



# Cobalt single atoms anchored on N-doped ultrathin carbon nanosheets for selective transfer hydrogenation of nitroarenes

Huining Li<sup>1,2</sup>, Changyan Cao<sup>1,2\*</sup>, Jian Liu<sup>1,2</sup>, Yang Shi<sup>1,2</sup>, Rui Si<sup>3</sup>, Lin Gu<sup>4</sup> and Weiguo Song<sup>1,2\*</sup>

**ABSTRACT** Selective transfer hydrogenation of nitroarenes to amines with transition metal nanocatalysts is appealing due to its low-cost, moderate reaction conditions, good activity and excellent selectivity. Single-atom catalysts (SACs) possessing advantages of maximum atom efficiency and particular electronic structure are expected to be more effective for this reaction, yet no report about it. Herein, cobalt single atoms anchored on N-doped ultrathin carbon nanosheets (denoted as CoSAs/NCNS) were produced and demonstrated as an outstanding SAC for selective transfer hydrogenation of nitroarenes to amines with formic acid as hydrogen donor. The turnover frequency (TOF) reached  $110.6 \text{ h}^{-1}$ , which was 20 times higher than the best results of cobalt nanoparticles reported in literatures under similar reaction conditions. Moreover, CoSAs/NCNS exhibited excellent selectivity for a variety of nitroarenes bearing other reducible functionalities, such as iodo, cyano, keto, vinyl, alkynyl and ester groups. The findings further highlight the ability and advantages of SACs in heterogeneous catalysis.

**Keywords:** single atom, catalysis, cobalt, hydrogenation, nitroarenes

## INTRODUCTION

During recent years, single-atom catalysis has become one of the most attractive new frontiers in catalysis as a model bridging homogeneous and heterogeneous catalysis [1–7]. With the aid of recent advances in synthetic methodologies, atomic-resolution characterization techniques and theoretical modelling, various single-atom catalysts (SACs) were produced and studied for catalysis

[8–20]. Compared with clusters and nanocatalysts, SACs usually exhibit superior activity and excellent selectivity in a wide variety of catalytic reactions owing to their maximum atom efficiency, unsaturated coordinate environment and particular electronic structures [21–28]. Thus, single-atom catalysis provides an ideal platform and opportunity to develop more efficient catalysts.

Functionalized amines are key intermediates for polymers, pharmaceuticals and fine chemicals [29,30]. Catalytic hydrogenation of nitroarenes with molecular hydrogen is the most straightforward and atom-economical route. Especially, heterogeneous catalysts based on transition metals (e.g., Fe and Co) have been demonstrated to be potential replacements for commonly used homogeneous catalysts and noble metal catalysts [31–37]. However, high  $\text{H}_2$  pressure and elaborate experimental setup (e.g.,  $110^\circ\text{C}$ , 5 MPa) were usually required. As an alternative to direct hydrogenation, transfer hydrogenation of nitroarenes with formic acid [38–43], alcohol [44–46] or hydrazine [47] has also attracted considerable attention because of the moderate reaction conditions and readily available hydrogen donors [48,49], which may be regarded as hydrogen carrier. Beller and co-workers [39,40] demonstrated that  $\text{Fe}_2\text{O}_3$  or  $\text{Co}_3\text{O}_4$  nanoparticles surrounded by nitrogen-doped graphene layers (denoted as  $\text{Fe}_2\text{O}_3/\text{NGr}@C$  or  $\text{Co}_3\text{O}_4/\text{NGr}@C$ ) were active catalysts for the activation of formic acid in the transfer hydrogenation of nitroarenes to anilines. Since then, several other kinds of cobalt catalysts were also reported [41,42]. Nevertheless, all the reported catalysts based on transition metals were nanoparticles by far and

<sup>1</sup> Beijing National Laboratory for Molecular Sciences Laboratory of Molecular Nanostructures and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>2</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup> Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

<sup>4</sup> Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

\* Corresponding authors (emails: [cycas@iccas.ac.cn](mailto:cycas@iccas.ac.cn) (Cao C); [wsong@iccas.ac.cn](mailto:wsong@iccas.ac.cn) (Song W))

their specific activities needed to be further improved. Taking consideration of the advantages of SACs described above, we envisioned that transition metal SACs would exhibit better activity for this reaction.

Herein, we report a reliable method to produce cobalt single atoms anchored on N-doped ultrathin carbon nanosheets (denoted as CoSAs/NCNS) for selective transfer hydrogenation of nitroarenes. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and synchrotron radiation X-ray absorption fine structure (XAFS) analysis confirm that all Co species exist as single atoms coordinated with four N atoms (CoN<sub>4</sub> site). The ultrathin and mesoporous structure favor the active Co single atoms to be accessible during the reaction, making the CoSAs/NCNS a superior active heterogeneous catalyst for transfer hydrogenation of nitrobenzene with formic acid as the hydrogen donor. The turnover frequency (TOF) reaches as high as 110.6 h<sup>-1</sup>, which is twenty times higher than the best results of cobalt nanoparticles reported in the literatures under similar reaction conditions. Moreover, the CoSAs/NCNS exhibits excellent selectivity to amines towards a variety of nitroarenes bearing reducible functionalities, such as iodo, cyano, keto, vinyl, alkynyl and ester groups.

