Chemical
Science

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Sun, Q. Zhu, J. Hu, X. Kang, J. Ma, H. Liu and B. Han, *Chem. Sci.*, 2017, DOI: 10.1039/C7SC01058C.

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View Article Online
DOI: 10.1039/C7SC01058C

Journal Name

ARTICLE

N,N-Dimethylation of Nitrobenzenes with CO_2 and Water by Electrocatalysis

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We proposed a strategy to synthesize N,N-dimethylanilines from nitrobenzene and its derivatives, CO_2, and water via electrochemical reaction under ambient conditions. H^+ generated from H_2O was used as hydrogen source. Pd/Co-N/carbon, in which Pd nanoparticles were supported on Co-N/carbon, were designed and used as electrocatalysts. It was found that the electrocatalysts were very efficient for the reaction in MeCN solution with 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim]Tf_2N) as the supporting electrolyte and 1-amino-methylphosphonic acid (AMPA) as thermal co-catalyst. A series of control experiments showed that Pd/Co-N/carbon and AMPA cooperated very well in accelerating the reaction. This synthetic route has some obvious advantages, such as using CO_2 and water as the reactants, ambient reaction condition, and high yields of the desired product. This opens a way to synthesize chemicals by the combination of electrocatalyst and thermal catalyst with organics, CO_2, and water as reactants.

Introduction

Carbon dioxide (CO_2) is an abundant, inexpensive, harmless and renewable C1 resource.[1,2] CO_2 chemistry has emerged as one of the most significant branches of chemistry. Owing to its thermodynamic stability and kinetic inertness, well designed activation of CO_2 and thermodynamic driving force are required for efficient conversion.[3-5] Transformation of CO_2 into different chemicals have been reported, such as direct hydrogenation of CO_2 to organic acids and alcohols.[6,7] In parallel, direct introduction of CO_2 into organic substrates is also an attractive goal in modern chemistry,[8-11] and exploration of new routes is very interesting.

N-Methylation and N,N-dimethylation reations are very important in chemical industry, which can obtain a series of useful intermediates for the synthesis of many valuable products, such as dyes, pesticides and perfumes.[12-20] Traditionally, they can be synthesized through the methylation of amines with methanol or formaldehyde.[19,20] Using CO_2 as C1 resource is a very promising route to synthesize N,N-dimethylanilines. In general, H_2 or $PhSiH_3$ has been used as reducing agent for the N-methylation reaction of anilines.[12-18] Anilines are usually synthesized by the hydrogenation of nitrobenzenes. Recently, direct N-methylation of nitrobenzenes have also been studied using H_2 as reducing agent at high temperature and high pressure (Fig. S1).[17] Obviously, searching for new reducing agents and performing the methylation reaction of nitrobenzenes under mild conditions are desirable.

Electrochemical method has been used to synthesize organic molecules from the past century.[21-25] It possess some obvious advantages, such as mild conditions, high functional group tolerance, and innate scalability and sustainability.[21] Water is an ideal hydrogen source. H^+ can be obtained *via* the oxygen evolution reaction (OER) at the anode electrode and tranferred to cathode electrode.[26] It is well known that the efficiency and selectivity of electrochemical reactions depend strongly on the properties of electrodes and electrolytes, and their coupling.[22] Therefore, designing a suitable electrocatalyst with abundant active sites and high electrical conductivity is the key to promoting electrocatalytic reactions.

Use of CO_2 and water as reactants simultaneously in organic reactions is very attractive. Herein, we developed a strategy for synthesis of N,N-dimethylanilines by N,N-dimethylation of nitrobenzene or its derivatives with CO_2 using H_2O as the hydrogen source. In the reactions, electrochemical reaction and thermal reaction were combined with Pd/Co-N/carbon as electrocatalyst and 1-amino-methylphosphonic acid (AMPA) as thermal catalyst. It was demonstrated that Pd/Co-N/carbon and AMPA had exellent synergistic effect and the reactions proceeded efficiently under ambient condition and high yields of the desired product could be reached. As far as we know, this is the first work on synthesis N,N-dimethylanilines using nitrobenzene (or its derivatives), CO_2, and water as reactants.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C7SC01058C

Results and discussion

The H-type reaction cell used was composed of a cathode, a platinum anode, and an Ag/Ag$^+$ reference electrode (Fig. S2), which was similar to that utilized in the previous works for electroreduction of CO_2.[27-31] The cathode and anode compartments were separated by a Nafion 117 proton exchange membrane (PEM). H_2SO_4 aqueous solution was used as anodic electrolyte. In the reaction, H$^+$ from water could be transferred from anode compartment to cathode compartment through the PEM, which acted as the hydrogen source for the reaction. The detailed description of the apparatus is given in the ESI.

