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COMMUNICATION

Copper nanoparticles modified silicon nanowires with enhanced cross-coupling catalytic ability†

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Copper nanoparticles modified silicon nanowires show enhanced catalytic activity for the coupling reaction of benzene halides (iodobenzene, bromobenzene, and chlorobenzene) and aniline.

Remarkable progress in nanocatalysis has been achieved by a great number of noble metal nanoparticles,[1–3] carbon and silicon nanostructures.[4–6] Among them, Si nanowires (SiNWs, easily converted to Si–H surface by HF treatment)[7,8] have numerous advantages: easy surface modification with metals, organic groups and oxides, large specific surface area, stability to the atmospheric environment.[9–12] These unique properties make SiNWs a promising candidate for the synthesis of hybrid nanocatalysts. Metal modified SiNWs hybrid nanomaterials[13] have attracted considerable attention, and also exhibit excellent catalytic activities in oxidation of hydrocarbon,[14,15] photo-degradation of organic pollutants[16] and electro-oxidation of methanol.[17,18]

Transition-metal catalyzed C–N bond formation is a powerful strategy for the synthesis of numerous compounds in the biological, pharmaceutical, and natural products.[19–21] The copper-mediated Ullmann condensation of aryl halides with amines[22,23] is the most frequently used pathway for coupling reactions. In the past decades, great progress in this field has been achieved with a variety of homogeneous catalysts,[24] such as Cu,[19,20,25,26] Pd[27,28] and Rh,[29,30] in the presence of different ligands. Among them, Cu[31] has attracted much more attention because it is as versatile as Pd and Rh, but much cheaper. However, these homogenous catalysts always suffer from serious limitations: (1) possible contamination of the products with metals; (2) difficult to separate the expensive catalysts from the products for reuse; (3) the use of toxic or expensive ancillary ligands; and (4) the loss of catalytic activity due to the metal aggregation and precipitation. These problems are of particular environmental and economic concern in large-scale synthesis, and limit their further applications.

As known, aryl iodides have been widely employed as substrates in heterogeneous coupling reactions. Based on the readily available and inexpensive nature, aryl chlorides and bromides should be regarded as important substrates in coupling reactions from a practical point of view.[32] But the obstacle restricting their uses as substrates is that they are more difficult to be activated than aryl iodides. To date, reports on the heterogeneous reactions using deactivated aryl chlorides and bromides are still quite scarce[33,34] Therefore, searching the efficient heterogeneous catalysts for this point is extremely important both fundamentally and technologically.

In light of the respective merits of metal nanoparticles[35] and SiNWs, Cu nanoparticles modified SiNWs (CuNPs@SiNWs) are expected to possess excellent catalytic properties on C–N coupling reaction. In this communication, we demonstrate the enhanced catalytic activity of CuNPs@SiNWs for the coupling reaction of benzene halides and aniline at 110 °C, without any ligands or additives. Specifically, besides the high catalytic ability on coupling iodobenzene and aniline (yield about 89%), CuNPs@SiNWs also show good catalytic ability on the coupling reaction for deactivated aryl bromides (yield about 54%) and inert chlorobenzene (yield about 11%).

In our experiments, SiNWs were fabricated by an oxide-assisted growth method[7] and the oxide layer of the as-grown SiNWs was removed by 2% HF. CuNPs@SiNWs were successfully prepared by immersing the SiNWs into $CuSO_4$ aqueous solution. The detailed synthesis process was shown in the supporting information (ESI†). The followed coupling reaction of aryl halides and aniline using CuNPs@SiNWs as the catalyst and dimethyl sulfoxide (DMSO) as the solvent, was performed under N_2 protection at 110 °C for 18 h. The progress of the reaction was monitored by thin-layer chromatography. For the detailed catalytic experiments also see the supporting information (ESI†).

The X-ray diffraction (XRD) patterns of SiNWs (black curve) and CuNPs@SiNWs (red curve) are shown in Fig. 1. For both

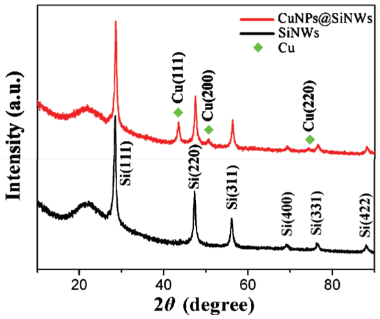

Fig. 1 The XRD patterns of SiNWs and CuNPs@SiNWs.