## EXPERIMENTAL SECTION

### Materials

Dopamine (DA) hydrochloride (99%), tris(hydroxymethyl)-aminomethane (Tris, 99%), 1,10-phenanthroline (anhydrous, 99%) and cobalt(II) acetate tetrahydrate (Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, 98%) were purchased from Alfa Aesar. Urea (AR) was purchased from Shanghai Chemical Reagents, China. Nitrobenzene (99+%) was obtained from Acros Organics. *n*-Tridecane (99%) and triethylamine (99%) were purchased from J&K scientific Co., Ltd. Formic acid was obtained from Xilong scientific Co., Ltd.

### Preparation of g-C<sub>3</sub>N<sub>4</sub> nanosheets

In a typical experiment, 10 g of urea was placed in a crucible with a cover, and then it was heated at 550°C with a rate of 5°C min<sup>-1</sup> in a muffle furnace for 2 h. The resultant yellow powder was collected for use without further treatment.

### Preparation of CoSAs/NCNS

Cobalt(II) acetate tetrahydrate (12.7 mg, 0.05 mmol) and 1,10-phenanthroline (18.4 mg, 0.1 mmol) were mixed and stirred in ethanol (25 mL) for approximately 30 min at room temperature. Then, 469 mg g-C<sub>3</sub>N<sub>4</sub> was added and

the whole reaction mixture was refluxed at 80°C for 4 h. The reaction mixture was cooled to room temperature and the ethanol was removed by a rotary evaporator (40°C, 60 rpm, 20 min). The obtained Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was dispersed in 150 mL methanol under ultrasound for five minutes. Separately, a freshly prepared tris methanol solution (1.81 g, 140 mL) and DA methanol solution (1.36 g, 60 mL) were added dropwise. After stirring for 6 h, the grey precipitates were collected by centrifugation and washed with methanol for three times and dried under vacuum at room temperature overnight. The powder of Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>@polydopamine (PDA) was transferred into a 30 cm × 60 cm rectangle crucible, which was covered by another identical crucible. The covered crucible was placed in a tube furnace (GSL-1100X-S, Hefei Kejing crystal material technology Co., LTD.) and then heated to 850°C for 2 h at the heating rate of 2°C min<sup>-1</sup> under flowing Ar gas and then naturally cooled to room temperature to obtain the CoSAs/NCNS.

### Preparation of Co(phen)<sub>2</sub>/GO@PDA and Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>

The Co(phen)<sub>2</sub>/GO@PDA was synthesized using a similar synthetic route, only changing the g-C<sub>3</sub>N<sub>4</sub> to the graphene oxide (24 mL, 10 mg mL<sup>-1</sup>); the Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was synthesized using a similar synthetic route except for the coating of PDA.

### Preparation of phen/NCNS

The phen/NCNS was synthesized using a similar synthetic route, without the addition of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O.

### Preparation of CoSAs/NCNS-AT (acid treatment)

The CoSAs/NCNS-AT was synthesized by acid etching of CoSAs/NCNS using aqua regia at 85°C for 20 h. 10 mg CoSAs/NCNS and 25 mL aqua regia were added to a 35-mL glass reaction tube without a lid (Beijing Synthware Glass, Inc. Pressure Vessel, HeavyWall). The mixture was stirred in a preheated 50°C oil bath for 30 min and then heated up to 85°C for 20 h. The catalyst was washed with water and ethanol for four times and dried under vacuum at room temperature for 12 h.

### Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max2500 with Cu Kα radiation (40 kV, 40 mA, 0.1541 nm). Brunauer-Emmett-Teller (BET) surface areas were obtained from N<sub>2</sub> adsorption/desorption isotherms at 77 K with a Micromeritics ASAP 2460 instrument. Before measurements, the samples were degassed at 150°C for 12 h. The Co content of the samples

was measured by inductively coupled plasma spectrometer (ICP-AES) on a SHIMAZU ICPE-9000 instrument. The surface morphology and the element distribution of the samples were obtained using a scanning electron microscope (SEM, HITACHI, S-4800) and a transmission electron microscope (TEM, JEOL, JEM-2100F) with energy-dispersive X-ray spectroscopy (EDS) analysis. HAADF-STEM images were obtained using a JEOL ARM200F (JEOL, Tokyo, Japan) STEM operated at 200 kV with cold filed emission gun and double hexapole Cs correctors (CEOS GmbH, Heidelberg, Germany). Atomic force microscope (AFM) images and height profiles were acquired through a Bruker dimension icon. Thermogravimetric analyses (TGA) were carried out on a TA-60 WS thermal analyzer heating from room temperature to 1,000°C at the rate of 2°C min<sup>-1</sup> under flowing nitrogen. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Scientific ESCALa-b220i-XL spectrometer using Al K $\alpha$  radiation.

