## NJC

## PAPER



Cite this: New J. Chem., 2014, 38, 6147

# Co<sub>0.85</sub>Se bundle-like nanostructure catalysts for hydrogenation of 4-nitrophenol to 4-aminophenol<sup>†</sup>

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This study demonstrated the preparation of  $Co_{0.85}Se$  bundle-like nanostructures (BNs) by a templatedirected approach under solvothermal conditions. The  $Co_{0.85}Se$  BNs were utilized as catalysts in the reduction of 4-nitrophenol in the presence of NaBH<sub>4</sub>. The kinetics of the reduction of 4-nitrophenol at three different reaction temperatures were investigated to evaluate the catalytic activity of the  $Co_{0.85}Se$ BNs. The activation energy ( $E_a$ ), activation enthalpy ( $\Delta H^{\ddagger}$ ), and activation entropy ( $\Delta S^{\ddagger}$ ) of the  $Co_{0.85}Se$ BNs and  $Co_{0.85}Se$  nanoparticles (NPs) are 14.66 kJ mol<sup>-1</sup>, 12.15 kJ mol<sup>-1</sup>, 42.51 J mol<sup>-1</sup> K<sup>-1</sup>, and 17.78 kJ mol<sup>-1</sup>, 16.55 kJ mol<sup>-1</sup>, 50.66 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. The above results revealed that the  $Co_{0.85}Se$  BNs exhibited a higher catalytic performance for the hydrogenation of 4-nitrophenol by NaBH<sub>4</sub> than that of the  $Co_{0.85}Se$  BNs at room temperature. It is believed that the prepared  $Co_{0.85}Se$  BNs have potential applications in catalysis.

Received (in Montpellier, France) 12th August 2014, Accepted 25th September 2014

DOI: 10.1039/c4nj01358a

www.rsc.org/njc

## 1. Introduction

In recent years, many effective strategies have been developed for the synthesis of transition metal chalcogenides because of their potential applications in catalysis,<sup>1,2</sup> solar cells,<sup>3,4</sup> gas separation,<sup>5</sup> environmental treatment,<sup>6</sup> and biochemical sensors.<sup>7</sup> Cobalt selenide, an important transition metal chalcogenide, has attracted a great deal of attention because of its good physical and chemical properties. Thus, Co<sub>x</sub>Se<sub>v</sub> materials with different sizes, compositions, morphologies, and phase structures have been prepared through different methods, such as wet chemical methods,8-11 thermal decomposition,12,13 laser irradiation,14 mechanical alloying,15,16 electrodeposition,17,18 and hydro-/ solvothermal methods.<sup>3,6,19–23</sup> In previous reports, the obtained Co<sub>r</sub>Se micro-/nanostructures have mainly been applied as catalysts for oxygen reduction reactions.<sup>9-11</sup> Wang and co-workers reported a facile one-step low-temperature hydrothermal approach for the in situ growth of Co<sub>0.85</sub>Se on a conductive glass substrate that can be utilized as a high-performance counter electrode for dyesensitized solar cells.<sup>3</sup> Recently, Song and co-workers reported that graphene-like hexagonal Co<sub>0.85</sub>Se nanostructures with high

specific surface area can be used as adsorbents in wastewater treatment.<sup>6</sup> More recently, tremelliform  $Co_{0.85}Se$  nanosheets<sup>22</sup> and polycrystalline  $Co_{0.85}Se$  nanotubes<sup>23</sup> have been used as efficient catalysts for the decomposition of N<sub>2</sub>H<sub>4</sub>. Although  $Co_{0.85}Se$  nanosheets and  $Co_{0.85}Se$ -Fe<sub>3</sub>O<sub>4</sub> nanocomposites had been developed to reduce 4-nitrophenol,<sup>18</sup> the synthesis of  $Co_{0.85}Se$  bundle-like nanostructures (BNs) and their efficiency for the catalytic reduction of nitro aromatics by NaBH<sub>4</sub> have been rarely researched.

In this work, Co<sub>0.85</sub>Se BNs were prepared using a facile two-step solvothermal process. Co<sub>0.85</sub>Se nanoparticles (NPs) were also obtained using a similar method. The reduction of 4-nitrophenol to 4-aminophenol is a model reaction that has been widely used for the quantification and comparison of the catalytic activity of noble metals or their alloys.<sup>24–28</sup> Herein, the as-obtained Co<sub>0.85</sub>Se BNs and NPs were applied as heterogeneous catalysts to reduce 4-nitrophenol to 4-aminophenol by NaBH<sub>4</sub> in aqueous solution under three different reaction temperatures. Based on the Arrhenius equation and Eyring equation, the apparent  $E_a$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  for the Co<sub>0.85</sub>Se BNs and NPs were obtained for the first time, respectively.

