

pubs.acs.org/cm

Cobalt Oxide Encapsulated in C₂N-h2D Network Polymer as a Catalyst for Hydrogen Evolution

Javeed Mahmood,[†] Sun-Min Jung,[†] Seok-Jin Kim,[†] Jungmin Park,[‡] Jung-Woo Yoo,[‡] and Jong-Beom Baek^{*,†}

[†]School of Energy and Chemical Engineering/Center for Dimension-Controllable Organic Frameworks, Ulsan National Institute of Science and Technology (UNIST), 100 Banyeon, Ulsan 689-798, South Korea

[‡]School of Materials Science and Engineering/Low-Dimensional Carbon Materials Center/KIST-UNIST Ulsan Center for Convergent Materials, Ulsan National Institute of Science and Technology (UNIST), 100 Banyeon, Ulsan 689-798, South Korea

Supporting Information

ABSTRACT: With cobalt oxides as promising catalysts for hydrogen generation, 2D network polymer-supported cobalt-oxide catalysts with good crystallinity are highly anticipated to enhance catalytic performance. Here we report the fabrication of a 2D nitrogenated network polymer-encapsulated cobalt-oxide ($Co@C_2N$) catalyst via an *in situ* solvothermal synthesis. $Co@C_2N$ exhibits outstanding catalytic activities for hydrogen (H_2) generation from the hydrolysis of alkaline sodium borohydride ($NaBH_4$) solutions. The rate of maximum hydrogen generation is comparable to the best reported values for catalysts containing other noble metals in alkaline solutions. Furthermore, $Co@C_2N$ can also catalyze the *in situ* reduction of a nitro group into an amino group (4-nitrophenol to 4-aminophenol) in the presence of NaBH₄. The origin of high catalytic activity with enhanced stability could be due to the strong interaction between the cobalt-oxide nanoparticle and the C_2N framework, which contains a large portion of nitrogen.



INTRODUCTION

Hydrogen is a clean and efficient fuel and can serve as an excellent alternative to fossil fuels. In fuel cell systems, hydrogen is the most eco-friendly anodic fuel for the generation of electricity. However, many problems are associated with the safe and convenient utilization of hydrogen fuel. One of the foremost issues is related to hydrogen storage, which must be efficient while also safely controlling the storage and release processes. Although sodium borohydride (NaBH₄) is currently regarded as a convenient way to store hydrogen at high densities, it is crucial to develop efficient catalysts for the release of hydrogen.¹ The catalytic decomposition of sodium borohydride in water is an easy method by which to obtain clean hydrogen, where the catalysts perform a vital role in controlling the speed and extent of hydrogen generation. The hydrogen evolution reaction of NaBH4 on the surface of a suitable catalyst under an ambient condition can be expressed by the following eq $1.^2$

$$NaBH_4 + 2H_2O \xrightarrow{Catalyst} NaBO_2 - 4H_2$$
(1)

The most popular catalysts for obtaining hydrogen from hydrides are mainly based on noble metals such as ruthenium (Ru) and platinum (Pt).^{3,4} However, due to the very high cost and limited supply of noble metals, many efforts have gone into looking for alternative catalysts composed of inexpensive materials.⁵ Nonprecious transition metal oxides are broadly studied as catalysts due to their diversity of oxidation states for efficient redox charge transfers.⁶ Cobalt oxides have been recognized for their nontoxicity, high stability, and low cost.^{7–14}

They are also used as catalysts for the oxygen reduction reaction (ORR) in fuel cells and for the oxygen evolution reaction (OER) necessary for water splitting. $^{15\!,16}$ In addition, cobalt oxides can serve as efficient catalytic precursors for NaBH₄ hydrolysis, as they can be reduced in situ to form active Co. B catalysts.^{17,18} Crystalline cobalt oxides with a high surface area are conducive to NaBH4 hydrolysis on the surface of the catalyst.^{19,20} Hence, cobalt oxides with high crystallinity and a large surface area are desirable for efficient catalysis. By implanting the crystalline metal oxide on a carbon support, the crystallinity and surface area can be enhanced. A number of techniques, such as electrochemical deposition,²¹ the hydro-thermal process,²² thermal decomposition,⁶ thermal oxida-tion,²³ and spray pyrolysis²⁴ have been applied in the production of nanostructured cobalt oxides.^{25–27} Recently, porous single-crystal and ordered mesoporous cobalt-oxide structures were developed using templates.^{28,29} However, cobalt oxide encapsulated in a two-dimensional (2D) network polymer framework has not been reported as catalyst for hydrogen evolution and heterogeneous reduction of nitro groups into amino groups at the same time.