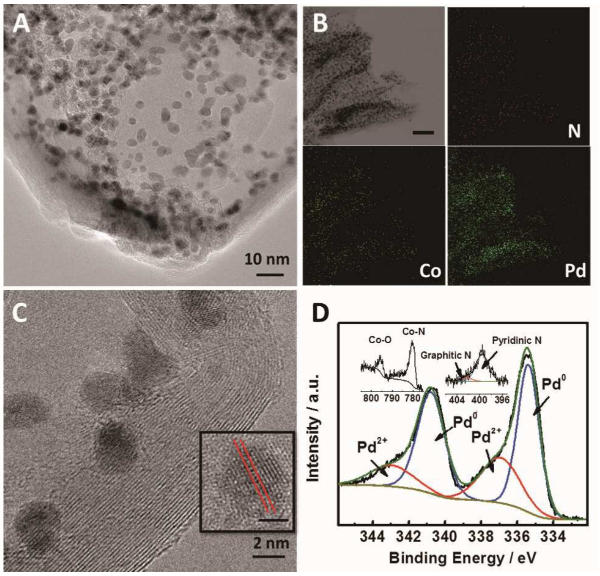


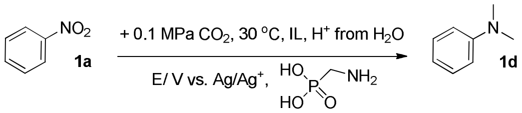
Fig. 1 Structural and elemental analysis of $Pd_{2.2}$/Co-N/carbon. A) TEM image of $Pd_{2.2}$/Co-N/carbon. B) Corresponding elemental mappings of $Pd_{2.2}$/Co-N/carbon (scale bar: 50 nm). C) HR-TEM image of $Pd_{2.2}$/Co-N/carbon. The scale bar of inset of C is 1 nm. D) XPS spectra of Pd 3d, Co 2p and N 1s orbits of $Pd_{2.2}$/Co-N/carbon.

Pd is an efficient electrocatalyst for the reduction of CO_2 to CO or formate.[32,33] It is known that nanoporous carbon materials have high specific surface area, high chemical and thermal stability, and good conductivity.[34,35] Zeolitic imidazolate frameworks (ZIFs) have been reported to be outstanding carbon precursors.[36,37] They can incorporate N atoms and metal species into the carbon lattice, which can enhance electric conductivity and electron-donor tendency, and act as the hard template during the carbonization process.[36] Meanwhile, the residual metals can also act as co-catalyst. We designed a new electrocatalysts Pd/Co-N/carbon using ZIF as carbon and nitrogen precursors, and detailed preparation procedures are given in the SI. Very briefly, Co-N/carbon support was first prepared by the carbonization of the Co-ZIF/graphene oxide (GO) at 800 °C under an Ar atmosphere.The Pd_x/Co-N/carbon electrocatalysts were obtained by immobilizing Pd nanoparticles on the support, in which x denotes the average size of Pd particles in nm. The size of Pd nanoparticles could be controlled by the reduction temperature and the ratio of sodium citrate (stabilizing agent) to $PdCl_2$. The size distributions of the Pd nanoparticles in different catalysts are shown in Fig. S3, which were obtained from counting more than 200 particles in the transmission electron microscopy (TEM) images. The support had specific surface area of 380 m^2 g^{-1} determined by N_2 adsorption/desorption method. The elemental analysis of Co-N/carbon support was conducted by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results showed that the contents of Co, C and N element in the support are 37.69 wt%, 30.73 wt% and 1.05 wt%, respectively. The surface composition of the support detected by X-ray photoelectron spectroscopy (XPS) is given in Table S1.

