_3O_4 core-shell NA/CF, the hydrolysis reactions were performed at different temperatures (Fig. 4a). It is quite clear that the higher reaction temperature leads to larger HGR. The E_a was determined as 56.38 KJ mol^{-1} according to Arrhenius plot of ln (HGR) vs. 1/T for the catalyst (Fig. 4b).[57] A HGR of 6162.55 mL/min/$g_{(CuO/Co3O4)}$ was achieved under 298 K and ambient pressure. This value compares favourably to the behaviours of most reported Co-based catalysts (Table S1). Such superior catalytic performances can be rationally attributed to the following two reasons: (1) the nanoarray format leads to more exposed active sites for catalysis;[31] (2) the 3D macroporous configuration of CF and the open spaces between the nanowires allow for enhanced diffusion of the fuel and hydrogen gas generated.[58]

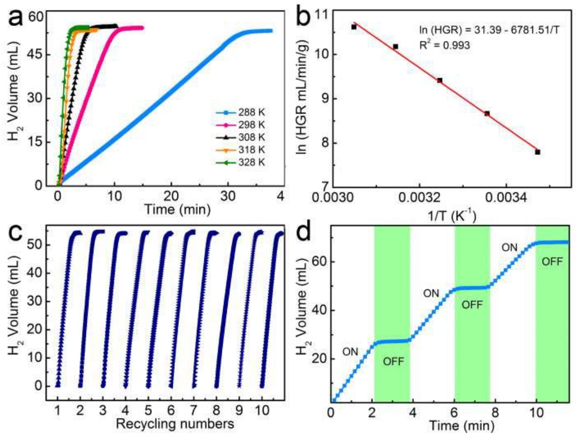


Fig. 4. (a) Hydrogen generation kinetics curves for alkaline $NaBH_4$ solutions (2 mL) catalyzed by CuO/Co_3O_4 NW/CF using the 1 wt.% NaOH and 1 wt.% $NaBH_4$ solution at different solution temperatures. (b) The corresponding Arrhenius plot. (c) Recycling of CuO/Co_3O_4 NW/CF in aqueous solution (2 mL) containing 1.0 wt% $NaBH_4$ and 1.0 wt% NaOH at 298 K and ambient pressure. (d) On-demand hydrogen generation in the fuel solution using CuO/Co_3O_4 NW/CF as an on/off switch (CuO/Co_3O_4 loading = 0.9 mg, [NaOH] = 1 wt%, $[NaBH_4]$ = 1 wt%, T = 298 K).

High recycle stability is really crucial for every practical catalyst. Therefore, hydrolysis experiments were performed to reuse the catalyst several times at room temperature for durability test. The catalytic activity remains unchanged after 10 cycles (Fig. 4c). Compared to powdery catalyst systems, the monolithic CuO/Co_3O_4 core-shell NA/CF can be easily separated from the fuel solution, promising its use as an efficient on/off switch for on-demand hydrogen generation.[59,28] Fig. 4d shows the temporal control of hydrogen generation by repeated activation of the catalyst system. In the absence of CuO/Co_3O_4 NA/CF (OFF), hydrolysis was terminated without hydrogen release. Hydrogen release occurs again when immersing CuO/Co_3O_4 core-shell NA/CF into the fuel solution (ON). XPS analysis for CuO/Co_3O_4 core-shell NA/CF suggests the valence state of Co does not change obviously after reaction (Fig. S7a). But, in contrast, two distinct peaks at BEs of 932.4 and 952.5 eV can be attributed to Cu(I),[60,61] which demonstrate some CuO was reduced to Cu_2O during reaction (Fig. S7b).

In summary, hierarchical CuO/Co_3O_4 core-shell nanowires array on copper foam has been proven as an efficient 3D monolithic catalyst with an E_a of 56.38 KJ/mol for on-demand

View Article Online
DOI: 10.1039/C6RA17340C

generation ration from the hydrolysis of alkaline $NaBH_4$ solution. It shows a high HGR of 6162.55 mL/min/$g_{(CuO/Co3O4)}$ with high recyclability and durability. Our study not only provides us an attractive low-cost catalyst material toward efficient $NaBH_4$ hydrolysis for mass production of hydrogen fuels, but would open new opportunities in designing and utilizing monolithically integrated nanoarrays as an on/off switch for on-demand hydrogen generation from borohydrides as fuel feed to cells in portable devices.[62]

