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Direct Reductive Coupling of Nitroarenes and Alcohols Catalysed by Co-N-C/CNT@AC

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A non-noble heterogeneous catalyst - Co, N and C composite encapsulated carbon nanotube grown in-situ on the surface of activated carbon (Co-N-C/CNT@AC) was fabricated via the pyrolysis - reduction process. The Co-N-C/CNT@AC catalyzed the reductive coupling of structurally diverse nitroarenes and alcohols to imines and secondary amines under exogenous base- and solvent- free conditions. BET, TEM, SEM, XRD and XPS characterizations displayed that the exceptional catalytic property of Co-N-C/CNT@AC could be explained by its nanostructure, Co-N and basic N species. Our protocol had advantages of low cost, environment-friendliness, and good applicability. Furthermore, a reaction route of nitroarenes, amines and alcohols as the starting materials was proposed to improve the atom economy of the reductive coupling of nitroarenes with alcohols.

Introduction

Carbon-nitrogen bonding is a very important transformation in organic chemistry since nitrogen-containing compounds, such as amines and imines, are the basic building blocks in the production of numerous fine chemicals¹. The formation of C-N or C=N bonds can be conducted by hydroamination^{2, 3}, hydroaminomethylation⁴, self-coupling of primary amine^{5, 6} and reductive amination^{7, 8}. Recently, the direct reductive coupling of nitroarenes with alcohols by using a hydrogen-borrowing strategy (also known as a hydrogen autotransfer process) to synthesis of amines was reported⁹. In this one-pot multistep transformation, the alcohol also serves as hydrogen source for nitro reduction except for the role of alkylating agent, avoiding the use of additional hydrogen donor. And alcohols and nitroarenes have the advantages of low-cost, good accessibility and stable chemical property¹⁰. Thus, the direct reductive coupling of nitroarenes with alcohols has aroused significant attention.

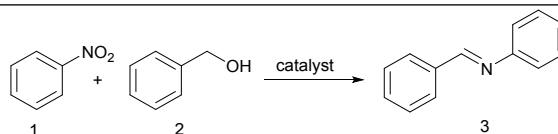
For the reductive coupling of nitroarenes with alcohols, photocatalysts such as Cd_xZn_{1-x}S¹¹, CdS/TiO₂^{12, 13}, TiO₂¹⁴, Pd/TiO₂¹⁵, Pd/H_{1.07}Ti_{1.73}O₄ · H₂O nanosheets¹⁶ and CdIn₂S₄¹⁷ have been studied owing to the characteristics of the mild reaction condition of the photocatalysis. Besides, thermal catalysis was also employed in this transformation. Zanardi et al⁹ successfully prepared imines from the direct reductive coupling of nitroarenes and alcohols over an Ir-Pd catalyst. Next, Ag-MCP-1^{10, 18, 19}, Ru complex²⁰⁻²², Au/Ag-Mo-NR²³, Pd/DNA²⁴, Pd/hydrotralcite²⁵, Ir-Au dimetallic complexes²⁶,

Au/TiO₂-VS²⁷, Ru hydroxide²⁸, RuCl₃ · 3H₂O²⁹ and Au-Pd/Ru-Pd³⁰ were reported. These catalytic systems achieved the N-alkylation of nitroarenes with alcohols, whereas there were different levels of drawbacks or limitations as follows: i) the costs of these catalysts were high on account of the use of noble metal, ii) excess exogenous base (K₂CO₃^{10, 22, 23, 29}, KOH²⁸, Cs₂CO₃^{9, 26}, t-BuOK²¹, KHCO₃²⁰, LiOH · H₂O²⁴), organic solvent (benzotrifluoride^{11, 17, 22}, acetonitrile¹², toluene^{10, 23, 25, 27, 28}, chlorobenzene²⁰, mesitylene^{18, 30}, xylene¹⁹ and/or hydrogen source (H₂^{18, 29}, glycerol^{10, 22, 23, 30}) were required, iii) most catalytic systems presented a narrow range of application, only a few cases were applied to synthesize different classes of amines such as imines, secondary amines and tertiary amines^{10, 21, 22}. In terms of economy and environmental friendliness, it would be highly desirable to develop an inexpensive, recyclable and universal catalytic system without solvent, exogenous base and hydrogen source for the reductive coupling of nitroarenes with alcohols. Based on our previous research^{31, 32}, herein we developed a non-noble heterogeneous catalyst- Co, N and C composite encapsulated multiwalled carbon nanotubes (CNT) grown in-situ on the surface of activated carbon, which was easily obtained by the successive pyrolysis and hydrogen reduction process of the mixture of the precursors. Benefiting from the composition and nanostructure of the catalyst, imines and secondary amines are efficiently synthesized through the reductive coupling of nitroarenes with alcohols in the absence of solvent, exogenous base and hydrogen source.