This study undertakes the *in situ* synthesis of a 2D network polymer in the presence of cobalt chloride $(CoCl_2)$ and thus the production of highly crystalline cobalt-oxide nanoparticles encapsulated in a 2D porous network polymer. The encapsulated cobalt-oxide nanoparticles in the 2D porous

Received: May 9, 2015

Revised: June 23, 2015

network polymer show outstanding catalytic activity for $NaBH_4$ hydrolysis in alkaline solutions relative to those of the other reported catalysts based on pure precious metals. The material was also evaluated as a catalyst for the *in situ* reduction of 4-nitrophenol into 4-aminophenol in the presence of $NaBH_4$.

EXPERIMENTAL SECTION

Chemicals. All solvents, chemicals, and reagents were purchased from Aldrich Chemical Inc., unless otherwise stated. Solvents were degassed with nitrogen purging prior to use. All the reactions were carried out under nitrogen atmosphere using oven-dried glassware. 1,2,3,4,5,6-Hexaaminobenzene was synthesized according to literature procedure.³⁰

Characterization. Thermogravimetric analysis (TGA) were conducted in air and nitrogen atmosphere at a heating rate of 10 °C/min using a Thermogravimetric Analyzer Q200 TA Instrument, U.S.A. The surface area was calculated by nitrogen adsorptiondesorption isotherms using the Brunauer-Emmett-Teller (BET) method on BELSORP-max (BEL Japan Inc.). Scanning electron microscope (SEM) images were taken on Field Emission Scanning Electron Microscope Nanonova 230 FEI, U.S.A. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Fisher K-alpha Spectrometer (UK). X-ray diffraction (XRD) patterns were taken on High Power X-ray Diffractometer D/MAZX 2500 V/PC (Cu K α radiation, 35 kV, 20 mA, $\lambda = 1.5418$ Å) Rigaku, Japan. High resolution transmission electron microscopy (HR-TEM) was performed by using JEM-2100F (JEOL, Japan) under an operating voltage of 200 keV. The samples for TEM were prepared by drop casting N-methyl-2pyrrolidone (NMP) dispersion on Quantifoil holey carbon TEM grid and dried in oven at 80 °C. Elemental analysis was conducted with Thermo Scientific Flash 2000. Nuclear magnetic resonance (NMR) spectra were taken using a FT-NMR 400 MHz Agilent Spectrometer in DMSO- d_6 as a solvent, and mass spectra were measured on Bruker Mass Spectrometer (Germany).

Synthesis of Co@C₂N. CoCl₂ (1.15 g) was first dissolved in anhydrous NMP (80 mL) on the ice bath in round-bottom flask and then added 1.68 g (5.403 mmol) of hexaketocyclohexane (HKH) followed by 1.5 g (5.403 mmol) of 1,2,3,4,5,6-hexaaminobenzene (HAB) trihydrochloride under the nitrogen atmosphere and refluxed for 8 h. The reaction mixture was then cooled to room temperature and sodium borohydride (NaBH₄) solution (10 wt %, 40 mL NMP) was slowly added into the reaction mixture and refluxed for additional 5 h. After the mixture was cooled, it was poured into water, and the precipitates were collected by filtration using PTFE membrane (0.45 μ m). The product was further purified by Soxhlet extraction with methanol and water for 24 h each. After freeze-drying, the black powder was annealed at 450 °C under argon atmosphere for 2 h.

Catalytic Hydrogen Evolution Test. In a typical experimental setup, an oven-dried flask containing the $Co@C_2N$ (10 mg) catalyst was flushed with nitrogen. Then, an aqueous mixture of NaBH₄ (10 wt %, 3 mL) solution and NaOH solution (5 wt %, 3 mL) was injected through the rubber plug sealed flask by a syringe. The volume of the H₂ generated was measured using water displacement method. The reaction temperature was controlled by immersing the flask in a temperature controlled oil bath.