References

1 M. Paladini, G. M. Arzac, V. Godinho, M. C. Jiménez De Haro and A. Fernández, *Appl. Catal. B: Environmental*, 2014, **158**, 400-409.
2 C. Tang, L. Xie, K. Wang, G. Du, A. M. Asiri, Y. Luo and X. Sun, *J. Mater. Chem. A*, 2016, **4**, 12407-12410.
3 S. B. Kalidindi, M. Indirani and B. R. Jagirdar, *Inorg. Chem.*, 2008, **47**, 7424-7429.
4 L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353-358.
5 Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai and H. Hayashi, *Int. J. Hydrogen Energy*, 2002, **27**, 1029-34.
6 J. Graetz, *Chem. Soc. Rev.*, 2009, **38**, 73-82.
7 C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279-293.
8 J. Fang, J. Li, B. Zhang, X. Yuan, H. Asakura, T. Tanaka, K. Teramura, J. Xie and N. Yan, *Nanoscale*, 2015, **7**, 6325-6333.
9 J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura and N. Yan, *ACS Catal.*, 2014, **4**, 1574-1583.
10 J. Zhang, Y. Yuan, K.J. Kilpin, Y. Kou, P.J. Dyson and N. Yan, *J. Mol. Catal. A: Chem.*, 2013, **371**, 29-35.
11 L. Chong, J. Zou, X. Zeng and W. Ding, *J. Mater. Chem. A*, 2013, **1**, 3983-3991.
12 K. Eom, K. Cho and H. Kwon, *J. Power Sources*, 2008, **180**, 484-490.
13 H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, 1953, **75**, 215-219.
14 S. I. Orimo, Y. Nakamori, J. R. Eliseo, A. Zuttel and C. M. Jensen, *Chem. Rev.*, 2007, **107**, 4111-4132.
15 S. C. Amendola, S. L. Sharp-Goldman, M. S. Janjua, M. T. Kelly, P. J. Petillov and M. Binder, *J. Power Sources*, 2000, **85**, 186-189.
16 Y. Bai, C. Wu, F. Wu and B. Yi, *Mater. Lett.*, 2006, **60**, 2236-2239.
17 V. I. Simagina, O. V. Netskina, O. V. Komova, G. V. Odegova, D. I. Kochubei and A. V. Ishchenko, *Kinet. Catal*., 2008, **49**, 568-573.
18 S. Özkar and M. Zahmakıran, *J. Alloys Compd.*, 2005, **404**, 728-731.
19 N. Patel, B. Patton, C. Zanchetta, R. Fernandes, G. Guella, A. Kale and A. Miotello, *Int. J. Hydrogen Energy*, 2008, **33**, 287-292.
20 B. Liu and Z. Li, *J. Power Sources*, 2009, **187**, 527-534.
21 U. B. Demirci and P. Miele, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14651-14665.
22 J. Yan, X. Zhang, H. Shioyama and Q. Xu, *J. Power Sources*, 2010, **195**, 1091-1094.
23 J. Yan, X. Zhang, T. Akita, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5326-5327.
24 V. I. Simagina, O. V. Komova, A. M. Ozerova, O. V. Netskina, G. V. Odegova, D. G. Kellerman, O. A. Bulavchenko and A. V. Ishchenko, *Appl. Catal. A: Gen.*, 2011, **394**, 86-92.
25 A. Lu, Y. Chen, J. Jin, G. Yue and D. Peng, *J. Power Sources*, 2012, **220**, 391-398.
26 O. V. Komova, V. I. Simagina, O. V. Netskina, D. G. Kellerman, A. V. Ishchenko and N. A. Rudina, *Catal. Today*, 2008, **138**, 260-265.
27 S. S. Muir and X. Yao, *Int. J. Hydrogen Energy*, 2011, **36**, 5983-5997.
28 L. Cui, X. Sun, Y. Xu, W. Yang and J. Liu, *Chem. Eur. J.*, 2016, doi: 10.1002/chem.201603087.
29 H. Kobayashi, M. Yamauchi, H. Kitagawa, Y. Kubota, K. Kato and M. Takata, *J. Am. Chem. Soc.*, 2008, **130**, 1818-1819.
30 Y. Lei and W. K. Chim, *J. Am. Chem. Soc.*, 2005, **127**, 1487-1492.
31 J. Tian, Q. Liu, N. Cheng, A.M. Asiri and X. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 9577-958.
32 C. Chen, J. Lin and T. Lai, *Chem. Commun.*, 2008, **40**, 4983-4985.
33 Z. Li, M. Shao, L. Zhou, R. Zhang, C. Zhang, J. Han, M. Wei, D.G. Evans and X. Duan, *Nano Energy*, 2016, **20**, 294-304.
34 R. Xu and H. Zeng, *J. Phys. Chem. B*, 2003, **107**, 12643-12649.
35 X. Xia, J. Tu, Y. Zhang, X. Wang, C. Gu, X. Zhao and H. Fan, *ACS Nano*, 2012, **6**, 5531-5538.
36 K H. Kim and S. K. Ihm, *J. Hazard. Mater.*, 2007, **146**, 610-616.
37 I. H. Tseng, J. Wu and H. Y. Chou, *J. Catal.*, 2004, **221**, 423-440.
38 S. Poulston, P. M Parlett, P. Stone and M. Bowker, *Surf. Interface Anal.*, 1996, **24**, 811-820.
39 M. Kuang, T. Li, H. Chen, S. Zhang, L. Zhang and Y. Zhang, *Nanotechnol.*, 2015, **26**, 304002-304011.
40 Y. Feng, L. Li, S. Niu, Y. Qu, Q. Zhang, Y. Li, W. Zhao, H. Li and J. Shi, *Appl. Catal. B: Environ.*, 2012, **111**, 461-466.
41 L. Zhang, X. Zhao, W. Ma, M. Wu, N. Qian and W. Lu, *CrystEngComm*, 2013, **15**, 1389-1396.
42 S. Xiong, C. Yuan, X. Zhang and B. Xi and Qian, Y, *Chem. Eur. J.*, 2009, **15**, 5320-5326.
43 J. Morales, L. Sanchez, F. Martin, J. R. Ramos-Barrado and M. Sanchez, *Thin Solid Films*, 2005, **474**, 133-140.
44 M. A. Dar, Y. S. Kim, W. B. Kim, J. M. Sohn and H. S Shin, *Appl. Surf. Sci.*, 2008, **254**, 7477-7481.
45 R. Fernandes, N. Patel and A. Miotello, *Int. J. Hydrogen Energy*, 2009, **34**, 2893-2900.
46 G. Guella, C. Zanchetta, B. Patton and A. Miotello, *J Phys. Chem. B*, 2006, **110**, 17024-17033.
47 Y. Zou, J. Cheng, Q. Wang, C. Xiang, H. Chu, S. Qiu, H. Zhang, F. Xu, S. Liu, C. Tang and L. Sun, *Int. J. Hydrogen Energy*, 2015, **40**, 13423-13430.
48 R. Retnamma, A. Q. Novais and C .M. Rangel, *Int. J. Hydrogen Energy*, 2011, **36**, 9772-9790.
49 J. C. Ingersoll, N. Mani, J. C. Thenmozhihal and A. Muthaiah, *J. Power Sources*, 2007, **173**, 450-457.
50 B. Liu, Z. Li and S. Suda, *J. Alloys Compd.*, 2006, **415**, 288-293.
51 E. Özdemir, *Int. J. Hydrogen Energy*, 2015, **40**, 14045-14051.
52 L. Ai, X. Gao and J. Jiang, *J. Power Sources*, 2014, **257**, 213-220.
53 Ö. Şahin, C. Saka, O. Baytar and F. Hansu, *J. Power Sources*, 2013, **240**, 729-753.
54 D. Xu, P. Dai, X. Liu, C. Cao and Q. Guo, *J. Power Sources*, 2008, **182**, 616-620.
55 Y. Shang, R. Chen and G. Jiang, *Int. J. Hydrogen Energy*, 2008, **33**, 6719-6726.
56 M. Rakap and S. Özkar, *Appl. Catal. B: Environmental*, 2009, **91**, 21-29.
57 Y. Li, Q. Zhang, N. Zhang, L. Zhu, J. Zheng and B. Chen, *Int. J. Hydrogen Energy*, 2013, **38**, 13360-13367.
58 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169-172.