#### XAS measurements

The X-ray absorption fine structure (XAFS) spectra at Co K ( $E_0 = 7,709$  eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under “top-up” mode with a constant current of 250 mA. The XAFS data were recorded under transmission mode with two Oxford ion chambers. The energy was calibrated accordingly to the absorption edge of pure Co foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies  $\mu(E)$  were processed by background subtraction and normalization procedures, and reported as “normalized absorption” with  $E_0 = 7,709.0$  eV for all tested samples and Co foil/CoO/Co<sub>3</sub>O<sub>4</sub> standard. For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed data in  $R$  space were analyzed by applying first-shell approximate model for Co-N contribution. The passive electron factors,  $S_0^2$ , were determined by fitting the experimental data on Co foil and fixing the coordination number (CN) of Co-Co to be 8+6, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin,  $E_0$ ) and local structure environment including CN, bond distance ( $R$ ) and Debye-Waller factor around the absorbing atoms were allowed to vary during the fit process. The fitted ranges for  $k$  and  $R$  spaces were selected to be  $k = 2.5\text{--}11.5 \text{ \AA}^{-1}$  with  $R = 1.0\text{--}2.0 \text{ \AA}$  ( $k_3$  weighted).

#### General catalytic test

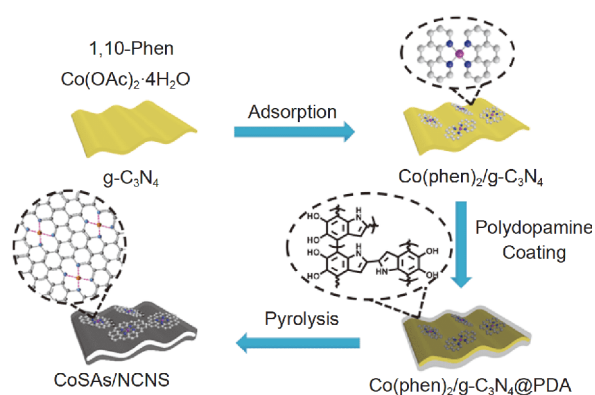
5.0 mg CoSAs/NCNS catalyst (0.78 mol% Co) and 3 mL tetrahydrofuran (THF) were added to a 15-mL glass reaction tube sealed with a Teflon lid (Beijing Synthware Glass, Inc. Pressure Vessel, HeavyWall). Then, the corresponding nitro compound (0.5 mmol), 3.5 mmol (7 equiv.) of HCOOH, 1.4 mmol of Et<sub>3</sub>N (HCOOH-Et<sub>3</sub>N (5:2) mixture) and 51  $\mu$ L *n*-tridecane as the internal standard were added sequentially. The reaction mixture was stirred in a preheated 100°C oil bath for a desired time. After the completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethanol. Then, the catalyst was filtered off, and the sample of the mixture was directly subjected to GC analysis with a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). The identity of the product was ascertained by GC-MS (Shimadzu GCMS-QP2010S) with a HP-5MS capillary column (0.25 mm in diameter, 30 m in length).

For the recyclability test, the reaction conditions were: 5 mg catalyst, 0.25 mmol nitrobenzene, 3.5 mmol (14 equiv.) HCOOH, 1.4 mmol Et<sub>3</sub>N (HCOOH-Et<sub>3</sub>N (5:2) mixture), 25  $\mu$ L *n*-tridecane, 100°C, 2 h. At the end of the catalytic reaction, the mixture was centrifuged and the solid was recovered, which was washed with THF five times, dried at 60°C under vacuum and then reused in a next run.

## RESULTS AND DISCUSSION

**Scheme 1** illustrates the preparation process for CoSAs/NCNS, which includes three-step procedures: (1) cobalt acetate and 1,10-phenanthroline are adsorbed onto g-C<sub>3</sub>N<sub>4</sub> nanosheets to form the Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>; (2) a thin layer of PDA is coated on Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> to form the Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>@PDA composite; (3) the obtained composite was pyrolyzed under a constant Ar flow at 850°C to form the final CoSAs/NCNS.

Typical TEM and SEM images of the obtained samples in each step are shown in Fig. S1. The final obtained CoSAs/NCNS shows ultrathin nanosheet structure and no nanoparticles are observed in the wide range low-magnification TEM image (Fig. 1a). The thickness of the catalyst is measured to be about 4.4 nm according to the representative atomic force microscopy (AFM) image (Fig. 1b and Fig. S2). Because PDA was coated on both sides and the g-C<sub>3</sub>N<sub>4</sub> nanosheets decomposed completely at 645°C under argon atmosphere (Fig. S3), the CoSAs/NCNS was actually composed of two layers with a very thin void space. Thus, the average thickness of the