Catalytic Reduction Reaction. In a two-neck flask, $Co@C_2N$ (10 mg) catalyst and deionized water (30 mL) were charged. Then, 4nitrophenol (2.0 g, 14.4 mmol) and aqueous NaBH₄ (10 wt %, 20 mL) solution were added. The mixture was stirred at room temperature until the yellowish solution completely disappeared after 30–60 min. After reaction completed, the reaction mixture was filtered through PTFE membrane (0.45 μ m) to recover the Co@C₂N catalyst. The filtrate was dried to give quantitative yield of 4-aminophenol. The product was characterized without further purification.

RESULTS AND DISCUSSION

The cobalt oxide encapsulated in C_2N holey two-dimensional network polymer ($Co(\partial C_2N)$ material was simply synthesized

by a condensation reaction between HKH) and HAB 30 in N-methyl-2-pyrrolidone $(\rm NMP)^{31}$ in the presence of cobalt chloride (CoCl_2) (Figure 1a; detailed synthesis and workup



Figure 1. (a) Schematic presentation of the $Co@C_2N$ synthesis; (b) the behavior of $Co@C_2N$ in the magnetic field. $Co@C_2N$ in a vial without a magnetic field (left); $Co@C_2N$ in the vial with a magnetic field (right), revealing the magnetic attraction of the black $Co@C_2N$ powder toward a magnet, with the material accumulated on the side of the glass wall of the vial; (c) SEM image of $Co@C_2N$; (d) low-magnification HR-TEM image, showing a uniform distribution of cobalt-oxide nanoparticles in the C_2N framework; (e) high-magnification HR-TEM image disclosing the Co nanoparticles tightly encapsulated by the C_2N framework.

procedures are described in the Experimental Section). The resultant black powder was annealed at 450 °C for 2 h under an argon atmosphere. Interestingly, the material shows strong attraction toward an external magnet (Figure 1b). The network polymer has empirical formula of C₂N for the repeating unit in the basal plane (Figure 1a); thus, the cobalt-oxide nanoparticles embedded in the C_2N structure are denoted as $Co@C_2N$. A scanning electron microscope (SEM) and a high-resolution transmission electron microscope (HR-TEM) were used to study the morphology of the Co@C2N structure. The SEM image of the $Co@C_2N$ shows granule-type morphology (Figure 1c). The HR-TEM image of the $Co@C_2N$ reveals the presence of well-distributed particles in the C_2N matrix (Figure 1d). The average diameter of the cobalt-oxide particles is in the range of 10–20 nm (Figure S1a). The high-resolution TEM (HR-TEM) image also shows that cobalt-oxide nanoparticles are very

tightly encapsulated with a well-defined C2N framework (Figure 1e). The number of coated C₂N layers varies from 2 to 12 in the Co@C₂N (Figures S1b and S2). The average number of C₂N layers encapsulating nanoparticles is approximately 3, and the average size of nanoparticles is approximately 6 nm. The Fast Fourier Transform (FFT) image of the Co@ C₂N can be assigned to the diffraction planes of the crystalline structure of the nanoparticles coated with C₂N layers (Figure 1e, inset). The C₂N layers can easily be identified around the outer surface of the cobalt-oxide nanoparticles with an interlayer spacing of 0.327 nm (Figure S3), which is very close to that of the parent C₂N-h2D.³¹ These results suggest that the encapsulation of the cobalt-oxide nanoparticles inside the well-defined C₂N framework efficiently protects the cobaltoxide nanoparticles and thus enhances the catalytic activity with long-term stability.

An elemental analysis (EA) further revealed that the Co@ C_2N contains ~28.5 wt % cobalt oxide with 71.05 wt % C_2N framework. A thermogravimetric analysis (TGA) also supports the EA results (Table S1, Figure S4); organic C_2N should be completely decomposed in air without leaving residue at temperatures above 400 °C, but Co@ C_2N displayed approximately 40 wt % of residue. The higher weight content (~40 wt %) from the TGA as compared to that (~28 wt %) from the EA is due to the further oxidation of cobalt into cobalt oxide in air at an elevated temperature.