Results and discussion

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ARTICLE

Table 1 Coupling reaction of nitrobenzene with benzyl alcohol to N-Benzylideneaniline^a

Entry	Catalyst	Condition	Conversion of 1 (%) ^b	yield of 3 (%) ^c
1	Co@AC	0.3g/140°C /solvent-free	6	1.7
2	Co-N-C/CNT@AC	0.3g/140°C /solvent-free	72	68
3	Co-N-C@AC	0.3g/140°C /solvent-free	58	52
4	N-C@AC	0.3g/140°C /solvent-free	1.5	1.5
5 ^d	Co-N-C/CNT@AC	0.3g/140°C /solvent-free	43	42
6	Co-N-C/CNT@AC	0.3g/140°C /p-xylene	51	47
7	Co-N-C/CNT@AC	0.3g/140°C /DMF	22	22
8	Co-N-C/CNT@AC	0.3g/160°C /solvent-free	92	88
9	Co-N-C/CNT@AC	0.4g/160°C /solvent-free	98	97
10	Co-N-C/CNT@AC	0.5g/160°C /solvent-free	98	96

^a Reaction conditions: nitrobenzene (5 mmol), benzyl alcohol (15 mmol), N₂ atmosphere, 18h.

^{b, c} Determined by GC.

^d open-air atmosphere.

In the beginning of our studies, the optimization of the catalytic systems and reaction conditions was first carried out. The imination of nitrobenzene and benzyl alcohol with 1:3 molar ratio was selected as the model reaction. Based on the intention of searching inexpensive catalyst, we attempted to prepare a non-noble metal Co@AC to catalyze this reaction, whereas the Co@AC catalyst exhibited poor catalytic performance (entry 1, Table 1). And nitrogen doping was implemented to further improve the catalytic activity of Co@AC by introducing DCD as N source. Amazingly, the obtained sample exhibited a much better catalytic activity in comparison with Co@AC (entry 2, Table 1). SEM images of the sample displayed the existence of carbon nanotubes (CNTs) (Figure 1). CNTs were formed in-situ and attached on the surface of AC during the pyrolysis of DCD under catalysis of cobalt species^{33, 34}. AC as support was able to effectively

scatter the CNTs in the Co-N-C/CNT@AC. To reveal the underlying factors of the catalytic property difference between these two catalysts, N₂ adsorption-desorption method was performed to characterize the textural properties of Co@AC and Co-N-C/CNT@AC.

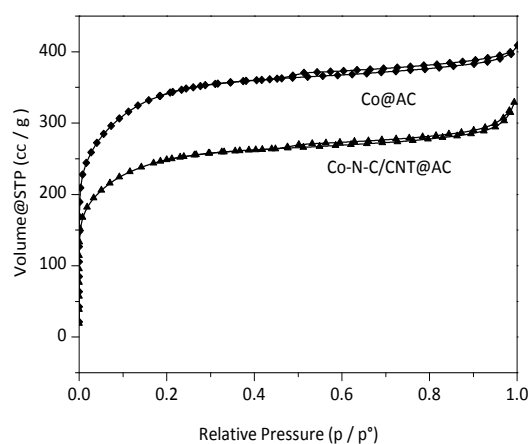
Figure 2 N₂ adsorption/desorption isotherms of catalysts.

Table 2 The textural properties of Co@AC and Co-N-C/CNT@AC catalysts.

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Mean pore size (nm)
Co-N-C/CNT@AC	846.6	0.51	1.21
Co@AC	1184.0	0.63	1.07

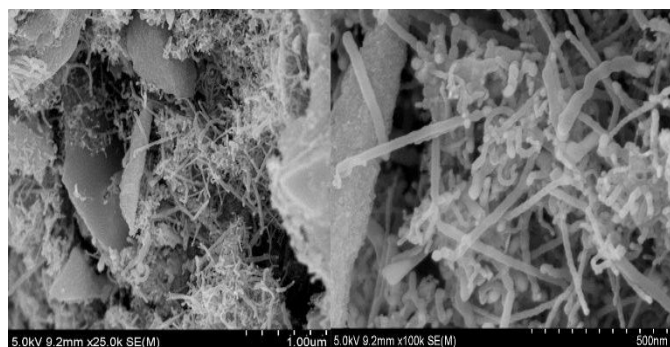


Figure 1 SEM images of Co-N-C/CNT@AC catalyst.