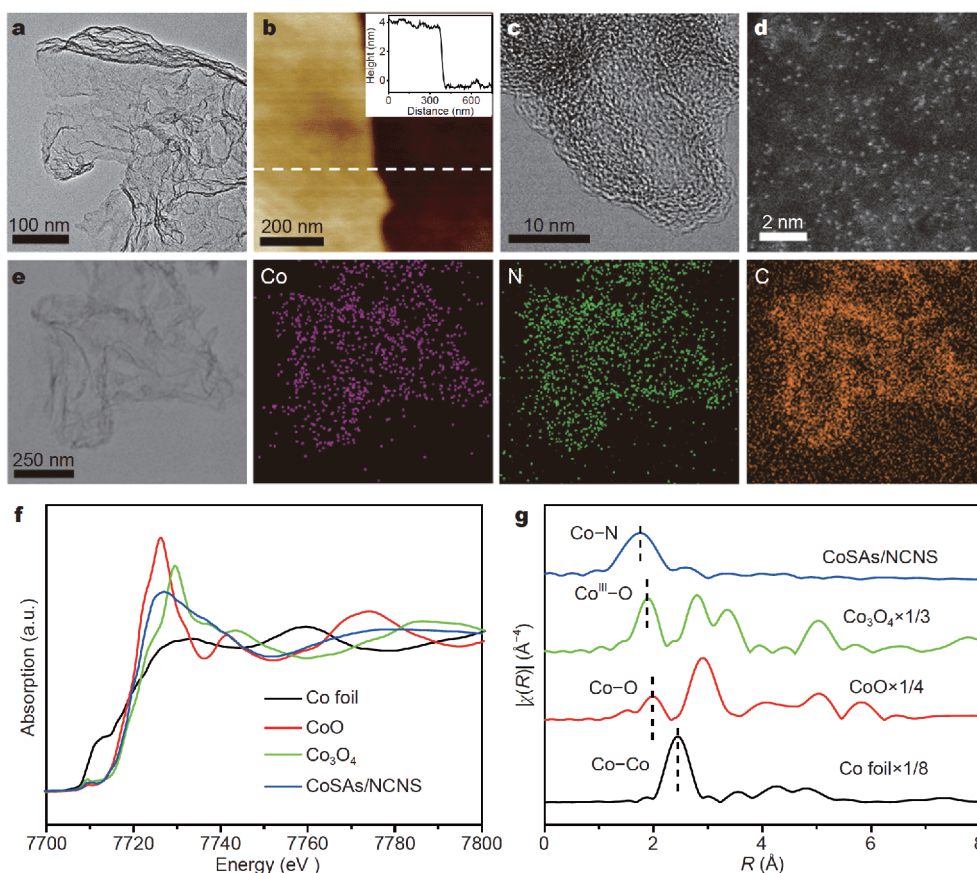


**Scheme 1** Schematic illustration of preparing CoSAs/NCNS. Key: cobalt atom (purple), nitrogen atom (blue), carbon atom (grey).

CoSAs/NCNS was only about 2.2 nm. High-resolution TEM image also shows no obvious nanoparticles (Fig. 1c) in CoSAs/NCNS. Meanwhile, the representative EDS analysis reveals that Co and N atoms are uniformly distributed in the carbon nanosheets (Fig. 1e). The Co

content in CoSAs/NCNS was measured to be about 4.57 wt% by ICP-AES. In addition, XRD pattern (Fig. S4) shows no peaks of cobalt metal or its compounds. All above results prove the presence of highly dispersed Co species.

Aberration-corrected HAADF-STEM study was further carried out to elucidate the exact form of Co atoms. As shown in Fig. 1d, the isolated bright dots corresponding to individual Co atoms dispersed in the carbon support could be clearly discerned due to the different atom Z-contrast. Synchrotron radiation XAFS was performed to identify the chemical state and coordination structure of Co atoms in CoSAs/NCNS. As shown in the XANES profiles (Fig. 1f), CoSAs/NCNS shows very similar lines to that of CoO standard sample, indicating the valence state of Co single atoms is close to  $\text{Co}^{2+}$ , in accordance with XPS analysis (Fig. S5). Further structural information associated to Co atoms can be obtained from the EXAFS. As shown in Fig. 1g, the peaks of Co-Co or Co-O coordination are absent in the Fourier transform



**Figure 1** (a) TEM, (b) AFM, (c) HR-TEM, (d) HAADF-STEM and (e) EDS mapping images of CoSAs/NCNS. (f) Co K-edge XANES profiles and (g) Fourier transformed EXAFS profiles in the  $R$  space of CoSAs/NCNS and standard samples.

curves of CoSAs/NCNS, showing that the Co species are atomically dispersed. EXAFS curve fitting analysis reveals that the coordination number of Co–N is 4.3 at a distance of 1.99 Å (Fig. S6 and Table S1), indicating the square-planar configuration of cobalt atoms in CoSAs/NCNS [50–55].

The g-C<sub>3</sub>N<sub>4</sub> nanosheet and PDA coating show synergistic effect in the formation of the final CoSAs/NCNS. The control sample produced without PDA coating (denoted as Co(phen)<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>) was first prepared to elucidate the role of PDA. It can be seen that cobalt nanoparticles are formed in this sample (Fig. S7b). Without PDA protection, complete decomposition of the g-C<sub>3</sub>N<sub>4</sub> nanosheet during pyrolysis results in aggregation of Co species. In order to elucidate the role of the g-C<sub>3</sub>N<sub>4</sub> nanosheet, another sample using graphene oxide (GO) instead of g-C<sub>3</sub>N<sub>4</sub> nanosheet (denoted as Co(phen)<sub>2</sub>/GO@PDA) was also prepared. As shown in Fig. S7a, cobalt nanoparticles dispersed on the carbon support are observed in this sample. The g-C<sub>3</sub>N<sub>4</sub> nanosheet possesses many N atoms for coordination, which is beneficial to the homogeneous distribution of Co atoms during pyrolysis. Moreover, it also acts as the template for final 2D ultrathin structure. The complete decomposition of g-C<sub>3</sub>N<sub>4</sub> nanosheet would generate large amount of gases during pyrolysis, which helps to introduce additional mesopores in the final CoSAs/NCNS. As shown in Fig. S8, the N<sub>2</sub> adsorption-desorption isotherms of CoSAs/NCNS display a typical type IV profile, confirming the existence of mesoporous structure. The BET surface area of CoSAs/NCNS was calculated to be 657 m<sup>2</sup> g<sup>-1</sup>. The relatively high

surface area and mesoporous structure as well as ultrathin structure are very favorable for mass transfer to access the active Co single atoms and thus beneficial to the catalytic activity.