SEM coupled energy-dispersive spectroscopy (SEM-EDS) (Figures S5) and TEM elemental mapping (Figure S6) were also used to confirm the elemental composition of $Co@C_2N$. A uniform distribution of cobalt-oxide nanoparticles in the $Co@C_2N$ framework was detected by elemental mappings in the SEM-EDS analysis. In addition to SEM-EDS, the XPS survey spectra of the $Co@C_2N$ show the presence of C, N, O, and Co (Figure 2a). Detailed data are summarized in Table S1.



Figure 2. XPS survey spectra: (a) full XPS survey spectrum. The inset shows the deconvoluted Co peak; deconvoluted survey spectra of (b) C 1s, (c) N 1s; (d) powder HP-XRD pattern of $Co@C_2N$.

The deconvoluted Co peak (Figure 2) reveals that the oxidation state of Co in the Co $@C_2N$ is mainly the Co³⁺ state with small amount of Co²⁺ (inset, Figure 2a).³² The powder X-ray diffraction (XRD) pattern of the Co $@C_2N$ after annealing at 450 °C reveals that its structure is highly crystalline (Figure 2b). The diffraction peaks marked with pink spots at 2θ values of 19.02°, 31.23°, 36.72°, 38.05°, 44.52°, 55.50°, 59.40°, and

65.06° for the crystal can be assigned to the (111), (220), (311), (222), (400), (422), (511), and (440) planes of cobaltoxide (Co₃O₄) crystal, respectively, whereas the peaks spotted with cyan at 2θ values of 42.40° and 61.52° for the cobalt-oxide (CoO) crystal can be assigned to the (200) and (220) planes of the CoO crystals, respectively. The XRD profile indicates mainly the presence of Co₃O₄ and CoO in the material as an active catalyst for hydrogen evolution (JCPDS 78-0431). From the XRD spectrum, it is clear that the population of Co₃O₄ is greater than that of CoO.

After annealing at 450 °C, the Co@C₂N was used as a catalyst for hydrogen production by means of NaBH₄ hydrolysis in alkaline media. Plots of the H₂ generation volume as a function of time at different temperatures are shown in Figure 3a. The H₂ generation rate clearly increases with respect



Figure 3. Catalytic hydrogen generation of $Co@C_2N$: (a) Hydrogen generation rate for $Co@C_2N$ at different temperature; (b) corresponding Arrhenius plot obtained from the data in (a).

to the temperature due to the accelerated movement of the $\mathrm{NaBH_4}$ molecules. 19 It can also be seen that the volume of the total H₂ generated always approaches 1500 mL, which corresponds to the maximum theoretical value for a NaBH₄ dosage.¹⁹ Furthermore, the Co@C₂N reaches a maximum H_2 generation rate of 8903 mL min⁻¹ g^{-1} at 303 K (ambient condition). For comparison, the maximum H_2 generation rates of different metal catalysts are summarized in the Table S3. As $Co@C_2N$ contains 30 wt % catalytic cobalt oxide, the actual H_2 generation rate must be much higher than the reported value.²⁰ These results indicate that Co@C2N has very high catalytic activity and that it can serve as an excellent alternative to the noble metal catalysts currently used during the catalytic generation of H₂ via the hydrolysis of NaBH₄. The Arrhenius activation energy (E_a) of the catalytic reaction can be calculated using the following eq 2:

$$r = k_{\rm o} \exp\left(-\frac{E_{\rm a}}{RT}\right) \tag{2}$$

Here *r* denotes the reaction rate, *R* is the ideal gas constant, k_0 represents the reaction constant, and *T* is the reaction temperature. The values of the rate constant *k* at different temperatures are calculated from the slope of the initial linear part of each plot. From the slope of the Arrhenius plot shown in Figure 3b, the Arrhenius activation energy of $Co@C_2N$ was determined to be approximately 66.174 kJ mol⁻¹. The low Arrhenius activation energy may be due to the synergic effect of Co nanoparticles and the two-dimensional (2D) C₂N structure. The stability of $Co@C_2N$ was explored during the hydrolysis of NaBH₄. The result revealed good stability, nearly maintaining its activity up to five runs (Figure 4a). The efficient catalytic properties may have two possible causes. The first may be the high surface area, which provides more active sites for catalytic reactions, and the second stems from the 2D C₂N polymer,



Figure 4. (a) Stability test of $Co@C_2N$ during catalysis at 303 K; (b) nitrogen absorption and desorption isotherm for $Co@C_2N$.

which protects the cobalt-oxide nanoparticles. The holey C_2N coating on the cobalt-oxide nanoparticles imparts a synergic effect by providing not only a large surface but also good isolation of the cobalt-oxide nanoparticles in the C_2N matrix (see Figure 1d).

