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Short communication

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Scalable production of Cu@C composites for cross-coupling catalysis



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1. Introduction

Micro- and nano-structured metal have received great attention because of their potential utilizations in a wide range of advanced applications in the field of sensor, catalytic, environment and energy storage [1–3]. Among them, the metal of copper is of particularly interest due to its fascinating properties while much lower cost compare to other noble metals of Pd, Pt and Au [4]. Until now, numerous approaches have been reported for preparing micro-/nano-structured Cu with different morphologies of cube, rod, disk and wire [5–7], as well as other Cu-based composites such as Cu@Si, Cu@CNT and Cu@TiO₂ [8,9]. As reported, these metal-particles with unique small size could be utilized as effective catalysts with high activities [11].

However, a formidable problem always remains, that is, the metal-particles have a strong trend to agglomerate in the processes of preparation and utilization by the strong surface tension [12]. One of the most promising strategies to this problem is the immobilization of catalysts on certain stable matrix. To date, the way of coating metal particle with a layer of carbon is of great interest, and the inert carbon resultant metal@C composite could exhibit excellent catalytic activities in many cases of photooxidation of alkanes [13], electrooxidation of methanol [14], lithium–oxygen battery [15], and so on. Distinct from homogenous catalyst, such heterogeneous catalysts have the

ABSTRACT

A novel Cu@C core-shell microstructure was prepared by reduction of $[Cu(NH_3)_4]^{2+}$ with glucose using a mild hydrothermal process. The carbon shell of such Cu@C composite can be tuned to different carbonization degrees just through varying the calcination conditions. The structural properties of as-prepared Cu@C were investigated in detail by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron micrographs (TEM) and Raman spectra. In addition, these Cu@C composites were firstly used to catalyze the C—N cross coupling of amines with iodobenzene. Among them, the catalytic ability of Cu@C composites increased as their surface carbon's carburization degree improved.

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advantages of easy separation, quick recycling and minimization of metal trace in the product. However, to the best of our knowledge, the synthesis of Cu@Carbon (i.e., Cu@C) with a core@shell microstructure is quite limited, especially processed in a one-step with a large-scale production [10].

To study this catalyst system better in light of the respective merits of metal particles and carbon structures, herein we present a facile one-pot hydrothermal procedure to synthesis Cu@C structure and also the carburization degrees of carbon shell were well controlled. Considering the copper-mediated Ullmann condensation of aryl halides with amines is the most frequently used pathway for coupling reactions [16,17]; therefore herein the coupling reaction of iodobenzene and aniline was applied with Cu@C as catalyst at 383 K to evaluate its catalytic performance. Promisingly, we found that the conversion yield was significantly improved as the graphitization degree of the carbon shell improved. Noteworthy, the yield was high to 73%, which is much higher than other similar nano/micro-particle catalyst [16,17].

2. Experimental

2.1. Preparation of Cu@C composites

In a typical procedure, solution A was prepared by adding 1.225 g $CuSO_4$ ·5H₂O and 2 g of glucose into 30 mL of distilled water, and solution B was prepared by mixing 5 mL of NH₃·H₂O (25%) with 35 mL of water. Then, solution A was added into solution B slowly under the stirring for 30 min. After that, the blue aqueous solution was transferred into stainless-steel autoclaves with Telfon. The

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autoclave was sealed and maintained at 453 K for 8 h, and then cool down to room temperature naturally. Finally, a red-dark product was collected by centrifugation and wash by deionized water and alcohol for several times. Vacuum dry the sample at 353 K for 24 h and it was named as pristine Cu@C composite.

To obtain composites with different carbonization degree of carbon shell, we further calcined the pristine Cu@C composite at 573, 873 and 1173 K under the N₂ atmosphere, under which the heating rate was 5 K min^{-1} and the heating time was 4 h. The products of Cu@C-573 K, Cu@C-873 K, and Cu@C-1173 K were obtained, respectively, in which the acronym of 573 K means calcinations the sample at 573 K.

2.2. Catalytic experiments

The coupling reaction of aniline and benzene halides using the as-prepared Cu@C composites (i.e., pristine Cu@C, Cu@C-573 K, Cu@C-873 K, and Cu@C-1173 K) as catalyst, DMSO as solvent, and KOH as alkali, was performed under N₂ protection. The reaction equation was shown insert in Fig. 4. Typically, the mixture was heated at 383 K for 18 h and the process of reaction was monitored by thin-layer chromatography (TLC). The reaction mixture was cooled to room temperature, and treated with 5 mL ethyl acetate and 2 mL water. The aqueous layer was separated and extracted with ethyl acetate. The combined organic solution was dried with Na₂SO₄ and purified on silica–gel column chromatography, using ethyl acetate and hexane as eluent. The conversion yields of product were calculated.

2.3. Characterization

The X-ray powder diffraction (XRD) patterns were recorded by using a X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer

with CuK α radiation (λ = 0.154178 nm). Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were collected under a FEI-quanta 200F scanning electron microscope with acceleration voltage of 20 kV. Fourier transform infrared spectroscopy (FTIR) was investigated by Hyperion 3000 (Bruker). Raman spectra were collected on a Laser confocal micro Raman spectrometer (HORIBA Jobin Yvon). Transmission electron micrographs (TEM) were taken on a FEI-Tecnai F20 (200 kV) transmission electron microscope.