Fig. 1 shows high-resolution transmission electron microscopy (HR-TEM) images of $Pd_{2.2}$/Co-N/carbon. It can be seen that the Pd nanoparticles were uniformly deposited on the Co-N/carbon support (Fig. 1A). Elemental distribution mappings also illustrate the co-existence of Pd and Co elements and Pd nanoparticles were dispersed on the support homogeneously (Fig. 1B). The typical Pd (111) plane with the characteristic lattice spacing of 0.23 nm could be observed (Fig. 1C). XPS spectra (Fig. 1D) showed the chemical nature of catalyst, including the peaks belonging to Pd^0 (Pd 3d: 340.7 and 335.4 eV), Pd^{2+} (Pd 3d: 343.0 and 336.9 eV), Co-N (Co 2p: 780.1 eV), Co-O (Co 2p: 795.4 eV), pyridinic N (N 1s: 399.5 eV) and graphitic N (N 1s: 402.2 eV).[36,38] The results provided direct evidence that most Pd nanoparticles existed in the form of Pd^0, and some electrochemical active sites for CO_2 reduction such as pyridinic N and Co-N_x moieties[39,40] existed in the support. Furthermore, the actual Pd loadings in all catalysts were 18.3 ± 0.6 wt%, as measured by ICP-OES as listed in Table S2. TEM and HR-TEM images of the other Pd_x/Co-N/carbon catalysts with different Pd sizes are shown in Fig. S4.

To prepare the electrodes, Pd_x/Co-N/carbon catalysts were suspended in acetone with Nafion D-521 dispersion to form a homogeneous ink with the aid of ultrasound, which was spread onto carbon paper (CP) to obtain the working electrodes. Ionic liquids (ILs) are efficient supporting electrolytes for the reduction of CO_2.[27,41] The initial screening was performed for the methylation reaction of nitrobenzene **1a** with CO_2 and H$^+$ from H_2O over $Pd_{2.2}$/Co-N/carbon using MeCN containing 0.5 M 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([Bmim]Tf_2N) as the electrolyte in the presence of AMPA. As expected, the reduction potential was crucial for the conversion of **1a** (Table 1, entries 1-6). The most effective potential was -2.3 V vs. Ag/Ag$^+$, and afforded full conversion of **1a** with a 92 % yield of N,N-dimethylaniline **1d** in 30 °C. Lowering the reaction temperature to 20 °C resulted in a yield of only 65 % after 10 h (Table S3). Increasing the temperature to 40 °C, 50 °C and 60 °C resulted in 81 %, 72% and 58 % yields of **1d** (Table S3) due mainly to the lower solubility of CO_2 in the electrolyte. Therefore, 30°C is an optimal temperature. Table 1 (entries 5, 7-10) and Fig. S5 indicated that reactant **1a** could be converted completely after 10 h. Subsequently, conversion of **1a** was also studied using MeCN containing other ILs as the supporting electrolytes, but their performances were not as good as [Bmim]Tf_2N (Table 1, entries 5, 11-16). Furthermore, the solutions of [Bmim]Tf_2N with AMPA in DMSO, DMF, $MeNO_2$ and 1,4-dioxane were also used as the electrolytes, and lower yields of **1d** were obtained (Table S4). The results indicated that [Bmim]Tf_2N in MeCN solution was the best electrolyte.

Table 1. Electrocatalytic methylation of nitrobenzene with CO_2 and water over $Pd_{2.2}$/Co-N/carbon.[a]



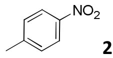
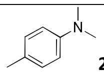
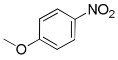
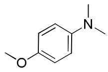
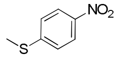
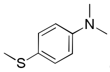
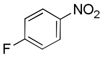
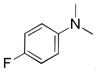
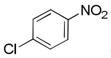
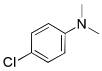
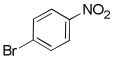
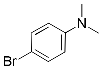
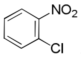
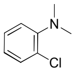
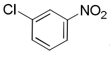
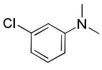
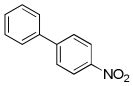
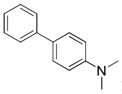
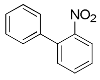
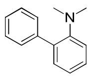
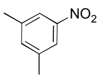
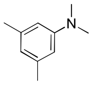
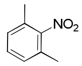
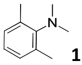
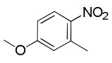
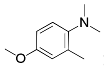
Entry	Electrolyte[b]	E / V[c]	t / h	Yield / %[d]
1	[Bmim]Tf_2N	-1.9	10	13
2	[Bmim]Tf_2N	-2.0	10	36
3	[Bmim]Tf_2N	-2.1	10	68
4	[Bmim]Tf_2N	-2.2	10	89
5	[Bmim]Tf_2N	-2.3	10	92
6	[Bmim]Tf_2N	-2.4	10	92
7	[Bmim]Tf_2N	-2.3	1	7
8	[Bmim]Tf_2N	-2.3	5	56
9	[Bmim]Tf_2N	-2.3	8	85
10	[Bmim]Tf_2N	-2.3	12	92
11	[Bmim]PF_6	-2.3	10	81
12	[Bmim]BF_4	-2.3	10	82
13	[Bmim]TfO	-2.3	10	85
14	[Bmim]ClO_4	-2.3	10	23
15	[Bmim]NO_3	-2.3	10	15
16	[Bmim]H_2PO_4	-2.3	10	30