## 2. Experimental section

#### 2.1. Synthesis of the Co<sub>0.85</sub>Se BNs and Co<sub>0.85</sub>Se NPs

All chemical reagents were analytical grade and were used without further purification. The  $Co_{0.85}Se$  BNs were prepared using a facile two-step process under solvothermal conditions (Scheme 1, route A). First, the synthesis of the  $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$  BN hard template is summarized as follows: 2 mmol  $CoCl_2 \cdot 6H_2O$  and 4 mmol urea were dissolved in a mixed solvent (20 mL H<sub>2</sub>O and 20 mL glycerin);



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<sup>†</sup> Electronic supplementary information (ESI) available: Fig. S1–S6 and Tables S1 and S2. See DOI: 10.1039/c4nj01358a

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then, the solution was transferred into a Teflon lined stainless steel autoclave with a capacity of 50 mL and heated at 433 K for 10 h. Afterward, the pink precipitates were washed with deionized water and ethanol several times each and dried under vacuum at 353 K for 5 h. The Co(CO<sub>3</sub>)<sub>0.35</sub>Cl<sub>0.20</sub>(OH)<sub>1.10</sub> BNs were then obtained. Subsequently, the Co<sub>0.85</sub>Se BNs were synthesized as follows: 100 mg of Co(CO<sub>3</sub>)<sub>0.35</sub>Cl<sub>0.20</sub>(OH)<sub>1.10</sub> BNs and 2 mL of freshly prepared NaHSe solution (1 M) were loaded into a Teflon lined stainless steel autoclave with 50 mL capacity, and the autoclave was then filled with ethanol up to 80% of its total volume. The autoclave was heated at 413 K for 5 h and cooled to room temperature naturally. The black precipitates were filtered off, washed with deionized water and absolute ethanol several times each, and dried under vacuum at 353 K for 5 h. In addition, the Co<sub>0.85</sub>Se NPs were also prepared (Scheme 1, route B).<sup>23</sup>

#### 2.2. Characterization

The structure, morphology and composition of the products were characterized by X-ray powder diffraction (XRD, Shimadzu XRD-6000, Japan), scanning electron microscopy (SEM, Hitachi S-4800, Japan), and energy dispersive X-ray spectroscopy (EDX, INCAx-Sight OXFORD) attached to SEM, transmission electron microscopy (TEM, JEM-2100, 200 kV, Japan), high resolution TEM (HRTEM), and selected-area electron diffraction (SAED), respectively. The X-ray photoelectron spectra (XPS) were recorded on a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI, US) with a non-monochromatized Al–Mg<sub>Ka</sub> radiation exciting source. The UV-vis measurements were performed on a U-4100 (Hitachi, Japan) spectrophotometer. The Brunauer–Emmett–Teller surface areas and the pore-size distributions were determined by Nova 2000E (US) at ~77 K.

#### 2.3. Catalytic reaction

The catalytic reaction process was similar to that in our previous reports.<sup>29</sup> In a typical catalytic reaction, 10 mL (0. 5 mM) of an aqueous solution of 4-nitrophenol and 10 mL (0.1 g  $L^{-1}$ ) of an aqueous dispersion of the Co<sub>0.85</sub>Se catalyst were mixed, and then purged with argon for 10 min to remove the dissolved oxygen. Afterward, 10 mL (0.02 M) of aqueous NaBH<sub>4</sub> solution purged with argon was added to the reaction mixture and time-dependent absorption spectra were recorded in the UV-vis spectrophotometer at 298 K. All of the measurements in this investigation were conducted in triplicate and average values with standard deviation were determined. In the same way as at 298 K, the reduction reaction was also carried out at two other temperatures of 308 K

and 318 K, respectively. Furthermore, the representative sample of the  $Co_{0.85}Se$  BNs was also tested for reusability in the reduction of 4-nitrophenol by NaBH<sub>4</sub>.