3. Results and discussion

3.1. Formation of Cu@C composites

A typical XRD pattern of the as-prepared Cu@C composite was shown in Fig. 1a. Three slightly broadened diffraction peaks can be indexed to the cubic phase of Cu, in accordance with the reported data (JCPDS No. 85-1326, a = 0.3615 nm). The broad peaks arising from 22° are attributed to the thin amorphous carbon layer on the surface of Cu. There was no characteristic peaks of impurities of Cu (OH)₂, CuO, and/or Cu₂O, suggesting that the CuSO₄ was fully deoxidized by glucose and generated elementary Cu. In addition, it also indicated that such Cu nanoparticles are very stable in air due to the protection of carbonaceous shells. The SEM image (Fig. 1b) provides direct information about the size and typical core@shell structure of the as-synthesized Cu@C composites. This core@shell structure is also confirmed by the sharp contrast between the pale edges and the dark centers under the TEM, as shown in Fig. 1c and d. The thickness of colorless colloidal carbon shell reached to 50 nm, and the diameter of Cu core ranging from 200 to 400 nm. The HRTEM image (Fig. S1) reveals that the Cu particles were indeed coated by a layer of amorphous carbon. However, we could not observe the clear lattice fringe image because the thick



Fig. 1. (a) XRD pattern, (b) SEM, (c) and (d) TEM images of Cu@C composite.



Fig. 2. (a) XRD patterns and SEM images of (b) Cu@C-573 K, (c) Cu@C-873 K, and (d) Cu@C-1173 K, the scale bar is 1 µm.

thickness of carbon and narrow lattice distance of Cu (e.g., only 0.2086 nm for (111) and 0.1806 nm for (200)). Additionally, the EDX spectrum and mapping images (Fig. S2) of Cu@C composite indicated that three kind elements of Cu, C, and O contained in composite and they have a uniformly distribution, in which the trace element of C is from the carbonaceous shell. This result was also confirmed by the FTIR spectrum (Fig. S2), in which a large numbers of functional groups such as —OH and C=O groups existed, and it might improve the linkage of bio-molecules or catalytic species to the surface in the future application.

In order to increase the carbonization degree of shell, the sample of Cu@C was calcined at different temperatures of 573, 873 and 1173 K under the N₂ atmosphere for 4 h. From the XRD patterns (Fig. 2a), it was confirmed that there is no crystalline phase change during the calcinations process. These samples almost keep the same morphologies after the calcinations as observed under the SEM images (Fig. 2b-d), and the only difference is that the carbon shells become thinner as the calcined temperature enhanced. The thickness of carbon shell is also confirmed by TEM images (Fig. S3), and the thickness of carbon shell decreased as the temperature increased. Note that for the sample of Cu@C-1173 K (Fig. 3d), there is a porous structure formed in the carbon shell, and it may benefit for the contact of Cu catalyst with the reactant. In addition, the high temperature calcinations give rise to better carbonization degree of carbon shell, as confirmed by the Raman spectra (Fig. 3), in which the intensity of the overall Raman spectra increased with increasing the temperature. Meanwhile, the graphitization degree of the carbon shell is also increased. In detail, the sample of Cu@C composite heated at 1173 K has the highest intensity ratio of the D and G band $(I_{\rm D}/I_{\rm C})$, which is a measurement of the order extent, as well as the ratio of sp2/sp3 carbon structure. Therefore, the higher calcination temperature endows the carbon shell more sp2 carbon structure, indicating more π - π chemical bonds formed [18].

3.2. Catalytic ability of Cu@C composites

Here, we select the coupling reaction of iodobenzene and aniline as the standard substrates to evaluate the catalytic properties of Cu@C composites, and the catalytic data are summarized in Fig. 4. The resultant product has been confirmed by ¹H NMR, ¹H NMR: (400 MHz, CDCl₃), δ 7.236–7.274 (m, 4H), 7.074-7.054 (d, 4H), 6.940-6.904 (m, 2H) and 5.773 (s, 1H). Detailed information is shown in Fig. S5. The catalysts of Cu@C. Cu@C-573 K, Cu@C-873 K, and Cu@C-1173 K composites are named as A, B, C and D, respectively. It could be find that the Cu@C-1173 K has the best catalytic ability may due to the higher graphitization degree of the carbon shell, in which the yield of the product can be as high as 73%. The reason should be ascribed to the follow aspects: (i) carbon shell could stabilize Cu particles and prevent them from aggregation; (ii) the synergistic effect of Cu and carbon may have a positive effect of the catalytic reaction; (iii) the higher carbonization degree and porous structure of carbon are helpful for the sufficient contact of catalyst and reactant and (iv) more



Fig. 3. Raman spectrum (λ_{ex} = 633 nm) of these Cu@C composites calcined at different temperatures.



Fig. 4. The product yields of these Cu@C composites in different carburization degree.

 π - π chemical bonds in higher graphitized carbon ensures a stronger electron field for accelerating this catalytic reaction [9,16,17]. The mechanism of this reaction is best viewed from the perspective of the Cu@C catalyst, as shown in Fig. S6. The first step is the oxidative addition of Cu@C to the halide **2** to form the Cu@C species **3**. Reaction with base gives intermediate **4**, which via transmetalation with complex **6** forms the Cu@C species **8**. Reductive elimination of the desired product **9** restores the original Cu@C catalyst **1**.

4. Conclusion

A scalable production of novel core@shell Cu@C microstructure has been constructed by using a one-step hydrothermal process without assistance of any surfactant. The new materials of Cu@C were utilized to catalyze the C—N cross coupling of amines with iodobenzene and a high yields of 73% were achieved. Besides, it was found that the catalytic ability of Cu@C nanocomposites increased with increasing the carbonization degree of shell, and it could make a progressive contribution to the development of such composite in catalytic field.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. materresbull.2015.04.043.

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