It was seen from Figure 2 that the isotherms of Co@AC and Co-N-C/CNT@AC catalysts all displayed a type-I sorption isotherm with H₄-type hysteresis loop, the high uptake at low relative pressure suggested the developed micropore structure of these two catalysts. The specific surface area and pore volume of Co-N-C/CNT@AC were lower than that of Co@AC (Table 2). The reason for this was probably that the pyrolysis products of DCD partly filled or covered pore organization of AC. In general, catalysts with low specific surface area exhibited weaker catalytic activity because of the insufficient exposure of active sites. However, Co-N-C/CNT@AC possessed higher catalytic activity, which indicated that the other factors dominated its catalytic behavior. Subsequently, the crystalline structures and the chemical valence states of Co@AC and Co-N-C/CNT@AC catalysts were displayed by XRD.

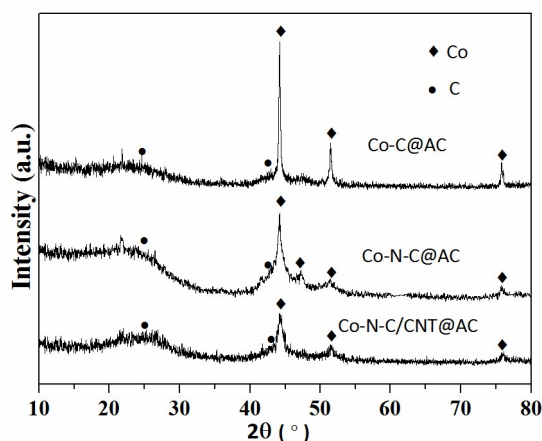


Figure 3 XRD patterns of Co@AC, Co-N-C@AC and Co-N-C/CNT@AC.

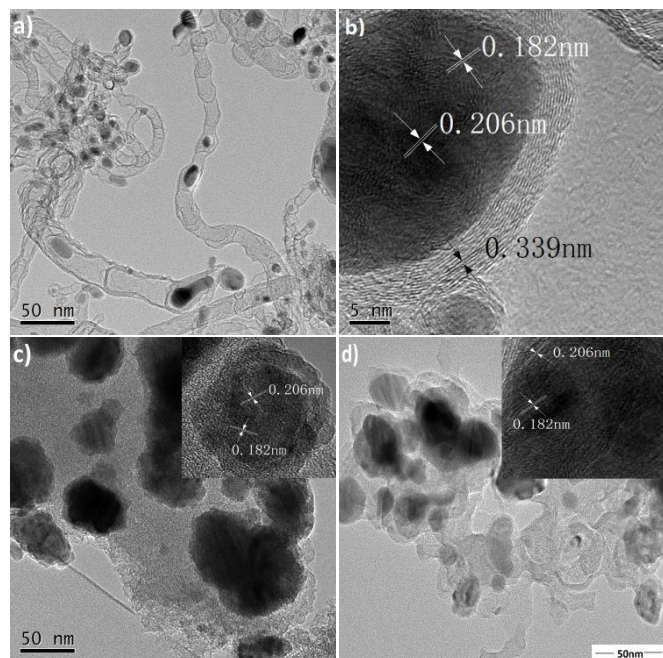
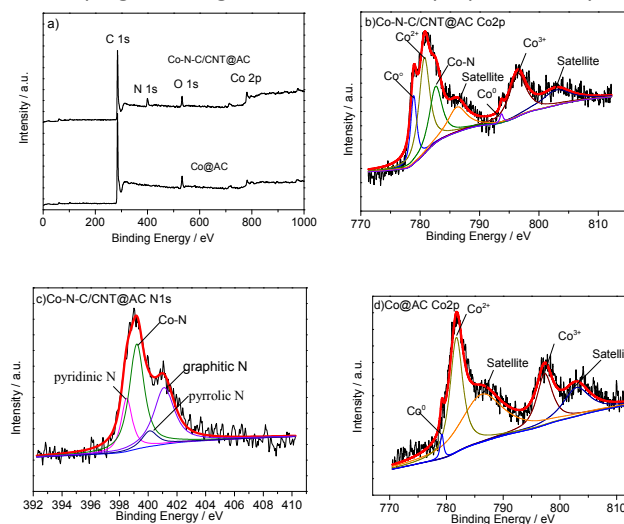


Figure 4 TEM images of Co-N-C/CNT@AC (a, b), Co@AC (c) and Co-N-C@AC (d).

As shown in Figure 3, XRD patterns of Co@AC and Co-N-C/CNT@AC exhibited the diffraction peaks at $2\theta = 24.0^\circ, 43.5^\circ$ signed to the crystal surface (002), (101) of graphite-type carbon³² and $44.2^\circ, 51.5^\circ, 75.8^\circ$ indexed to the (111), (200),