To prove this scenario, the Brunauer-Emmett-Teller (BET) surface area was measured through a nitrogen adsorption-desorption analysis of Co@C2N (Figure 4b). The specific surface area was measured to be 231 $m^2 g^{-1}$ with an average pore diameter 4.54 nm. To further understand the interaction between cobalt-oxide nanoparticle and C2N framework, the magnetic properties of $Co@C_2N$ were recorded using a Quantum Design SQUID-VSM. Figure S7 displays the hysteresis loop of the sample measured at 5 and 300 K. As shown in the inset of Figure S7, the magnetization of the sample clearly displays strong ferromagnetic behavior with nonzero coercivity and remanence even at 300 K. Indeed, this strong ferromagnetic behavior is somewhat surprising, as XRD indicates that the cobalt in our sample mostly presents as cobalt-oxide (Co_3O_4) crystal, which is a well-known antiferromagnet in the bulk form. Nanoparticles of Co₃O₄ have been shown to be weak ferromagnets due to uncompensated surface spins.³³ Based on ~28.5 wt % cobalt in the sample (Table S1), the saturation of the magnetization at 5 K and 7 T reaches ~0.8 $\mu_{\rm B}$. Unlike typical Co₃O₄ nanoparticles, nearly all of the spins in the Co^{2+} in our sample were involved in collinear ordering. In general, the electronic and magnetic configurations of nanosized particles can be dramatically influenced by the chemisorbed surface ligand. Such a ligand field can induce strong pinning of the surface spins, which even can be transferred into the core of the particles via exchange interactions.^{34,35} The remarkable change of magnetic configuration in our sample reflects strong interaction between the valence electrons in the Co ions and π -conjugated electrons in the C₂N layer, which may lead to enhanced performance as a catalyst.

Furthermore, 4-nitrophenol is widely present in wastewater, originating from agricultural and industrial sources. It is regarded to be one of the most widespread organic pollutants.³⁶ Hence, the transformation from the nitro to the amino forms has great potential industrial value in, for instance, aniline and paracetamol production.³⁴ The catalytic reduction of 4-nitrophenol into 4-aminophenol by NaBH₄ was initially reported by Pal in 2002 using silver nanoparticles as a catalyst.³⁷ The reduction reaction is a commonly used reaction to test the catalytic activity of an aqueous solution under mild conditions.³⁸ Co@C₂N was also used as a heterogeneous catalyst to catalyze the hydrogenation of 4-nitrophenol into 4-aminophenol, is an important synthon for the chemical and pharmaceutical industries. It is mainly produced by the hydrogenation of nitrobenzene over

precious metals in the presence of hydrogen under relatively high pressure.³⁹ Interestingly, $Co@C_2N$ itself can catalyze very efficiently the reduction of 4-nitrophenol into 4-aminophenol at room temperature in the presence of NaBH₄ with an almost quantitative yield. The product was characterized by NMR and mass spectrometry without purification (Figure S8–S11, Table S2), indicating that the yield is indeed quantitative.

CONCLUSIONS

In summary, a facile and scalable method is reported for the synthesis of cobalt oxide encapsulated in 2D network polymer ($Co@C_2N$). The synthesized $Co@C_2N$ was used as a catalyst for hydrogen evolution of NaBH₄, exhibiting outstanding catalytic activity. The maximum H₂ evolution rate of the $Co@C_2N$ catalyst exceeds most reported values of catalysts containing transition metals and/or noble metals carried out under similar conditions. Thus, the hydrolysis of NaBH₄ can be achieved in an ambient condition and hydrogen gas can be evolved at an appreciable rate. $Co@C_2N$ also has great potential to be used as a novel catalyst for the reduction of nitro groups in organic compounds. The results here suggest that $Co@C_2N$ is a promising candidate to replace noble metal-based catalysts for the hydrogen evolution of NaBH₄ and the reduction of nitro groups into amino groups at the same time.