The catalytic property of CoSAs/NCNS for the transfer hydrogenation with nitrobenzene as the substrate and formic acid as the hydrogen donor was first studied. As shown in Table 1, no conversion was observed without catalyst or without cobalt metal (Table 1, entries 1–2). The CoSAs/NCNS catalyst shows 14.3% conversion and 99% selectivity to aniline in 0.17 h, yielding a TOF as high as 110.6 h<sup>-1</sup> (Table 1, entry 4), which is much higher than the results of nanoparticles reported in literatures (Table 1, entries 6–10). Nitrobenzene could be completely converted with > 99% selectivity to aniline in 2 h with the CoSAs/NCNS catalyst under the optimized reaction condition (Table 1, entry 5). The corresponding TOF under the complete conversion could still reach 64.4 h<sup>-1</sup>, which is also substantially higher than those of transition metal nanocatalysts. The CoSAs/NCNS catalyst after etching with aqua regia shows no activity (Table 1, entry 3), further confirming that the active species are cobalt single atoms in this reaction.

Besides nitrobenzene, nitroarenes bearing electron-donating groups (*n*-butyl and methoxy) or withdrawing groups (trifluoromethyl) could all be readily transformed into the desired aniline derivatives with high yields (Table 2, entries 1–3), indicating the outstanding efficiency of the CoSAs/NCNS. A striking selectivity was observed with several nitroarenes substrates bearing easily reducible moieties, such as iodo, cyano, keto, vinyl

**Table 1** Comparison for the transfer hydrogenation of nitrobenzene<sup>a</sup>

Entry	Catalyst	$T$ (°C)	Time (h)	Conv. (%)	TOF (h <sup>-1</sup> )
1	-	100	2	0	
2	Phen/NCNS	100	2	0	
3	CoSAs/NCNS-AT	100	2	0	
4	CoSAs/NCNS	100	0.17	14.3	110.6
5	CoSAs/NCNS	100	2	>99	64.6
6 <sup>[39]</sup>	Fe <sub>2</sub> O <sub>3</sub> /NGr/C	120	24	>99	0.83
7 <sup>[40]</sup>	Co <sub>3</sub> O <sub>4</sub> -NGr/C	100	15	>99	3.3
8 <sup>[42]</sup>	Co@NPC	100	6	97	3.36
9 <sup>[41]</sup>	Co@NC-600	90	4	99	1.98
10 <sup>[38]</sup>	Ni-N <sub>x</sub> C <sub>y</sub> -800	85	2.5	>99	0.8

a) Reaction conditions: 0.5 mmol nitrobenzene, 5.0 mg catalyst, 3.5 mmol (7 equiv.) of HCOOH, 1.4 mmol of Et<sub>3</sub>N (HCOOH–Et<sub>3</sub>N (5:2) mixture), 3 mL THF.

**Table 2** Transfer hydrogenation of substituted nitroarenes with CoSAs/NCNS as catalyst<sup>a</sup>

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			4	99	>99
2			2.5	99	>99
3			2.5	>99	>99
4			2.5	99	>99
5			4	99	>99
6			2.5	99	>99
7			4	99	>99
8			2	>99	>99
9			2.5	99	>99
10			4	99	98
11			10	>99	98
12			2.5	>99	>99
13			10	>99	>99
14			10	>99	>99

a) Reaction conditions: 0.5 mmol nitroarene, 5.0 mg catalyst, 3.5 mmol (7 equiv.) of HCOOH, 1.4 mmol of Et<sub>3</sub>N (HCOOH–Et<sub>3</sub>N (5:2) mixture), 3 mL THF. The patterns of GC and GC-MS of some products are shown in Figs S10–S15.

and alkynyl groups. These nitroarenes could all be converted into the corresponding amines with high selectivity with the CoSAs/NCNS catalyst (Table 2, entries 4–11). Hydrogenation of nitroheteroarenes was also tested since these compounds are valuable building blocks in synthesizing a variety of pharmaceuticals and agrochemicals. 2-Nitrofluorene and 5-nitroindole were hydrogenated to the targeted heteroaromatic amines with prolonged reaction time, and no by-products were detected in the reaction mixtures (Table 2, entries 13–14).

Finally, the CoSAs/NCNS catalyst could be easily separated from the solution by centrifugation and shows good stability with a slight decrease in activity after reused for five times. The activity decrease comes from the loss of Co content in the CoSAs/NCNS under such reaction condition. This degradation phenomenon was also observed in other literatures using Co-based catalysts. However, satisfactory yields could be obtained after prolonged the reaction time (Fig. S9). The TOF of the reused catalysts is still as high as  $32.2 \text{ h}^{-1}$ , which is still ten times higher than the results reported in literatures.