(220) crystalline planes of the face-centered cubic metallic cobalt (JCPDS 15-0806)³⁵ respectively, which manifested the formation of graphite carbon and Co⁰ during the pyrolysis of the precursor. The difference was that the intensity of diffraction peaks of Co⁰ in Co@AC was stronger than that of Co-N-C/CNT@AC catalyst, demonstrating the smaller grain size of Co⁰ in Co@AC. These were supported by TEM images, as shown in Figure 4. The formation of Co⁰ was confirmed by two fringes spacing of 0.205 nm and 0.182 nm corresponding to the (111) and (200) plane of Co⁰ (Figure 4b, 4c, inset). The CNTs of Co-N-C/CNT@AC presented bamboo-like structures with different lengths varying from several hundreds of nanometers to several micrometers and diameters of 10-40 nm. Most Co⁰ nanoparticles were encapsulated in the CNTs, and Co⁰ nanoparticles were tightly wrapped by a few graphitic layers with an interlayer spacing of 0.339 nm corresponding to the (002) plane of graphite (Figure 4b). In addition, Co-N-C@AC catalyst was prepared for comparison by a similar method with urea as N source. There were no CNTs in Co-N-C@AC from TEM image (Figure 4d). Co particles were present in larger size and concentrated state relative to Co-N-C/CNT@AC, which was also judged based on the intensity of diffraction peaks in Figure 3. Apparently, CNTs were helpful to hinder the Co nanoparticles growth. And Co-N-C@AC exhibited a moderate catalytic activity in these three catalysts (entry 3, Table 1). According to the above analysis, it was found that besides smaller size and higher dispersion of cobalt particles, N doping could significantly improve catalytic performance. Thus, XPS was carried out to gain more details on N doping affecting the activities of as-prepared catalysts.



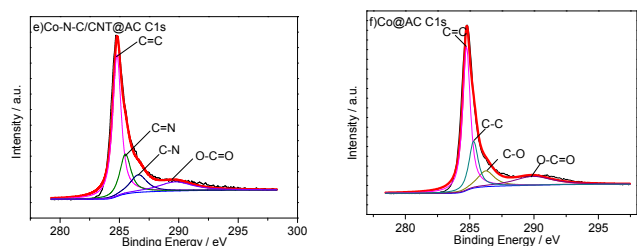
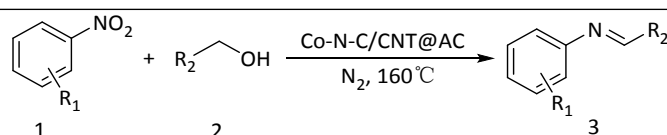


Figure 5 XPS spectra of Co@AC and Co-N-C/CNT@AC (a); XPS spectrum of Co-N-C/CNT@AC with the Co 2p (b), N 1s (c) and C 1s (e); XPS spectrum of Co@AC with the Co 2p (d) and C 1s (f).

XPS survey data was displayed in Figure 5. The elements-Co, C and O were identified in the Co@AC and Co-N-C/CNT@AC from Figure 5a. The occurrence of O most likely arised from the partial oxidation of metallic Co when the catalysts exposed to air. Especially, no N 1s signal was detected due to the extremely low content of N in the Co@AC, and N content in Co-N-C/CNT@AC catalyst was 7.83 at%, confirming the successful doping of nitrogen. In order to check the chemical state of elements, XPS spectra of Co@AC and Co-N-C/CNT@AC were carefully analyzed. The Co 2p_{3/2} spectrum of Co-N-C/CNT@AC catalyst could be resolved to four peaks at 778.7 eV, 780.6 eV, 782.6 eV, and 786.2 eV, corresponding to Co⁰, Co-O, Co-N and the satellite peak of Co-O, respectively (Figure 5b)³⁶. Meanwhile, the fitting peak at 399.2 eV assigned to Co-N was found in the deconvoluted result of N1s spectrum (Figure 5c)³⁴. These corroborated the presence of Co-N species in Co-N-C/CNT@AC catalyst. While only similar three peaks at 778.7eV, 781.3eV and 786.2eV representing Co⁰ and Co-O were observed in Co 2p_{3/2} spectrum of Co@AC^{36, 37}, demonstrating the inexistence of Co-N species in Co@AC (Fig. 5d). The Co loading in Co@AC and Co-N-C/CNT@AC determined by ICP are 9.5% and 8.3%, respectively. Base on this, the turnover numbers (TONs) here were calculated by the moles of imine produced per mole of active metal in the whole catalyst. For Co@AC catalyst, the TON value of imine in terms of metal Co was only 0.18 in 18 h (entry 1, Table 1). These results indicated that Co⁰ and Co-O species possessed very poor catalytic activities. Whereas, the TON of imine in terms of metal Co for Co-N-C/CNT@AC was 8 (entry 2, Table 1), which was much larger than that of Co@AC. Meanwhile, the metal-free N-C@AC catalyst gave only 1.5% yield of imine (entry 4, Table 1) manifesting that basic N species alone did not catalyze the reductive coupling of nitroarenes with alcohols. Also, it was clear that the direct reductive coupling of nitroarenes with alcohols involved the following tandem steps:

Table 3 Reductive imination of nitrobenzenes with alcohols catalyzed by Co-N-C/CNT@AC^a



Entry	Substrate 1	Substrate 2	Time (h)	Product 3	Conversion	Selectivity
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dehydrogenation of alcohols, transfer hydrogenation of nitroarenes and the condensation of amines with aldehydes³⁸, and previous studies had revealed that transition metal nitrides had a high hydrogenation/ dehydrogenation activity^{39, 40}. To sum up, we could identify that Co-N species were the main active phase for oxidation-reduction of nitroarenes with alcohols. Based on this, if calculating in terms of Co-N species without regard to the inactive Co⁰ and Co-O species, the TON of imine was 46 (entry 9, Table 1. the content of Co-N species from XPS deconvolution).

In addition, there were three peaks with binding energies of 398.5, 400.1 and 401.2 eV assigned to pyridinic groups, pyrrolic groups and graphitic-N severally except for the peak of Co-N in the high-resolution N 1s spectrum of Co-N-C/CNT@AC (Figure 5c)^{34, 37}, and the XPS of C 1s could be divided into four peaks at 284.7, 285.7, 286.6 and 289.8eV belonging to C=C, C=N, C-N and O-C=O^{41, 42}. These denoted the presence of basic N species in the Co-N-C/CNT@AC⁴³. For Co@AC catalyst, no XPS peak of N was also found in four resolving peaks centered at 284.7 eV (C=C), 285.3 eV (C-C), 286.3 eV (C-O) and 289.8 (O-C=O) eV of the C 1s spectrum (Figure 5f)^{41, 44}. Some former researches showed that basic N species were active in catalytic oxidation of alcohols^{42, 45, 46}. We also found that the conversion of benzyl alcohol to benzaldehyde reached 8.6% although N-C@AC almost had no activity in the reductive coupling of nitroarenes with alcohols (entry 4, Table 1). Moreover, no intermediate aniline was detected in the experiment of both N-C@AC and Co-N-C/CNT@AC as catalyst, indicating that basic N species also effectively promoted the coupling of amines with aldehydes, which was supported by Morales report⁴⁷. Therefore, it was reasonable to conclude that these basic N species assisted Co-N species in catalysing the reductive coupling of nitroarenes with alcohols in our catalytic system so that the use of exogenous base was avoided.

In sum, the superior catalytic performance of Co-N-C/CNT@AC catalyst benefited from its Co-N, nanostructure and basic N species.

Next, the model reaction was performed over Co-N-C/CNT@AC under air atmosphere, and low conversion of nitrobenzene was afforded (entry 5, Table 1). Effect of solvents was also investigated, the desired product could be obtained in solvents. Nevertheless, the best yield was still achieved under solvent-free condition (entries 6-7, Table 1). In the optimized experiments of the amount of catalyst, it was found that the 0.4g dosage of Co-N-C/CNT@AC was sufficient to promote the reaction under the given reaction condition (entries 8-10, Table 1).

					(%) ^b	(%) ^c
					View Article Online DOI: 10.1039/C8GC03818J	
1			18		98	99
2			24		98	94
3			28		100	97
4			20		100	90
5			30		98	98
6			36		97	98
7			42		91	97
8			40		95	96
9			36		96	98
10			22		100	99
11			28		75	22
12			24		21	44
13			24		12	10

^a Reaction conditions: nitrobenzenes (5 mmol), alcohols (15 mmol), Co-N-C/CNT@AC (0.4 g), N₂ atmosphere, 160°C, solvent-free.

^b Conversion was calculated based on substrate 1.

^c Selectivity was calculated based on products 3.

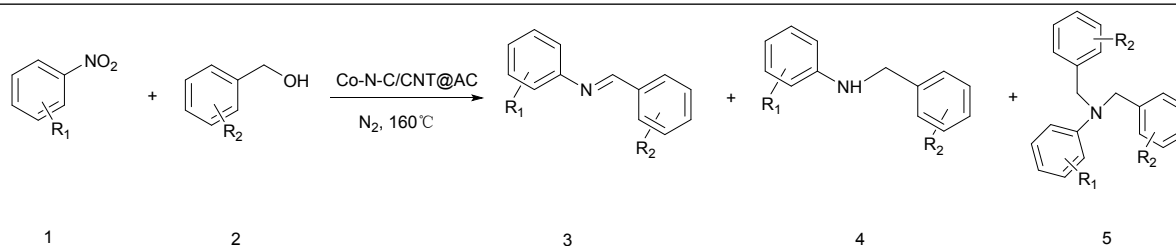
With the optimized reaction conditions, we explored the universality of our procedure for the synthesis of imines by a wide range of structurally diverse nitrobenzenes and alcohols as starting materials. The results were summarized in Table 3. Firstly, the nitrobenzenes reacted smoothly with both electron-donating (-Me, -OMe) and electron-withdrawing groups (-Cl) substituted benzyl alcohols, giving the imine products with high conversion and selectivity (entries 2-4, Table 3). Whereas the reactivities of substituted benzyl