[a] Reaction conditions: nitrobenzene (1.0 mmol), AMPA (0.06 mmol), CO_2 (0.1 MPa), temperature (30 °C); [b] Electrolyte (30 mL) is CO_2-saturated MeCN containing 0.5 M IL; [c] All potentials are reported with respect to Ag/Ag^+. [d] Yield determined by ^1H NMR spectroscopy.

Fig. S6 summarizes the yields of **1d** from the electrochemical conversion of **1a** over the Pd_x/Co-N/carbon catalysts with different Pd particle sizes at different potentials. The electronic properties of nanoparticles can be tuned by controlling the sizes.[42,43] Generally, smaller nanoparticles have the lower d-band center, which in turn results in a decrease in its adsorption energy.[44] With respect to the reduction of CO_2, lowering of the d-band center reduces the binding energy of hypothetical intermediates,[45] thereby enhancing the rate of CO_2 reduction and the conversion of nitrobenzene.

The methylation of various substituted nitrobenzenes over $Pd_{2.2}$/Co-N/carbon were investigated (Table 2). The electron-donating methyl, methoxy and methylthio groups in the 4-position of aromatic ring of **1a** reduced the reactivity with yields of 75 % (**2d**), 74 % (**3d**) and 71 % (**4d**), respectively (Table 2, entries 1-3). For halogen-substituted nitrobenzenes, the desired products were obtained in 82-90 % yields (Table 2, entries 4-8). When 4-nitrobiphenyl **10a** and 2-nitrobiphenyl **11a** were used, the corresponding products were generated in 78 % (**10d**) and 76 % (**11d**) yields, respectively (Table 2, entries 9-10). Di-substituted nitrobenzene such as 5-nitro-m-xylene (**12a**), 2,6-dimethylnitrobenzene (**13a**) and 3-methyl-4-nitroanisole (**14a**) also showed high reactivity, which gave the desired products in 75-82 % yields (Table 2, entries 11-13). To our delight, N,N-dimethylation of benzonitrile and its derivatives could also be carried out with moderate yields (Table S5).

Table 2. Electrocatalytic methylation of substituted nitrobenzenes with CO_2 and water over $Pd_{2.2}$/Co-N/carbon.[a]

Entry	Substrates	Products	Yield / %[b]
1	 **2a**	 **2d**	75
2	 **3a**	 **3d**	74
3	 **4a**	 **4d**	71
4	 **5a**	 **5d**	90
5	 **6a**	 **6d**	87
6	 **7a**	 **7d**	82
7	 **8a**	 **8d**	82
8	 **9a**	 **9d**	86
9	 **10a**	 **10d**	78
10	 **11a**	 **11d**	76
11	 **12a**	 **12d**	78
12	 **13a**	 **13d**	82
13	 **14a**	 **14d**	75

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DOI: 10.1039/C7SC01058C

[a] Reaction conditions: substituted nitrobenzene (1.0 mmol), AMPA (0.06 mmol), CO_2 (0.1 MPa), electrolyte (30 mL, CO_2-saturated MeCN containing 0.5 M $[Bmim]Tf_2N$), -2.3 V vs Ag/Ag^+, 30 °C, 10 h; [b] Yield determined by ^1H NMR spectroscopy.

Some control experiments were conducted in order to get some evidences to study the mechanism. Fig. S7 shows that very small amount of AMPA could promote the reaction for producing N,N-dimethylaniline efficiently. However, only aniline was formed in the absence of AMPA (Fig. S8), and aniline could not be further converted even extending the reaction time (Table S6). These results indicate that the AMPA is necessary and acts as a co-catalyst. To further understand the role of AMPA, NMR analysis was performed on aniline and its mixture with AMPA, respectively (Fig. S9), it was found that ^1H signal of N-H in aniline shifted downfield from 4.88 to 5.11 ppm due to mixing with AMPA. The shift of ^1H signal of N-H in aniline was also affected by the amount of AMPA and the result was consistent with the reaction result that the yield of the product increased with the increase of the amount of AMPA from 0 to 0.06 mmol (Fig. S7). From these results, it can be concluded that AMPA as a Brønsted base could activate the proton on the aniline to promote the formation of N,N-dimethylaniline. In this way, the C atom on the intermediates obtained from CO_2 electroreduction could show an easier electrophilic attack to the N atom on aniline, *i.e.* AMPA acted as the co-catalyst to promote the reaction of aniline with the intermediate from CO_2 electroreduction to form N-phenylformamide or N-methyl-N-phenylformamide. As a result, the next reaction that N-methyl-N-phenylformamide reacted with H^+ from water to synthesize N,N-dimethylaniline could proceed successfully. More details will be discussed in the mechanism part below.