View Article Online
DOI: 10.1039/C6RA17340C

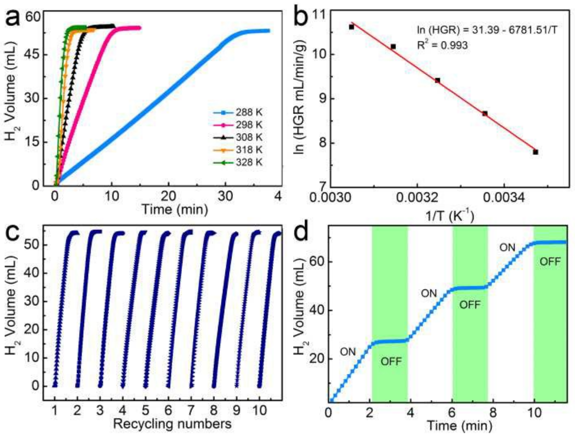
59 F. Erogbogbo, T. Lin, P. M. Tucciarone, K. M. LaJoie, L. Lai, G. D. Patki, P. N. Prasad and M. T. Swihart, *Nano Lett.*, 2013, **13**, 451-456.

60 M. C. Biesinger, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2010, **257**, 887-898.

61 J. P. Espinós, J. Morales, A. Barranco, A. Caballero, J. P. Holgado and A. R. González-Elipe, *J. Phys. Chem. B*, 2002, **106**, 6921-6929.

62 W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2012, **134**, 17462-17465.

View Article Online
DOI: 10.1039/C6RA17340C



3D hierarchical CuO/Co_3O_4 core-shell nanowires array works as a robust and high-active catalyst toward the hydrolytic dehydrogenation of $NaBH_4$ for on-demand hydrogen generation under alkaline solutions, with a maximum hydrogen generation rate of 6162.55 mL/min/$g_{(CuO/Co3O4)}$ at ambient conditions and an activation energy of 56.38 KJ/mol.