Above catalytic reaction results suggest the high efficiency of the CoSAs/NCNS catalyst in selective transfer hydrogenation of nitroarenes. Together with the appealing feature of selective transfer hydrogenation reaction in moderate reaction conditions (as shown in Tables 1 and 2, the reactions were carried out at  $100^\circ\text{C}$  under ambient pressure), this system is cost-effective and certainly safer.

## CONCLUSIONS

We produced cobalt single atoms anchored on N-doped ultrathin carbon nanosheets and demonstrated it as a superior heterogeneous catalyst for selective transfer hydrogenation of nitroarenes to amines with formic acid as the hydrogen donor. Owing to the ultrathin and mesoporous structure, which is favorable for mass transfer to access the active Co single atoms, the catalytic activity of CoSAs/NCNS is 20 times higher than those of transition metal nanoparticles reported in literatures under similar reaction conditions. Furthermore, it shows outstanding selectivity toward various nitro compounds bearing other reducible moieties. All these features make this single cobalt atom catalyst an excellent candidate for transfer hydrogenation reactions.

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- 1 Qiao B, Wang A, Yang X, *et al.* Single-atom catalysis of CO oxidation using  $\text{Pt}_1/\text{FeO}_x$ . *Nat Chem*, 2011, 3: 634–641
- 2 Yang XF, Wang A, Qiao B, *et al.* Single-atom catalysts: A new

- frontier in heterogeneous catalysis. *Acc Chem Res*, 2013, 46: 1740–1748
- 3 Bayatsarmadi B, Zheng Y, Vasileff A, *et al.* Recent advances in atomic metal doping of carbon-based nanomaterials for energy conversion. *Small*, 2017, 13: 1700191
  - 4 Cui X, Li W, Ryabchuk P, *et al.* Bridging homogeneous and heterogeneous catalysis by heterogeneous single-metal-site catalysts. *Nat Catal*, 2018, 1: 385–397
  - 5 Liu L, Corma A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chem Rev*, 2018, 118: 4981–5079
  - 6 Zhang H, Liu G, Shi L, *et al.* Single-atom catalysts: Emerging multifunctional materials in heterogeneous catalysis. *Adv Energy Mater*, 2018, 8: 1701343
  - 7 Yan H, Su C, He J, *et al.* Single-atom catalysts and their applications in organic chemistry. *J Mater Chem A*, 2018, 6: 8793–8814
  - 8 Kyriakou G, Boucher MB, Jewell AD, *et al.* Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations. *Science*, 2012, 335: 1209–1212
  - 9 Guo X, Fang G, Li G, *et al.* Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science*, 2014, 344: 616–619
  - 10 Grundner S, Markovits MAC, Li G, *et al.* Single-site trinuclear copper oxygen clusters in mordenite for selective conversion of methane to methanol. *Nat Commun*, 2015, 6: 7546
  - 11 Wang L, Guan E, Zhang J, *et al.* Single-site catalyst promoters accelerate metal-catalyzed nitroarene hydrogenation. *Nat Commun*, 2018, 9: 1362
  - 12 Jones J, Xiong H, DeLaRiva AT, *et al.* Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. *Science*, 2016, 353: 150–154
  - 13 Liu P, Zhao Y, Qin R, *et al.* Photochemical route for synthesizing atomically dispersed palladium catalysts. *Science*, 2016, 352: 797–800
  - 14 Chen Y, Ji S, Sun W, *et al.* Discovering partially charged single-atom Pt for enhanced anti-markovnikov alkene hydrosilylation. *J Am Chem Soc*, 2018, 140: 7407–7410
  - 15 Liu G, Robertson AW, Li MMJ, *et al.*  $\text{MoS}_2$  monolayer catalyst doped with isolated Co atoms for the hydrodeoxygenation reaction. *Nat Chem*, 2017, 9: 810–816
  - 16 Lin L, Zhou W, Gao R, *et al.* Low-temperature hydrogen production from water and methanol using  $\text{Pt}/\alpha\text{-MoC}$  catalysts. *Nature*, 2017, 544: 80–83
  - 17 Fang X, Shang Q, Wang Y, *et al.* Single Pt atoms confined into a metal-organic framework for efficient photocatalysis. *Adv Mater*, 2018, 30: 1705112
  - 18 Marcinkowski MD, Darby MT, Liu J, *et al.* Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation. *Nat Chem*, 2018, 10: 325–332
  - 19 Tang Y, Li Y, Fung V, *et al.* Single rhodium atoms anchored in micropores for efficient transformation of methane under mild conditions. *Nat Commun*, 2018, 9: 1231
  - 20 Chen Y, Li Z, Zhu Y, *et al.* Atomic Fe dispersed on N-doped carbon hollow nanospheres for high-efficiency electrocatalytic oxygen reduction. *Adv Mater*, 2019, 31: 1806312
  - 21 Liu J. Catalysis by supported single metal atoms. *ACS Catal*, 2016, 7: 34–59
  - 22 Giannakakis G, Flytzani-Stephanopoulos M, Sykes ECH. Single-atom alloys as a reductionist approach to the rational design of heterogeneous catalysts. *Acc Chem Res*, 2019, 52: 237–247