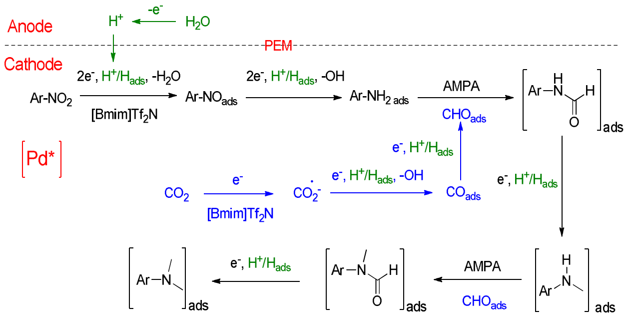

Fig. 2. Possible pathway for electrochemical reaction of nitrobenzene with CO_2 and water to form N,N-dimethylaniline of over Pd/Co-N/carbon.

On the basis of the experimental results and the related knowledge in the literature, we propose a speculative mechanism for N,N-dimethylation of nitrobenzene, which is shown schematically in Fig. 2. Two parallel processes, CO_2 and nitrobenzene hydrogenation occur in the cathode compartment in the first step. For CO_2 activation and reduction, a $[Bmim\text{-}CO_2]^+$ complex can form quickly via the hydrogen bonding interaction between CO_2 and IL cation,[46] which can reduce the reaction barrier for electron transfer to CO_2.[27] $[Bmim\text{-}CO_2]^+$ can be adsorbed on the electrode surface and the CO_2 is reduced to $CO_2^{\bullet-}$, which forms CO_{ads} after receiving the second electron. Pd nanoparticles facilitate these processes.[32] After accepting an electron and proton, CO_{ads} can be adsorbed on the support, and pyridinic N as well as $Co\text{-}N_x$ moieties can further drive CO_{ads} to generate CHO_{ads}.[31,39-40] The next step is the insertion of CHO_{ads} into $ArNH_2Pd^*$ to form adsorbed N-phenylformamide in the presence of the Brønsted base, AMPA. $ArNH_2Pd^*$ can be obtained through the pathway of nitrobenzene → nitrosobenzene → N-phenylhydroxylamine → aniline on the electrode surface. It is usually observed in the electrochemical reduction of nitrobenzene to aniline.[47] The adsorbed N-phenylformamide can be quickly hydrogenated into N-methylaniline. Following this, N-methylaniline can be adsorbed onto the electrode surface and reacted with CHO_{ads} to form the adsorbed N-methyl-N-phenylformamide. Finally, the protonation of the adsorbed N-methyl-N-phenylformamide leads to the formation of N,N-dimethylaniline.

To further verify the reaction mechanism proposed, we conducted the experiments using some intermediates in Fig. 2 as starting reactants, including aniline, N-phenylformamide, N-methylaniline and N-methyl-N-phenylformamide (Fig. S10). 92 % N,N-dimethylaniline, 5 % N-methylaniline and a small amount of aniline, N-phenylformamide and N-methyl-N-phenylformamide can be detected in reaction (I). In reaction (II), the products contained 93 % N,N-dimethylaniline, about 3 % N-methylaniline as well as a small amount of N-phenylformamide and N-methyl-N-phenylformamide. The results were similar to those in reaction (I), suggesting that nitrobenzene was first converted to aniline completely in a short time. In reactions (III) and (V), when N-phenylformamide or N-methyl-N-phenylformamide was used as the strating reactant, the desired products N-methylaniline or N,N-dimethylaniline could be obtained. At the same time, most N-methylaniline could be transformed to N,N-dimethylaniline with the aid of AMPA in reaction (IV). In addtion, a small amount of N-phenylformamide or N-methyl-N-phenylformamide as reaction intermediates could be also detected in reactions (III) and (IV). All these evidences support the proposed reaction mechanism.