### Results and discussion

#### 3.1. Characterization of the Co<sub>0.85</sub>Se BNs and NPs

In order to obtain the  $Co_{0.85}Se$  BNs, we first fabricated the Co-precursor sacrificial template using a facile solvothermal method in a mixed solvent. Fig. S1a (ESI<sup>†</sup>) shows a typical X-ray powder diffraction (XRD) pattern of the sample that served as the precursor. All of the reflection peaks can be indexed to  $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$  (JCPDS No. 38-0547), which are similar to previous reports.<sup>23,30</sup> The Co-precursor with BNs and smooth surface was obtained through the scanning electron microscopy (SEM) image (Fig. S1b, ESI<sup>†</sup>). Moreover, we can clearly see that the bundle-like Co-precursor assembled with nanorods and grew from the center in a horizontal direction. Energy dispersive X-ray (EDX) spectroscopy further confirms the Co-precursor, and the element signals of Co, Cl, O, and C can be found in Fig. S1c (ESI<sup>†</sup>).

The phase, crystallinity and purity of the as-obtained Co<sub>0.85</sub>Se samples were examined by the XRD technique. Fig. 1a shows the XRD pattern of the Co<sub>0.85</sub>Se sample. The characteristic peaks at  $2\theta$  values of 33.3°, 44.8°, and 50.9° correspond to the hexagonal close packed (hcp)  $Co_{0.85}$ Se nanostructure crystal planes of (101), (102), and (110), respectively (JCPDS No. 52-1008). No impurity peaks from other phases can be detected, indicating that the precursor has been totally converted into Co<sub>0.85</sub>Se. The surface composition and quality of the Co<sub>0.85</sub>Se samples were determined by EDX spectrometry and X-ray photoelectron spectra (XPS) are shown in Fig. 1b-d and Fig. S2 (ESI<sup>†</sup>). The EDX results (Fig. 1b) showed that the chemical elements Co and Se were detected, and the ratio of Co to Se is 45.1:54.9. Some C and O from the air or carbon support films can also be observed. Fig. S2 (ESI<sup>+</sup>), Fig. 1c and d show the XPS spectrum of the Co<sub>0.85</sub>Se sample, which mainly exhibits the peaks of Co2p and Se3d, respectively, and the ratio of Co to Se is 46.4:53.6. The binding



Fig. 1 XRD pattern (a), EDX spectrum (b), XPS spectrum of the Co2p region (c) and Se3d region (d) of the as-obtained  $Co_{0.85}$ Se BNs.



Fig. 2 SEM image (a), TEM image (b), HRTEM image (c), and SAED pattern (d) of the as-obtained  $Co_{0.85}$ Se BNs.

energies of ~780.8, ~779.0, ~797.2 and ~794.0 eV are  $Co^{2+}$  2p3/2,  $Co^{3+}$  2p3/2,  $Co^{2+}$  2p1/2 and  $Co^{3+}$  2p1/2, respectively, which are similar to the reported values, <sup>23,31*a*</sup> and the binding energy of ~55.4 eV is close to the previously reported value for Se3d. <sup>23,31*b*</sup>

The morphology and size of the as-obtained Co<sub>0.85</sub>Se BNs were further examined by SEM and transmission electron microscopy (TEM). Fig. 2a shows the SEM image of the products, which clearly reveals that the as-obtained Co<sub>0.85</sub>Se product is BNs with an unsmooth surface. The TEM image (Fig. 2b) further confirms that the products are BNs with lengths and diameters of about 1.5 µm and 300 nm. The typical high resolution TEM (HRTEM) image in Fig. 2c also shows that the nanorods in the BNs are composed of domains of nanocrystallites. From the HRTEM, the lattice spacing is 0.27 nm (Fig. 2c), which can be indexed to the (101) spacing of hcp Co<sub>0.85</sub>Se structures (JCPDS No. 52-1008). Moreover, the corresponding selected-area electron diffraction (SAED) pattern (Fig. 2d) indicates the polycrystalline nature of the nanorods, and the diffraction rings can be easily indexed to the (102), (110), (103), and (112) planes of the hcp  $Co_{0.85}$ Se. As a comparison, the  $Co_{0.85}$ Se samples with a particlelike shape (Fig. S3, ESI<sup>+</sup>) were obtained in the previous report.<sup>23</sup>

#### 3.2. Catalytic performances of the Co<sub>0.85</sub>Se BNs and NPs

4-Aminophenol is an important intermediate in the preparation of paracetamol, acetanilide, phenacetin, and so on.<sup>29,32,33</sup> A series of noble metal catalysts were developed to reduce 4-nitrophenol into 4-aminophenol,<sup>24–28</sup> however, the process was much more costly in this reaction. The reduction reaction was used as a model system to quantitatively evaluate the catalytic activities of the Co<sub>0.85</sub>Se crystals with different morphologies, such as BNs and NPs. As is well-known, this reaction did not occur without a catalyst (Fig. S4, ESI†). The typical UV-vis absorption change of the reaction mixture upon the addition of Co<sub>0.85</sub>Se BNs and NPs are shown in Fig. 3a and b, respectively. The colour of the above mixed solution gradually faded and was ultimately bleached after the addition of the Co<sub>0.85</sub>Se catalysts, and the peak at 400 nm