- 23 Liang Z, Qu C, Xia D, *et al.* Atomically dispersed metal sites in MOF-based materials for electrocatalytic and photocatalytic energy conversion. *Angew Chem Int Ed*, 2018, 57: 9604–9633
- 24 Lin R, Albani D, Fako E, *et al.* Design of single gold atoms on nitrogen-doped carbon for molecular recognition in alkyne semi-hydrogenation. *Angew Chem Int Ed*, 2019, 58: 504–509
- 25 Podyacheva OY, Bulushev DA, Suboch AN, *et al.* Highly stable single-atom catalyst with ionic Pd active sites supported on n-doped carbon nanotubes for formic acid decomposition. *ChemSusChem*, 2018, 11: 3724–3727
- 26 Sun G, Zhao ZJ, Mu R, *et al.* Breaking the scaling relationship via thermally stable Pt/Cu single atom alloys for catalytic dehydrogenation. *Nat Commun*, 2018, 9: 4454
- 27 Li H, Wang L, Dai Y, *et al.* Synergetic interaction between neighbouring platinum monomers in CO<sub>2</sub> hydrogenation. *Nat Nanotech*, 2018, 13: 411–417
- 28 Yan H, Lv H, Yi H, *et al.* Understanding the underlying mechanism of improved selectivity in Pd<sub>1</sub> single-atom catalyzed hydrogenation reaction. *J Catal*, 2018, 366: 70–79
- 29 Downing RS, Kunkeler PJ, van Bekkum H. catalytic syntheses of aromatic amines. *Catal Today*, 1997, 37: 121–136
- 30 Blaser HU, Steiner H, Studer M. Selective catalytic hydrogenation of functionalized nitroarenes: An update. *ChemCatChem*, 2009, 1: 210–221
- 31 Jagadeesh RV, Surkus AE, Junge H, *et al.* Nanoscale Fe<sub>2</sub>O<sub>3</sub>-based catalysts for selective hydrogenation of nitroarenes to anilines. *Science*, 2013, 342: 1073–1076
- 32 Westerhaus FA, Jagadeesh RV, Wienhöfer G, *et al.* Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes. *Nat Chem*, 2013, 5: 537–543
- 33 Wei Z, Wang J, Mao S, *et al.* *In situ*-generated Co<sup>0</sup>-Co<sub>3</sub>O<sub>4</sub>/N-doped carbon nanotubes hybrids as efficient and chemoselective catalysts for hydrogenation of nitroarenes. *ACS Catal*, 2015, 5: 4783–4789
- 34 Zhang S, Chang CR, Huang ZQ, *et al.* High catalytic activity and chemoselectivity of sub-nanometric Pd clusters on porous nanorods of CeO<sub>2</sub> for hydrogenation of nitroarenes. *J Am Chem Soc*, 2016, 138: 2629–2637
- 35 Liu L, Concepción P, Corma A. Non-noble metal catalysts for hydrogenation: A facile method for preparing Co nanoparticles covered with thin layered carbon. *J Catal*, 2016, 340: 1–9
- 36 Schwob T, Kempe R. A reusable Co catalyst for the selective hydrogenation of functionalized nitroarenes and the direct synthesis of imines and benzimidazoles from nitroarenes and aldehydes. *Angew Chem Int Ed*, 2016, 55: 15175–15179
- 37 Sun X, Olivos-Suarez AI, Osadchii D, *et al.* Single cobalt sites in mesoporous N-doped carbon matrix for selective catalytic hydrogenation of nitroarenes. *J Catal*, 2018, 357: 20–28
- 38 Shalom M, Molinari V, Esposito D, *et al.* Sponge-like nickel and nickel nitride structures for catalytic applications. *Adv Mater*, 2014, 26: 1272–1276
- 39 Jagadeesh RV, Natte K, Junge H, *et al.* Nitrogen-doped graphene-activated iron-oxide-based nanocatalysts for selective transfer hydrogenation of nitroarenes. *ACS Catal*, 2015, 5: 1526–1529
- 40 Jagadeesh RV, Banerjee D, Arockiam PB, *et al.* Highly selective transfer hydrogenation of functionalised nitroarenes using cobalt-based nanocatalysts. *Green Chem*, 2015, 17: 898–902
- 41 Zhou P, Zhang Z. One-pot reductive amination of carbonyl compounds with nitro compounds by transfer hydrogenation over Co-N<sub>x</sub> as catalyst. *ChemSusChem*, 2017, 10: 1892–1897
- 42 Duan Y, Song T, Dong X, *et al.* Enhanced catalytic performance of cobalt nanoparticles coated with a N, P-codoped carbon shell derived from biomass for transfer hydrogenation of functionalized nitroarenes. *Green Chem*, 2018, 20: 2821–2828
- 43 Xu X, Luo J, Li L, *et al.* Unprecedented catalytic performance in amine syntheses via Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst-assisted transfer hydrogenation. *Green Chem*, 2018, 20: 2038–2046
- 44 Gawande MB, Rathi AK, Branco PS, *et al.* Regio- and chemoselective reduction of nitroarenes and carbonyl compounds over recyclable magnetic ferritenickel nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-Ni) by using glycerol as a hydrogen source. *Chem Eur J*, 2012, 18: 12628–12632
- 45 Cabrero-Antonino JR, Adam R, Junge K, *et al.* Cobalt-catalysed transfer hydrogenation of quinolines and related heterocycles using formic acid under mild conditions. *Catal Sci Technol*, 2017, 7: 1981–1985
- 46 Jia WG, Ling S, Zhang HN, *et al.* Half-sandwich ruthenium phenolate–oxazoline complexes: Experimental and theoretical studies in catalytic transfer hydrogenation of nitroarene. *Organometallics*, 2018, 37: 40–47
- 47 Jagadeesh RV, Wienhöfer G, Westerhaus FA, *et al.* Efficient and highly selective iron-catalyzed reduction of nitroarenes. *Chem Commun*, 2011, 47: 10972–10974
- 48 Brieger G, Nestrück TJ. catalytic transfer hydrogenation. *Chem Rev*, 1974, 74: 567–580
- 49 Wang D, Astruc D. The golden age of transfer hydrogenation. *Chem Rev*, 2015, 115: 6621–6686
- 50 Cao Y, Chen S, Luo Q, *et al.* Atomic-level insight into optimizing the hydrogen evolution pathway over a Co<sub>1</sub>-N<sub>4</sub> single-site photocatalyst. *Angew Chem Int Ed*, 2017, 56: 12191–12196
- 51 Han A, Chen W, Zhang S, *et al.* A polymer encapsulation strategy to synthesize porous nitrogen-doped carbon-nanosphere-supported metal isolated-single-atomic-site catalysts. *Adv Mater*, 2018, 30: 1706508
- 52 Huang P, Huang J, Pantovich SA, *et al.* Selective CO<sub>2</sub> reduction catalyzed by single cobalt sites on carbon nitride under visible-light irradiation. *J Am Chem Soc*, 2018, 140: 16042–16047
- 53 Pan Y, Lin R, Chen Y, *et al.* Design of single-atom Co–N<sub>5</sub> catalytic site: a robust electrocatalyst for CO<sub>2</sub> reduction with nearly 100% CO selectivity and remarkable stability. *J Am Chem Soc*, 2018, 140: 4218–4221
- 54 Zhu C, Shi Q, Xu BZ, *et al.* Hierarchically porous M–N–C (M = Co and Fe) single-atom electrocatalysts with robust MN<sub>x</sub> active moieties enable enhanced ORR performance. *Adv Energy Mater*, 2018, 8: 1801956
- 55 Zhang H, Wei J, Dong J, *et al.* Efficient visible-light-driven carbon dioxide reduction by a single-atom implanted metal-organic framework. *Angew Chem Int Ed*, 2016, 55: 14310–14314