Conclusions

In conclusion, N,N-dimethylanilines can be synthesized by methylation of nitrobenzene (or substituted nitrobenzenes) with CO_2 and water. Pd/Co-N/carbon electrode and the electrolyte composed of MeCN, $[Bmim]Tf_2N$, and AMPA is very efficient electrolysis system at ambient condition. The N,N-dimethylation of a range of substrates, including nitrobenzene, substituted nitrobenzene and benzonitrile, can proceed smoothly with satisfactory yields. In the reaction, Pd/Co-N/carbon catalyzes the reduction of nitrobenzene to aniline quickly, which is further converted to the N,N-dimethylaniline catalyzed cooperatively by electrocatalyst Pd/Co-N/carbon and thermal catalyst AMPA. We believe that this route has potential of application for producing N,N-dimethylanilines due to some obvious advantages. In addition, combination of

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DOI: 10.1039/C7SC01058C

electrocatalysts and thermal catalysts can realize other reactions that cannot be conduct with only electrocatalysts or thermal catalysts.

Experimental section

Preparation of Co-ZIF/GO

In this work, GO was prepared by modified Hummer method according to the reference.[48] 1.2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 1 mmol of 2-methylimidazole were dissolved in 12 mL and 20 mL of methanol, respectively. $Co(NO_3)_2$ solution was added into the 2-methylimidazole solution to obtain a clear purple solution under continuous stirring. Then, 10 mL of GO dispersion (10 mg GO in 10 mL methanol/water, v/v, 4:1) was immediately added to the above purple solution. After stirring for 3 h, the precipitation was collected by centrifugation and washing with methanol, followed by drying at 50 °C for 10 h. Co-ZIF/GO was obtained.

Preparation of Co-N/carbon support

The resulting Co-ZIF/GO precursor was heated in the tube furnace at 10 °C min^{-1} in argon (Ar) medium to 800 °C and kept at this temperature for 3 h. Then the composites were immersed in 2 M HCl aqueous solution for 24 h. The precipitation was collected by centrifugation and washing with water, followed by drying at 80 °C for 24 h. Co-N/carbon support was obtained, of which the elemental composition is given in Table S1.

Preparation of Pd_x/Co-N/carbon catalysts

Pd/Co-N/carbon catalysts were synthesized with sodium borohydride as a reductive agent, sodium citrate as a stabilizing agent and Co-N/carbon as support. The sizes of the Pd nanoparticles in the catalysts were controlled by varying the ratio of sodium citrate to $PdCl_2$ as well as the reduction temperature.[32] The average particle size was determined by counting more than 200 particles from TEM images. Herein, preparation of $Pd_{2.2}$/Co-N/carbon is described in detail. 0.5 mmol of $PdCl_2$ in 0.1 M HCl solution and 4 mmol sodium citrate were dissolved in 200 mL water under continuous stirring for 30 min. Then, 200 mg as-prepared Co-N/carbon support was added into the mixture with sonication for 1 h. Then, 50 mL of 0.1 M sodium borohydride aqueous solution was added into the above suspension dropwise at 0 °C under vigorous stirring to reduce the Pd^{2+}. After stirring for 8 h, the black precipitation was collected by centrifugation and washing with water for 3 times, $Pd_{2.2}$/Co-N/carbon was obtained after freeze drying.

The other Pd/Co-N/carbon catalysts were prepared by controlling the reduction temperature and adjusting the ratio of sodium citrate (stabilizing agent) to $PdCl_2$. For $Pd_{3.6}$/Co-N/carbon and $Pd_{4.5}$/Co-N/carbon, the temperatures to reduce Pd^{2+} were 25 °C and 60 °C, respectively, and the ratio of sodium citrate to $PdCl_2$ was the same as that for preparing $Pd_{2.2}$/Co-N/carbon. For $Pd_{6.4}$/Co-N/carbon and $Pd_{7.9}$/Co-N/carbon, the ratios of sodium citrate to $PdCl_2$ were 2 and 0, respectively, and the reduction temperature was 25 °C. $Pd_{10.2}$/Co-N/carbon was obtained by bubbling $Pd_{3.6}$/Co-N/carbon with H_2 for 12 h in 0.1 M HCl aqueous solution at 25 °C.