Fig. 3 Time-dependent UV-vis absorption spectrum changes for the reduction of 4-nitrophenol into 4-aminophenol by (a) Co<sub>0.85</sub>Se BNs and (b) Co<sub>0.85</sub>Se NPs as the catalysts (conditions: 4-nitrophenol, 0.5 mM; Co<sub>0.85</sub>Se catalyst, ~0.1 g L<sup>-1</sup>; NaBH<sub>4</sub>, 0.02 M; temperature, 298 K).

gradually disappeared with the concomitant appearance of a new peak at 300 nm, which substantiates the formation of 4-aminophenol.<sup>29,32–35</sup>

As shown in Fig. 3a, the complete reduction of 4-nitrophenol into 4-aminophenol can be finished within 10 min using Co<sub>0.85</sub>Se BNs as the catalyst. However, the conversion time of 4-nitrophenol into 4-aminophenol was within 14 min using the same quantity of Co<sub>0.85</sub>Se NPs as the catalyst (Fig. 3b), which was lower than that of the Co<sub>0.85</sub>Se BNs. In this catalytic reaction, the amount of NaBH4 was much higher than that of 4-nitrophenol and the concentration of BH<sub>4</sub><sup>-</sup> can be regarded as a constant. Thus, the pseudo-first-order kinetics can be applied for the evaluation of rate constants.<sup>24–29,32–35</sup> The linear relations of  $\ln(C_t/C_0)$  against time that were observed for the Co<sub>0.85</sub>Se catalysts at three different temperatures are shown in Fig. 4a and b, and Fig. S5 (ESI<sup>+</sup>). According to the linear relationship (Table S1, ESI<sup>†</sup>), the average reaction rate constants (Table 1) were calculated from three measurements for each Co<sub>0.85</sub>Se catalyst at temperatures of 298, 308 and 318 K, respectively. The catalytic rate of the Co<sub>0.85</sub>Se BNs at 298 K  $(0.457 \text{ min}^{-1})$  was slightly faster than that of the Co<sub>0.85</sub>Se NPs  $(0.331 \text{ min}^{-1})$  and  $\text{Co}_{0.85}$ Se-Fe<sub>3</sub>O<sub>4</sub> nanocomposites  $(0.3931 \text{ min}^{-1})$ ,<sup>18</sup> and was much faster than that of the Co<sub>0.85</sub>Se nanosheets



**Fig. 4** Plots of  $\ln(C_t/C_0)$  against time for (a)  $C_{0.85}$ Se BNs and (b)  $C_{0.85}$ Se NPs as catalysts at different reaction temperatures of 298, 308, and 318 K; (c) The Arrhenius plots vs. 1000/T and (d) Eyring plots vs.  $\ln(1000/T)$  for reactions catalyzed by  $C_{0.85}$ Se BNs (I) and  $C_{0.85}$ Se NPs (II), respectively.

Table 1Summary of the k,  $E_a$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  for the Co<sub>0.85</sub>Se BNs and NPsas catalysts (conditions: 4-nitrophenol, 10 mL, 0.5 mM; Co<sub>0.85</sub>Se catalyst,10 mL, ~0.1 g L<sup>-1</sup>; NaBH<sub>4</sub>, 10 mL, 0.02 M), respectively

Samples	Т (К)	k (min <sup>-1</sup> )	$\stackrel{E_{\mathrm{a}}}{(\mathrm{kJ}\ \mathrm{mol}^{-1})}$	$\Delta H^{\ddagger}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\ddagger}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Co <sub>0.85</sub> Se BNs	298 308 318	0.457 0.513 0.673	14.66	12.15	42.51
Co <sub>0.85</sub> Se NPs	298 308 318	0.331 0.434 0.530	17.78	16.55	50.66