ASSOCIATED CONTENT

Supporting Information

Additional figures (particle distribution graph, TEM images, TGA graph, EDS both from TEM and SEM, magnetization, reduction of nitrophenol, mass and NMR spectra) and Tables S1, S2 and S3 are included in this section. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.Sb01734.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jbbaek@unist.ac.kr. Tel: +82-52-217-2510. Fax: +82-52-217-2019.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by Creative Research Initiative (CRI), Mid-Career Researcher (MCR), BK21 Plus and Basic Research Laboratory (BRL) programs funded by the National Research Foundation (NRF) of Korea, and the US Air Force Office of Scientific Research through the Asian Office of Aerospace R&D (AFOSR-AOARD).

REFERENCES

(1) Clark, T. J.; Whittell, G. R.; Manners, I. Highly Efficient Colloidal Cobalt- and Rhodium-Catalyzed Hydrolysis of $H_3N \cdot BH_3$ in Air. *Inorg. Chem.* **2007**, *46*, 7522–7527.

(2) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen. *J. Am. Chem. Soc.* **1953**, *75*, 215–219.

(3) Wu, C.; Zhang, H.; Yi, B. Hydrogen Generation from Catalytic Hydrolysis of Sodium Borohydride for Proton Exchange Membrane Fuel Cells. *Catal. Today* **2004**, *93–95*, 477–483.

(4) Özkar, S.; Zahmakıran, M. Hydrogen Generation from Hydrolysis of Sodium Borohydride Using Ru(0) Nanoclusters as Catalyst. J. Alloys Compd. 2005, 404–406, 728–731.

(5) Tong, D.-G.; Han, X.; Chu, W.; Chen, H.; Ji, X.-Y. Preparation and Characterization of Co-B Flowers with Mesoporous Structure. *Mater. Res. Bull.* **2008**, *43*, 1327–1336.

(6) Ryu, J.; Kim, S.-W.; Kang, K.; Park, C. B. Synthesis of Diphenylalanine/Cobalt Oxide Hybrid Nanowires and Their Application to Energy Storage. *ACS Nano* **2009**, *4*, 159–164.

(7) Rakhi, R. B.; Chen, W.; Cha, D.; Alshareef, H. N. Substrate Dependent Self-Organization of Mesoporous Cobalt Oxide Nanowires with Remarkable Pseudocapacitance. *Nano Lett.* **2012**, *12*, 2559–2567.

(8) Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-Temperature Oxidation of CO Catalysed by Co_3O_4 Nanorods. *Nature* **2009**, 458, 746–749.

(9) Zhu, Z.; Li, X.; Zeng, Y.; Sun, W.; Zhu, W.; Huang, X. Application of Cobalt Oxide Nanoflower for Direct Electrochemistry and Electrocatalysis of Hemoglobin with Ionic Liquid as Enhancer. *J. Phys. Chem. C* 2011, *115*, 12547–12553.

(10) Melaet, G.; Ralston, W. T.; Li, C.-S.; Alayoglu, S.; An, K.; Musselwhite, N.; Kalkan, B.; Somorjai, G. A. Evidence of Highly Active Cobalt Oxide Catalyst for the Fischer–Tropsch Synthesis and CO₂ Hydrogenation. J. Am. Chem. Soc. **2014**, 136, 2260–2263.

(11) Polshettiwar, V.; Baruwati, B.; Varma, R. S. Self-Assembly of Metal Oxides into Three-Dimensional Nanostructures: Synthesis and Application in Catalysis. *ACS Nano* **2009**, *3*, 728–736.

(12) Huang, X.-l.; Wang, R.-z.; Xu, D.; Wang, Z.-l.; Wang, H.-g.; Xu, J.-j.; Wu, Z.; Liu, Q.-c.; Zhang, Y.; Zhang, X.-b. Homogeneous CoO on Graphene for Binder-Free and Ultralong-Life Lithium Ion Batteries. *Adv. Funct. Mater.* **2013**, *23*, 4345–4353.