Materials characterization

XPS analysis was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. The actual loading of Pd in the catalysts was determined by ICP-OES (Vista-MPX). The N_2 adsorption/desorption isotherms of the Co-N/carbon nanosheets were determined using a Quadrasorb SI-MP system. The microstructures of the catalysts were studied using JEOL-2100F HR-TEM operated at 200 kV.

Preparation of electrode and electrochemical reaction

To prepare an electrode, the corresponding Pd_x/Co-N/carbon catalyst was suspended in acetone with Nafion D-521 dispersion to form a homogeneous ink assisted by ultrasound, which was spread onto carbon paper (CP: 1×1 cm^{-2}) to obtain the working electrodes. The loading of catalyst was 2.0 ± 0.1 mg cm^{-2}. Before experiment, all the auxiliary electrodes were sonicated in acetone for 3 min and then washed with water and ethanol, followed by drying in N_2 atmosphere.

An electrochemical workstation (CHI 6081E, Shanghai CH Instruments Co., China) was used in all the experiments. The electrolysis experiments were conducted in a typical H-type cell that was similar to that used in the previous works,[28,29] which is schematically shown in Fig. S2. It consisted of a cathode (working electrode), an anode (platinum gauze auxiliary electrode), and an Ag/Ag^+ reference electrode. The cathode and anode compartments were separated by a Nafion 117 proton exchange membrane. 0.5 M H_2SO_4 aqueous solution was used as anodic electrolyte. H^+ can be transferred from anode compartment to cathode compartment through Nafion 117 proton exchange membrane, which is the hydrogen source. Under the continuous stirring, CO_2 was bubbled through the catholyte (2 mL/min) for 30 min before electrolysis. Then, the electrolysis experiments were carried out with CO_2 bubbling (2 mL/min). In a typical reaction procedure, 1.0 mmol nitrobenzene and 0.06 mmol AMPA were added into 30 mL electrolyte (CO_2-saturated MeCN containing 0.5 M $[Bmim]Tf_2N$). The reaction was performed at 30 °C for desired time under magnetic stirring. After the reaction, MeCN in the system was removed by rotary evaporation and the IL was extracted by ether. The isolated product was obtained and purified by column chromatography using petroleum ether/ethyl acetate (150:1).

Product analysis

The gaseous product of electrochemical experiments was collected and analyzed by gas chromatography (GC, HP 4890D), which was equipped with FID and TCD detectors using helium as the internal standard. For methylation of nitrobenzene, the liquid product was analyzed by ^1H NMR (Bruker Avance III 400 HD spectrometer) in chloroform-d with TMS as an internal standard.

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DOI: 10.1039/C7SC01058C

Acknowledgements

The authors thank the National Natural Science Foundation of China (21533011, 21403253, 21673248) and Chinese Academy of Sciences (QYZDY-SSW-SLH013).