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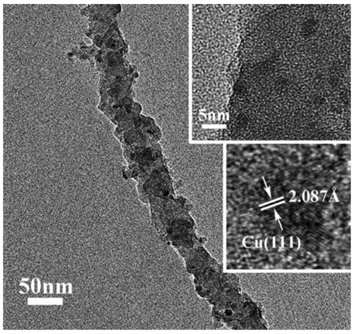


Fig. 2 TEM and HRTEM images of CuNPs@SiNWs.

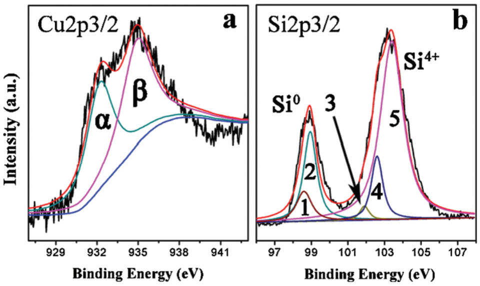


Fig. 3 XPS spectra for (a) Cu and (b) Si in CuNPs@SiNWs.

curves, the broad peaks arising from 22° are attributed to the thin amorphous SiO_2 layer on the surface of SiNWs. The diffraction peaks can be indexed to a cubic phase with lattice constant $a = 5.419$ Å for SiNWs and a cubic phase with lattice constant $a = 3.615$ Å for CuNPs, respectively. The peaks at 43.5, 50.5 and 74.2° belonged to Cu (111), Cu (200) and Cu (220), respectively. No signals of other elements are observed in the energy dispersive X-ray (EDX) spectroscopy of CuNPs@SiNWs (Fig. S1, inset†), except Si, Cu and O. The peak intensity of Si is much higher than that of Cu, and the atomic ratio of Si to Cu is close to 7 : 1. The transmission electron microscopy (TEM) images (Fig. 2) of CuNPs@SiNWs clearly show that the SiNWs (50 nm in diameter) take the shape of wire after the modification by CuNPs, and the CuNPs are randomly attached to the surface of the SiNWs with sizes ranging from 10 to 30 nm. The high-resolution TEM (HRTEM) image (inset in Fig. 2) reveals the single-crystalline nature of the CuNPs on the SiNWs, and well-resolved fringe spacing of 0.208 nm corresponds to the Cu (111) interplanar spacing.

X-Ray photoelectron spectroscopy (XPS) was carried out to check the surface composition and chemical environment of the obtained CuNPs@SiNWs, and the binding energies obtained in the XPS analysis were standardized for specimen charging by calibrating the C1s peak to 284.6 eV. As shown in Fig. 3a, the peaks at about 933.6 eV (Fig. 3a) are attributed to Cu 2p3/2, which can be deconvoluted typically into two component peaks (marked as α and β) with binding energies at about 932.3 eV (Cu^0 or Cu^+) and 934.7 eV (Cu^{2+}), respectively. This indicates that there is a copper oxides mixture on the surface of CuNPs. In Fig. 3b, the peaks at 98.8 eV and 103.5 eV are attributed to Si^0 and Si^{4+} of Si 2p3/2, respectively. As shown, five Gaussians were resolved after a curve-fitting procedure. And notably, the obvious peak 3 at about 101.9 eV may be ascribed to Si binding with Cu.[36] All of the above characterization results are consistent with each other and adequately prove that the SiNWs have been successfully modified with CuNPs, and there is copper oxides mixture on the surface of CuNPs.

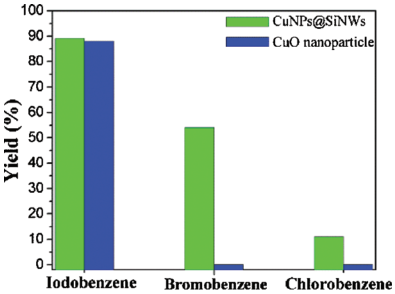
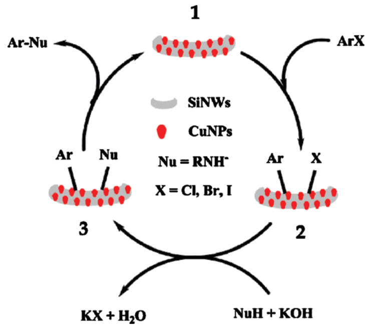