(13) Varghese, B.; Zhang, Y.; Dai, L.; Tan, V. B. C.; Lim, C. T.; Sow, C.-H. Structure-Mechanical Property of Individual Cobalt Oxide Nanowires. *Nano Lett.* **2008**, *8*, 3226–3232.

(14) Seo, W. S.; Shim, J. H.; Oh, S. J.; Lee, E. K.; Hur, N. H.; Park, J. T. Phase- and Size-Controlled Synthesis of Hexagonal and Cubic CoO Nanocrystals. *J. Am. Chem. Soc.* **2005**, *127*, 6188–6189.

(15) Liu, J.; Jiang, L.; Zhang, B.; Jin, J.; Su, D. S.; Wang, S.; Sun, G. Controllable Synthesis of Cobalt Monoxide Nanoparticles and the Size-Dependent Activity for Oxygen Reduction Reaction. *ACS Catal.* **2014**, *4*, 2998–3001.

(16) Liao, L.; Zhang, Q.; Su, Z.; Zhao, Z.; Wang, Y.; Li, Y.; Lu, X.; Wei, D.; Feng, G.; Yu, Q.; Cai, X.; Zhao, J.; Ren, Z.; Fang, H.; Robles-Hernandez, F.; Baldelli, S.; Bao, J. Efficient Solar Water-Splitting Using a Nanocrystalline CoO Photocatalyst. *Nat. Nanotechnol.* **2014**, *9*, 69–73.

(17) Krishnan, P.; Advani, S. G.; Prasad, A. K. Cobalt Oxides as Co_2B Catalyst Precursors for the Hydrolysis of Sodium BoroHydride Solutions to Generate Hydrogen for PEM Fuel Cells. *Int. J. Hydrogen Energy* **2008**, *33*, 7095–7102.

(18) Simagina, V. I.; Komova, O. V.; Ozerova, A. M.; Netskina, O. V.; Odegova, G. V.; Kellerman, D. G.; Bulavchenko, O. A.; Ishchenko, A. V. Cobalt Oxide Catalyst for Hydrolysis of Sodium Borohydride and Ammonia Borane. *Appl. Catal., A* **2011**, *394*, 86–92.

(19) Lu, A.; Chen, Y.; Jin, J.; Yue, G.-H.; Peng, D.-L. CoO Nanocrystals as a Highly Active Catalyst for the Generation of Hydrogen from Hydrolysis of Sodium Borohydride. *J. Power Sources* **2012**, *220*, 391–398.

(20) Pfeil, T. L.; Pourpoint, T. L.; Groven, L. J. Effects of Crystallinity and Morphology of Solution Combustion Synthesized Co_3O_4 as a Catalyst Precursor in Hydrolysis of Sodium Borohydride. *Int. J. Hydrogen Energy* **2014**, *39*, 2149–2159.

(21) Meng, Z.; Liu, B.; Zheng, J.; Sheng, Q.; Zhang, H. Electrodeposition of Cobalt Oxide Nanoparticles on Carbon Nanotubes, and Their Electrocatalytic Properties for Nitrite Electrooxidation. *Microchim. Acta* **2011**, *175*, 251–257. (22) Jiang, J.; Liu, J.; Ding, R.; Ji, X.; Hu, Y.; Li, X.; Hu, A.; Wu, F.; Zhu, Z.; Huang, X. Direct Synthesis of CoO Porous Nanowire Arrays on Ti Substrate and Their Application as Lithium-Ion Battery Electrodes. J. Phys. Chem. C 2009, 114, 929–932.

(23) Varghese, B.; Teo, C. H.; Zhu, Y.; Reddy, M. V.; Chowdari, B. V. R.; Wee, A. T. S.; Tan, V. B. C.; Lim, C. T.; Sow, C. H. Co_3O_4 Nanostructures with Different Morphologies and Their Field-Emission Properties. *Adv. Funct. Mater.* **2007**, *17*, 1932–1939.

(24) Lupo, F.; Kamalakaran, R.; Gulino, A. Viable Route for Cobalt Oxide–Carbon Nanocomposites. J. Phys. Chem. C 2009, 113, 15533– 15537.

(25) Risbud, A. S.; Snedeker, L. P.; Elcombe, M. M.; Cheetham, A. K.; Seshadri, R. Wurtzite CoO. *Chem. Mater.* **2005**, *17*, 834–838.