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**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Supporting data are available in the online version of the paper.



**Huining Li** received her BSc degree from Hebei Normal University in 2014. Now, she is a PhD student under the supervision of Prof. Weiguo Song at the Institute of Chemistry, Chinese Academy of Sciences, China. Her research interests mainly focus on the design and fabrication of single-atom catalysts for heterogeneous catalysis.



**Changyan Cao** obtained his PhD degree from Harbin Institute of Technology in 2011. Since then he did postdoctoral research under the supervision of Prof. Weiguo Song at the Institute of Chemistry, Chinese Academy of Sciences. Currently, he is an associate professor in Prof. Weiguo Song's group. His current research interest mainly focuses on the design and controllable synthesis of nanocatalysts with high performance.



**Weiguo Song** obtained his BSc degree from Peking University in 1992 and his PhD degree from the University of Southern California in 2001. Now, he is a full professor in the Institute of Chemistry, Chinese Academy of Sciences. His current research interest mainly focuses on the synthesis of nanostructured materials and their applications in heavy metal ions adsorption and nanocatalysis.

## 负载于超薄氮掺杂碳纳米片上的钴单原子催化芳香硝基化合物氢转移反应

李会宁<sup>1,2</sup>, 曹昌燕<sup>1,2\*</sup>, 刘剑<sup>1,2</sup>, 施杨<sup>1,2</sup>, 司锐<sup>3</sup>, 谷林<sup>4</sup>, 宋卫国<sup>1,2\*</sup>

**摘要** 过渡金属催化芳香硝基化合物氢转移反应制备胺类化合物, 具有成本低廉、反应条件温和、高活性、高选择性等优点. 单原子催化剂具有最大的原子利用率和独特的电子结构, 有望进一步提升其催化反应性能, 但目前还没有关于单原子催化剂应用于该反应的文献报道. 本文制备了负载于氮掺杂超薄碳纳米片上的钴单原子催化剂(简称为CoSAs/NCNS), 并将其应用于芳香硝基化合物氢转移反应中, 在与文献报道类似的反应条件下, 该催化剂的TOF达 $110.6 \text{ h}^{-1}$ , 是已报道结果的20倍; 且该催化剂对一系列具有其他不饱和官能团(如: 卤素, 氰基, 醛基, 乙烯基和乙炔基等)的硝基化合物具有优异的选择性.