alcohols were lower than that of benzyl alcohol (entries 1-4, Table 3). Furthermore, the reactions of regioisomers of methyl nitrobenzene with benzyl alcohols were investigated, it was found that the yields were dependent on the substituted position on the benzene ring with the order as follows: para > meta > ortho isomer, manifesting that the reaction was sensitive to the steric hindrance (entries 5-7, Table 3). In the next set of experiments, nitrobenzenes with substituents (-F, -Cl, -Br) and benzyl alcohol reacted, furnishing the

corresponding imines in 91-99% yields, and the reactivity of the electron-withdrawing groups substituted benzyl alcohol with nitrobenzene decreased in the order of $-F > -Cl > -Br$, which revealed the presence of an electron-withdrawing inductive effect (entries 8-10, Table 3). For the reaction of allyl alcohol with nitrobenzene, selectivity of allyl imine was very low on Co-N-C/CNT@AC since carbon-carbon double bond of allyl alcohol was easily oxidized leading to the formation of by-

Table 4 Reductive amination of nitrobenzenes with alcohols catalyzed by Co-N-C/CNT@AC ^a

product N-benzylidene-aniline (entries 11, Table 3). The reaction of aliphatic alcohols with nitrobenzene were also examined, a considerable amount of intermediate anilines were detected, so the yields of imines were unsatisfactory (entries 12, 13, Table 3).



Entry	Substrate 1	Substrate 2	Time (h)	Yield (%) ^b		
				Product 3	Product 4	Product 5
1			38	7	82	11
2			44	8	83	9
3			46	14	85	1
4			46	16	74	10
5			48	4	84	12
6			48	4	86	10

^a Reaction conditions: nitrobenzenes (2 mmol), alcohols (24 mmol), Co-N-C/CNT@AC (0.24 g), N₂ atmosphere, 160°C, solvent-free.

^b GC Yield was calculated based on nitrobenzene.

On the strength of the one-pot synthesis of imines from the reductive coupling of nitrobenzenes with alcohols, it would be a useful extension if the imines could be hydrogenated to provide the corresponding secondary amines. Much to our joy, this transformation was successfully achieved by increasing alcohols/nitrobenzenes molar ratio. The nitrobenzenes were completely converted and structurally varied secondary amines were obtained with 74-86% yields (Table 4). Note that in this transformation course, the secondary amines were partly alkylated to afford the corresponding tertiary amines (1-12%). So, it was reasonably believed that our protocol could be applied to synthesize tertiary amines by strengthening reaction conditions.

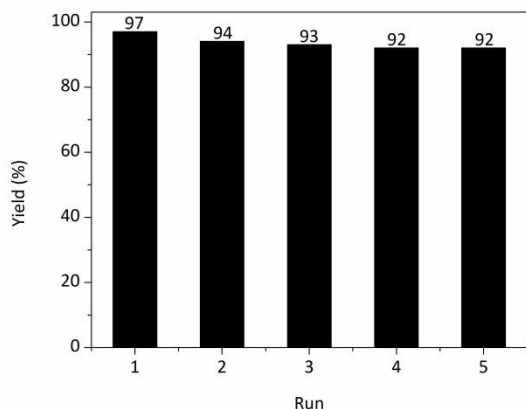


Figure 6 Reusability of the Co-N-C/CNT@AC catalyst. Reaction conditions: nitrobenzene (10 mmol), benzyl alcohol (30 mmol), Co-N-C/CNT@AC (0.8 g), N₂ atmosphere, 160°C, solvent-free, GC yields.

Moreover, we explored the reusability of Co-N-C/CNT@AC catalyst by a simple filtration from the reaction mixture. Prior to reuse in the next run, the catalyst needed to be refluxed at 80°C for 30min and sonicated in ethanol orderly, then followed the reactivation in H₂ atmosphere at 375°C for 1 h. In the reusability test, a slight activity loss after five rounds was found (97-92%), which demonstrated the excellent thermal and chemical stability of Co-N-C/CNT@AC catalyst (Figure 6). Further, we performed XRD and TEM characterization for the spent catalyst after 2 cycles. No significant change was observed from XRD patterns, and CNTs could still remain except for minor morphology change compared to fresh catalyst (Figure 4a vs. Figure 7).