(26) An, K.; Lee, N.; Park, J.; Kim, S. C.; Hwang, Y.; Park, J.-G.; Kim, J.-Y.; Park, J.-H.; Han, M. J.; Yu, J.; Hyeon, T. Synthesis, Characterization, and Self-Assembly of Pencil-Shaped CoO Nanorods. *J. Am. Chem. Soc.* **2006**, *128*, 9753–9760.

(27) Li, D.; Ding, L.-X.; Wang, S.; Cai, D.; Wang, H. Ultrathin and Highly-Ordered CoO Nanosheet Arrays for Lithium-ion Batteries with High Cycle Stability and Rate Capability. *J. Mater. Chem. A* **2014**, *2*, 5625–5630.

(28) Ren, Y.; Bruce, P. G.; Ma, Z. Solid-Solid Conversion of Ordered Crystalline Mesoporous Metal Oxides Under Reducing Atmosphere. J. Mater. Chem. 2011, 21, 9312–9318.

(29) Tüysüz, H.; Weidenthaler, C.; Schüth, F. A Strategy for the Synthesis of Mesostructured Metal Oxides with Lower Oxidation States. *Chem. - Eur. J.* 2012, *18*, 5080–5086.

(30) Mahmood, J.; Kim, D.; Jeon, I.-Y.; Lah, M. S.; Baek, J.-B. Scalable Synthesis of Pure and Stable Hexaaminobenzene Trihydrochloride. *Synlett* **2013**, *24*, 246–248.

(31) Mahmood, J.; Lee, E. K.; Jung, M.; Shin, D.; Jeon, I.-Y.; Jung, S.-M.; Choi, H.-J.; Seo, J.-M.; Bae, S.-Y.; Sohn, S.-D.; Park, N.; Oh, J. H.; Shin, H.-J.; Baek, J.-B. Nitrogenated holey two-dimensional structures. *Nat. Commun.* **2015**, *6*, 6486.

(32) Dominguez, M.; Taboada, E.; Idriss, H.; Molins, E.; Llorca, J. Fast and Efficient Hydrogen Generation Catalyzed by Cobalt Talc Nanolayers Dispersed in Silica Aerogel. *J. Mater. Chem.* **2010**, *20*, 4875–4883.

(33) Moro, F.; Yu Tang, S. V.; Tuna, F.; Lester, E. Magnetic Properties of Cobalt Oxide Nanoparticles Synthesised by a Continuous Hydrothermal Method. *J. Magn. Magn. Mater.* **2013**, 348, 1–7.

(34) Fenger, R.; Fertitta, E.; Kirmse, H.; Thunemann, A. F.; Rademann, K. Size Dependent Catalysis with CTAB-Stabilized Gold Nanoparticles. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9343–9349.

(35) Li, S.-D.; Bi, H.; Fang, J.-L.; Zhong, W.; Du, Y.-W. Surface Spins Pinning Effect on the Magnetic Properties in Co_3O_4 Nanocrystallites Covered with Polymer Decomposition Residues. *Chin. Phys. Lett.* **2004**, *21*, 737.

(36) Nemanashi, M.; Meijboom, R. Synthesis and Characterization of Cu, Ag and Au Dendrimer-Encapsulated Nanoparticles and Their Application in the Reduction of 4-Nitrophenol to 4-Aminophenol. *J. Colloid Interface Sci.* **2013**, *389*, 260–267.

(37) Pradhan, N.; Pal, A.; Pal, T. Silver Nanoparticle Catalyzed Reduction of Aromatic Nitro Compounds. *Colloids Surf., A* **2002**, *196*, 247–257.

(38) Herves, P.; Perez-Lorenzo, M.; Liz-Marzan, L. M.; Dzubiella, J.; Lu, Y.; Ballauff, M. Catalysis by Metallic Nanoparticles in Aqueous Solution: Model Reactions. *Chem. Soc. Rev.* **2012**, *41*, 5577–5587.

(39) Gelder, E.; Jackson, S. D.; Lok, C. M. A Study of Nitrobenzene Hydrogenation over Palladium/Carbon Catalysts. *Catal. Lett.* **2002**, *84*, 205–208.

Article