(0.1721 min<sup>-1</sup>).<sup>18</sup> To investigate in more detail, we obtained the apparent  $E_a$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  based on the Arrhenius equation  $\ln k = \ln A - E_a/(RT)$  (Fig. 4c) and Eyring equation  $\ln(k/T) = \ln(k_B/h) +$  $\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/(RT)$  (Fig. 4d),<sup>35</sup> respectively, and a summary of these data are shown in Table S1 (ESI<sup>+</sup>) and Table 1. It should be noted that the Co<sub>0.85</sub>Se BNs require lower  $E_a$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  than that of the Co<sub>0.85</sub>Se NPs for 4-nitrophenol reduction (Table 1). Here, the Brunauer-Emmett-Teller (BET) surface areas of the Co<sub>0.85</sub>Se crystals were determined as 15.4  $m^2 g^{-1}$  for the Co<sub>0.85</sub>Se BNs, and 54.9 m<sup>2</sup> g<sup>-1</sup> for the Co<sub>0.85</sub>Se NPs. However, the Co<sub>0.85</sub>Se BNs with a small surface-to-volume ratio show a higher catalytic activity than the Co<sub>0.85</sub>Se NPs with a large surface-to-volume ratio in the test. Using the BJH method (Fig. S6, ESI†), the pore size of the  $Co_{0.85}$ Se BNs (~19.7 nm) were found to be larger than the pore size of the  $Co_{0.85}$ Se NPs (~17.8 nm). However, the nitrogen adsorption and desorption measurements (Fig. S6, ESI<sup>†</sup>) showed that the pores should come from the crevices in the 3D structures (Fig. S6a, ESI<sup>†</sup>) of the Co<sub>0.85</sub>Se BNs or aggregation (Fig. S6b, ESI<sup> $\dagger$ </sup>) of the Co<sub>0.85</sub>Se NPs. Therefore, the Co<sub>0.85</sub>Se BNs with 3D structures provide more excellent channels and more active sites for the catalytic reduction of 4-nitrophenol, and as a result, the as-prepared Co<sub>0.85</sub>Se BNs exhibit a higher activity for 4-nitrophenol reduction than the Co<sub>0.85</sub>Se NPs. On the other hand, the Co<sub>0.85</sub>Se NPs could be aggregated into large particles, and as a result, the catalytic activity of the Co<sub>0.85</sub>Se NPs should be reduced. As an example, the reusability experiments for the Co<sub>0.85</sub>Se BNs were performed. Little loss of activity was observed for the Co<sub>0.85</sub>Se BNs after the first 3 cycles, but only a 45% conversion of 4-nitrophenol at the end of the fifth cycle was observed (Table S2, ESI<sup>†</sup>). Furthermore, the activation energies for different metal nanocatalysts are given in Table 2, which

Table 2Comparison of activation energies ( $E_a$ ) of different metal or alloynanoparticle catalysts used in the reduction of 4-nitrophenol

Catalysts	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	Ref.	
Co <sub>0.85</sub> Se BNs	14.66	This work	
Co <sub>0.85</sub> Se NPs	17.78	This work	
P(AMPS)-Cu composites	28.16	35 <i>a</i>	
P(AMPS)-Co composites	27.8	35 <i>b</i>	
P(AMPS)–Ni composites	25.70	35 <i>c</i>	
P(AAm)–CB–Ag composites	15.25	35 <i>d</i>	
Pt nanoparticles	40	26	
Au nanoparticles	49	36	
Fe <sub>3</sub> O <sub>4</sub> /Au	51.2	37	

suggest that  $Co_{0.85}Se$  catalyst systems are as good as other transition metals<sup>35</sup> or noble metal catalysts.<sup>26,36,37</sup> These results indicate that the catalytic performance of  $Co_{0.85}Se$  crystals could be greatly enhanced by controlling the shape,<sup>18</sup> but effectively improving the stability and percentage recovery of the  $Co_{0.85}Se$  catalysts needs further investigation.

## 4. Conclusions

Polycrystalline  $Co_{0.85}Se$  bundle-like nanostructures have been successfully synthesized through a facile and effective two-step hydrothermal method. Based on the Arrhenius equation and Eyring equation at three different temperatures, the activation energy, activation enthalpy, and activation entropy of the  $Co_{0.85}Se$  bundle-like nanostructures and nanoparticles were obtained for the first time. The  $Co_{0.85}Se$  bundle-like nanostructures required a lower activation energy than that of the  $Co_{0.85}Se$ nanoparticles for 4-nitrophenol reduction, and as a result, the  $Co_{0.85}Se$  bundle-like nanostructures showed a higher catalytic activity than that of the  $Co_{0.85}Se$  nanoparticles. Therefore, the good catalytic properties of the  $Co_{0.85}Se$  bundle-like nanostructures will make them attractive for potential applications in the field of catalysis and other applications.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (No. 21071005, 21271006), the Research Culture Funds of Anhui Normal University (No. 2011rcpy038, 2014xmpy13), the Innovation Funds of Anhui Normal University (No. 2014cxjj13), and the Undergraduate Innovation Training Plan of Anhui Normal University (No. 201310370080, 201410370199).

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