Notes and references

1 J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem. Int. Ed.*, 2016, **55**, 7296.
2 M. He, Y. Sun and B. Han, *Angew. Chem. Int. Ed.*, 2013, **52**, 9620.
3 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259.
4 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
5 J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631.
6 M. Cui, Q. Qian, Z. He, Z. Zhang, J. Ma, T. Wu, G. Yang and B. Han, *Chem. Sci.*, 2016, **7**, 5200.
7 Q. Qian, J. Zhang, M. Cui and B. Han, *Nat. Commun.*, 2016, **7**, 11481.
8 Z. Z. Yang, L. N. He, J. Gao, A. H. Liu and B. Yu, *Energy Environ. Sci.*, 2012, **5**, 6602.
9 J. Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu and B. Han, *Angew. Chem. Int. Ed.*, 2015, **54**, 5399.
10 M. Cui, Q. Qian, Z. He, J. Ma, X. Kang, J. Hu, Z. Liu and B. Han, *Chem. Eur. J.*, 2015, **21**, 15924.
11 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
12 K. Beydoun, T. vom Stein, J. Klankermayer and W. Leitner, *Angew. Chem. Int. Ed.*, 2013, **52**, 9554.
13 Y. Li, X. Fang, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 9568.
14 Y. Li, I. Sorribes, T. Yan, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 12156.
15 I. Sorribes, J. R. Cabrero-Antonino, C. Vicent, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2015, **137**, 13580.
16 E. Blondiaux, J. Pouessel and T. Cantat, *Angew. Chem. Int. Ed.*, 2014, **53**, 12186.
17 X. Cui, X. Dai, Y. Zhang, Y. Deng and F. Shi, *Chem. Sci.*, 2014, **5**, 649.
18 O. Jacquet, X. Frogneux, C. Das Neves Gomes and T. Cantat, *Chem. Sci.*, 2013, **4**, 2127.
19 P. S. Niphadkar, P. N. Joshi, H. R. Gurav, S. S. Deshpande and V. V. Bokade, *Catal. Lett.*, 2009, **133**, 175.
20 F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas, A. A. Romero and M. R. Urbano, *J. Catal.*, 1997, **172**, 103.
21 E. J. Horn, B. R. Rosen and P. S. Baran, *ACS Cent. Sci.*, 2016, **2**, 302.
22 J.-i. Yoshida, K. Kataoka, R. Horcajada and A. Nagaki, *Chem. Rev.*, 2008, **108**, 2265.
23 T. Morofuji, A. Shimizu and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2015, **137**, 9816.
24 M. Rafiee, K. C. Miles and S. S. Stahl, *J. Am. Chem. Soc.*, 2015, **137**, 14751.
25 H. C. Xu and K. D. Moeller, *J. Am. Chem. Soc.*, 2010, **132**, 2839.
26 D. D. Zhu, J. L. Liu and S. Z. Qiao, *Adv. Mater.*, 2016, **28**, 3423.
27 B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis and R. I. Masel, *Science*, 2011, **334**, 643.
28 X. Sun, Q. Zhu, X. Kang, H. Liu, Q. Qian, Z. Zhang and B. Han, *Angew. Chem. Int. Ed.*, 2016, **55**, 6771.
29 Q. Zhu, J. Ma, X. Kang, X. Sun, H. Liu, J. Hu, Z. Liu and B. Han, *Angew. Chem. Int. Ed.*, 2016, **55**, 9012.
30 S. Zhang, P. Kang, S. Ubnoske, M. K. Brennaman, N. Song, R. L. House, J. T. Glass and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 7845.
31 J. L. DiMeglio and J. Rosenthal, *J. Am. Chem. Soc.*, 2013, **135**, 8798.
32 D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang and X. Bao, *J. Am. Chem. Soc.*, 2015, **137**, 4288.
33 X. Min and M. W. Kanan, *J. Am. Chem. Soc.*, 2015, **137**, 4701.
34 X. Kang, X. Sun and B. Han, *Adv. Mater.*, 2016, **28**, 1011.
35 X. Sun, X. Kang, Q. Zhu, J. Ma, G. Yang, Z. Liu and B. Han, *Chem. Sci.*, 2016, **7**, 2883.
36 J. Wei, Y. Hu, Y. Liang, B. Kong, J. Zhang, J. Song, Q. Bao, G. P. Simon, S. P. Jiang and H. Wang, *Adv. Funct. Mater.*, 2015, **25**, 5768.
37 Q. Yang, Q. Xu, S.-H. Yu and H.-L. Jiang, *Angew. Chem. Int. Ed.*, 2016, **55**, 3685.
38 R. Nie, J. Shi, W. Du and Z. Hou, *Appl. Catal. A-Gen.*, 2014, **473**, 1.
39 A. S. Varela, N. Ranjbar Sahraie, J. Steinberg, W. Ju, H.-S. Oh and P. Strasser, *Angew. Chem. Int. Ed.*, 2015, **54**, 10758.
40 J. Shen, R. Kortlever, R. Kas, Y. Y. Birdja, O. Diaz-Morales, Y. Kwon, I. Ledezma-Yanez, K. J. P. Schouten, G. Mul and M. T. M. Koper, *Nat. Commun.*, 2015, **6**, 8177.
41 G. P. S. Lau, M. Schreier, D. Vasilyev, R. Scopelliti, M. Grätzel and P. J. Dyson, *J. Am. Chem. Soc.*, 2016, **138**, 7820.
42 H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser and B. R. Cuenya, *J. Am. Chem. Soc.*, 2014, **136**, 16473.
43 M. Hou, Q. Mei and B. Han, *J. Colloid Interf. Sci.*, 2015, **449**, 488.
44 W. P. Zhou, A. Lewera, R. Larsen, R. I. Masel, P. S. Bagus and A. Wieckowski, *J. Phys. Chem. B*, 2006, **110**, 13393.
45 A. Chen and C. Ostrom, *Chem. Rev.*, 2015, **115**, 11999.
46 C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.*, 2004, **126**, 5300.
47 C. Lagrost, L. Preda, E. Volanschi and P. Hapiot, *J. Electroanal. Chem.*, 2005, **585**, 1.
48 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.