Fig. 4 Catalytic activity of CuNPs@SiNWs for the coupling reaction of aryl halides with aniline. The comparison is for CuO nanoparticle catalyst.[37]

Here, we employ the coupling reaction of benzene halides (iodobenzene, bromobenzene and chlorobenzene) and aniline as the standard substrates to evaluate the catalytic properties of CuNPs@SiNWs, and the catalytic data are summarized in Table S1.† We found that the iodobenzene exhibited greater reactivity (diphenylamine yield up to 89%) compared to bromobenzene and chlorobenzene. When iodobenzene was replaced by bromo- and chlorobenzene, the reactions were moderately effective providing diphenylamine in 54% and 11% yield, respectively. The parallel experiment using HF (2%) treated SiNWs as catalyst (24 h, no reaction) indicates that the CuNPs are necessary for the catalytic reaction. Furthermore, we use a plot (Fig. 4) to compare the yields of diphenylamine with different aryl halides as substrates using CuNPs@SiNWs and CuO nanoparticles as catalysts, respectively. The catalytic data of CuO nanoparticles were taken from a previous report by Jammi *et al.* They described the CuO nanoparticles as commercially available (Aldrich: particle size 33 nm and surface area 29 $m^2\ g^{-1}$).[37] It is worth noting that in the case of CuO nanoparticles, the coupling reactions between bromo-/chlorobenzene and aniline are difficult with yields about 0%. While in the presence of CuNPs@SiNWs, the reaction easily happens with diphenylamine yields up to 54% (for bromobenzene) and 11% (for chlorobenzene), respectively. The catalytic experimental results demonstrate that the CuNPs@SiNWs could significantly improve the activity of deactivated aryl bromides and chlorides.

Here, we ascribe the excellent catalytic property of CuNPs@SiNWs to the following aspects. (1) The unique ability of H-SiNWs in anchoring metal NPs firmly and in a dispersed fashion on SiNWs surfaces. Due to the reaction between Si–H and $CuSO_4$ aqueous solution, CuNPs can be well stabilized or anchored on SiNWs, and isolated or separated from each other, which are the key factors for the enhanced catalytic activity. (2) For catalysis by heterogeneous catalyst is a surface phenomenon, the high surface area of CuNPs@SiNWs can increase the chance for reactant to react on the catalytic active sites. (3) The mixture of Cu oxides on CuNPs surface,[38] which is confirmed by XPS characterization above. As the coupling reaction is catalyzed by Cu, especially Cu^+ and Cu^{2+} species, the different oxidation



Scheme 1 Possible reaction mechanism for coupling reaction between aryl halide and aniline catalyzed by CuNPs@SiNWs.

states of the Cu atoms and the crystallographic planes of Cu/Cu_2O/CuO exposed on the surface would provide more catalytic active sites than CuO nanoparticle. (4) The unique Si binding with Cu should respond for the enhanced catalytic ability of CuNPs@SiNWs.

According to the literature,[37] the reaction may occur *via* oxidative addition followed by reductive elimination. The possible catalytic process is shown in Scheme 1 and outlined as follows: stabilization of CuNPs@SiNWs by DMSO may lead to an active cluster intermediate **1**, which may undergo oxidative addition with aryl halide to give intermediate **2** (positive charge developed may be shared among the CuNPs@SiNWs). Intermediate **2** may then undergo reaction with nucleophile to give intermediate **3**, which can complete the catalytic cycle by reductive elimination of the C-heteroatom cross-coupled product.

In conclusion, CuNPs@SiNWs have been developed for use as highly active and practical heterogeneous catalysts for the coupling reaction of benzene halides and aniline. Significantly, the deactivated aryl bromides and inert chlorobenzene were successfully coupled under mild conditions with diphenylamine yields about 54% and 11%, respectively. The advantages of SiNWs as substrate support are ascribed to stabilize and isolate CuNPs from each other, which can extremely enhance the catalytic activity of CuNPs@SiNWs. Our findings not only show that the metal modified SiNWs are superior heterogeneous catalysts for the coupling reaction, but also that SiNWs are powerful substrate supports for nanocatalysts, which may provide a new approach to high-efficiency catalyst design for applications in energy technology.

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