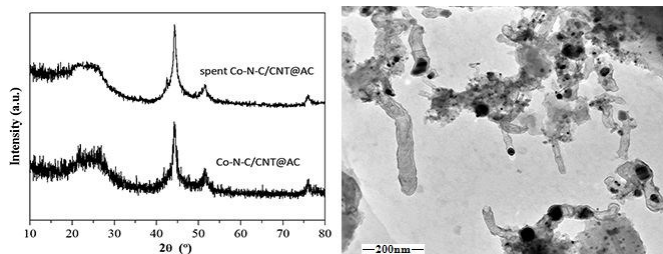
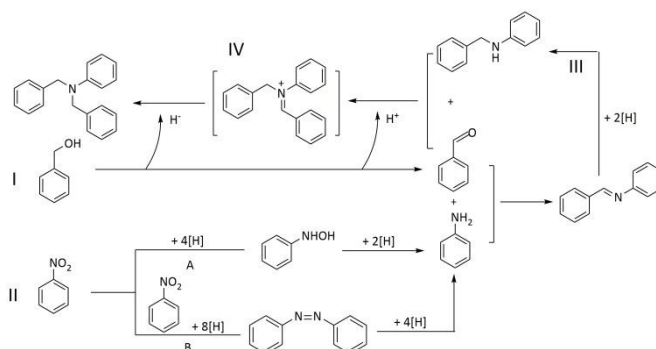


Figure 7 XRD and TEM image of spent Co-N-C/CNT@AC catalyst.

To examine the practical applicability of our protocol, the imination of nitrobenzene and benzyl alcohol was conducted on a 0.2 mol nitrobenzene scale under the above optimized conditions. The reaction proceeded for 24h and gave imine with 91% GC yield.

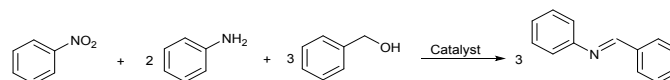
Based on our experiment results and previous literature reports, a tentative reaction mechanism to rationalize this transformation was depicted in Scheme 1. The direct reductive coupling of nitroarenes with alcohols involved the following four steps: I) the dehydrogenation of alcohols afforded aldehydes, and released proton and hydride which migrated to the substrate under the action of Co-N and basic N species^{48, 49}. II) transfer hydrogenation of nitrobenzenes. Two possible reaction pathways were widely accepted for this step. One is the direct reduction of nitrobenzenes to anilines undergoing hydroxylamine intermediates via a sequential hydrogenation/dehydration process (A). The second route

involves a condensation reaction leading to azo compound, which is then hydrogenated/dehydrated, finally generating the anilines (B)^{22, 26}. By tracing the reaction with GC-MS, very small amounts of azobenzene and/or aniline could be detected in some synthetic reaction. And we also performed the reaction starting from azobenzene in the presence of benzyl alcohol under reaction condition, imine was obtained with high yield. This fact implied that transfer hydrogenation of nitrobenzenes to anilines was via a condensation process of nitrobenzene over Co-N-C/CNT@AC catalyst. III) the coupling of amines with aldehydes gave imines promoted by basic N species⁴⁷, and imines could be further hydrogenated to secondary amines. IV) the secondary amines were alkylated to the corresponding tertiary amines.



Scheme 1 A tentative mechanism for the direct alkylation of nitroarenes.

It's worth pointing out that large amounts of aldehydes were produced by dehydrogenation of alcohols in the reductive amination of nitroarenes with alcohols, which increased the difficulty of product separation on the one hand and did not meet the requirement of atomic economy on the other hand although aldehydes were valuable products. Based on our effort in the economic synthesis of N-substituted amine, we tried to aminate excess alcohols by introducing amines. For this, a model reaction was made via nitrobenzene, aniline and benzyl alcohol with 1: 2: 3 molar ratio as the starting materials for the synthesis of imine (Scheme 2). The result exhibited that all reactants were almost quantitatively reacted to afford the desired imine with 96% yield, and only trace amount of benzaldehyde was detected. This methodology provided an alternative for the atom-economic reductive amination reaction of nitroarenes with alcohols.



Reaction conditions: nitrobenzene (5 mmol), aniline (10mmol), benzyl alcohol (15mmol) and catalyst (0.8 g), 160 °C, N₂ atmosphere, 30h.

Scheme 2 Coupling reaction of nitrobenzene, aniline and benzyl alcohol to N-Benzylideneaniline

Experimental

Materials

Activated Carbon (Norit RX 3 Extra) was obtained from Cabot Corporation. Other chemicals were purchased from Sinopharm

Chemical Reagent Co., Ltd. and Aladdin Reagent Co. Ltd. (Shanghai, China). Beyond that, all chemicals were of analytical grade or higher and were used without further purification.

Preparation of the Catalyst

Dicyandiamide (DCD, 10 g) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.34 g) were dissolved in deionized water (120 mL), activated Carbon powder (AC, 5g) was added to the above solution. Then, the mixture was continually stirred at 60 °C until the solution completely evaporated. The resulting solid sample was calcined in the following consecutive steps: 1) The solid sample was heated to 550°C with a rate of 5 °C/min under flowing N_2 and held at 550°C for 1 h. 2) The solid sample was further raised to 700°C (3°C/min) and kept the temperature for 30 min in N_2 flow. Then the temperature was naturally lowered to 375°C. 3) The material was reduced for 2h under flowing high-purity H_2 at 375°C, following natural cooling to 200°C. 4) The sample was passivated in N_2 flow from 200°C to room temperature to obtain final products, which was named as Co-N-C/CNT@AC.

Co@AC and N-C@AC catalyst were prepared based on the above method in the absence of DCD and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, respectively. In addition, Co-N-C@AC catalyst without CNT was prepared for comparison by a similar method using urea as N source.

Characterization techniques

Powder X-ray diffraction patterns (XRD) of the catalysts were carried out on a Rigaku diffractometer (Ultima IV, 3 kW) by Cu K α radiation (40 kV, 30 mA, 0.1543 nm). The N_2 adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 instrument. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, the pore volume and pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) method. The morphologies and structures of the catalysts were observed by scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 and JEOL 2100F). The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi Spectrometer for excitation to characterize the chemical compositions or elemental structure type of the catalysts surface. The contents of elements were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Shimadzu ICPE-9000).

General procedure for the coupling reaction of nitroarenes with alcohols

In a 50mL round bottomed flask equipped with a condenser, nitroarenes, primary alcohol and catalyst were added and the mixture was stirred at 160°C under N_2 atmosphere for the given time. After completion of the reaction, the temperature was cooled to 80°C, toluene was added into the mixture until the product was completely dissolved. Then, the mixture was hot filtered to separate the catalyst. A small amount of toluene was used to wash the residue again and collected. The dodecane was added to the filtrate as GC internal standard, and the clear solution was marked up to a specific volume according to the amount of reactant. The supernatant was then analyzed by using Shimadzu GC-2010 Plus with FID

detector and Agilent GC-MS 7890. The conversions, yields and selectivities were calculated by the following equations:

$$\text{Conversion (\%)} = [(C_0 - C_r) / C_0] \times 100$$

$$\text{Selectivity (\%)} = [C_p / (C_0 - C_r)] \times 100$$

$$\text{Yield (\%)} = C_p / C_0 \times 100$$

Here, C_0 represented the initial concentration of the reactants; C_r and C_p are the concentrations of the residual reactants and the corresponding amines, respectively.

Conclusions

A non-noble nanostructured Co-N-C/CNT@AC catalyst was fabricated via the successive pyrolysis and reduction of the mixture of the precursors. The imines and secondary amines were synthesized successfully through the route of the reductive coupling of nitroarenes and alcohols over Co-N-C/CNT@AC under exogenous base- and solvent- free conditions. And the reusability and amplification experiments confirmed the decent applicability of Co-N-C/CNT@AC. In short, our catalytic system had the merits of cost effectiveness, wide universality, environmental benignity and good reproducibility. More work is under way to further improve catalytic performance, explore reaction mechanism and expand the scope of application of our catalyst.

Conflicts of interest

There are no conflicts to declare.

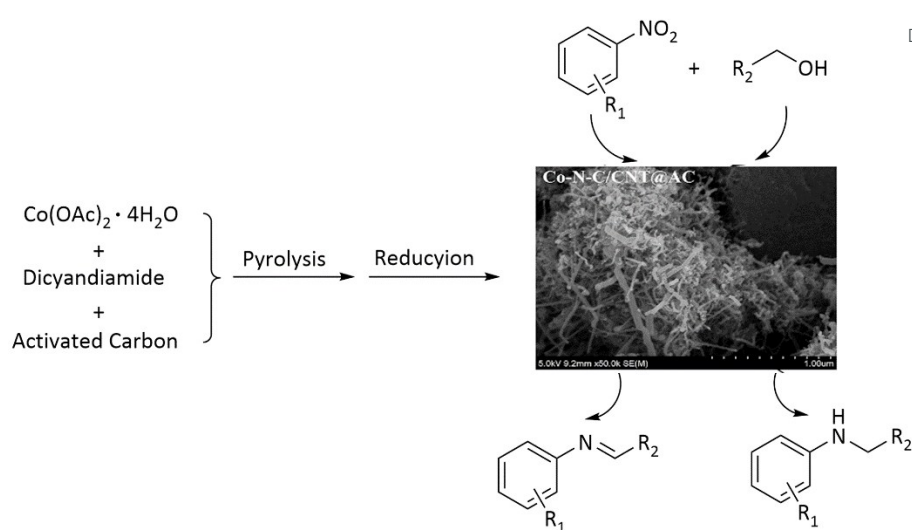
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Imines and amines were synthesized on Co-N-C/CNT@AC by the coupling of nitroarenes and alcohols under base- and solvent- free conditions.