CuNi Nanoparticles Assembled on Graphene for Catalytic Methanolyis of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds

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Supporting Information

ABSTRACT: We report a solution-phase synthesis of 16 nm CuNi nanoparticles (NPs) with the Cu/ Ni composition control. These NPs are assembled on graphene (G) and show Cu/Ni composition-dependent catalysis for methanolyis of ammonia borane (AB) and hydrogenation of aromatic nitro (nitrile) compounds to primary amines in methanol at room temperature. Among five different CuNi NPs studied, the G-CuNi64 NPs are the best catalyst for both AB methanolyis (turnover frequency (TOF) of 49.1 mol H2 molCuNi⁻¹ min⁻¹ and an activation energy (Ea) of 24.4 kJ/mol) and hydrogenation reactions (conversion yield of >97%). The G-CuNi compound represents a unique noble-metal-free catalyst for hydrogenation reactions in a green environment without using pure hydrogen.

Advances in nanoparticle (NP) synthesis methodology have made it possible to develop many different types of NPs with dimension and composition controls at near-atomic-level precision. Such controls allow the rational tuning and optimization of physical and chemical properties of NPs for optical, magnetic, biomedical, and catalytic applications.1–6 Recently, monodisperse NPs have attracted even more attention as catalysts for energy conversions and other important chemical reactions.7–13 The precise dimension controls achieved from the syntheses render these NPs ideal candidates for studying both electronic and geometric effects on a specific reaction and for identifying catalytic active sites on the NP surface to optimize catalytic activity and selectivity.14–17 The monodisperse NPs can also be assembled on a graphene (G) surface, and NP–G interactions, as well as the strong adsorption power of the G surface, can be exploited to promote the catalytic reaction and to enrich the reactants around the NP proximity, further enhancing the NP catalysis.18–22 Here, we report the synthesis of CuNi alloy NPs, their assembly on G, and their catalysis for tandem methanolyis of ammonia borane (BH3·NH3, denoted hereafter as AB) and hydrogenation of nitro (R-NO2) or nitrile (R-CN) compounds to primary amines. AB has been explored extensively as a new hydrogen storage material (hydrogen content of 19.6 wt %) for easy hydrogen transportation.23–26 Hydrogen is released via AB hydrolysis or methanolyis, both of which can be catalyzed by a nanostructured catalyst of noble metal13,32–34 or first-row transition metal Ni (or Cu) under ambient conditions.35–38 Recently, this reaction was found to show good reducing power to convert R-NO2 to R-NH2 or R-CN to R-CH2NH2 in the presence of a noble metal catalyst, especially MPd alloy NPs (M = Ni, Co, Fe) deposited on G.24,59–62 Opening up a new approach to the production of primary amines without using pure hydrogen at elevated temperature and under high-pressure conditions.33–47 Working to develop a noble-metal-free catalyst for the same tandem reaction, we found the CuNi alloy NPs deposited on G, denoted as G-CuNi, showed Cu/Ni composition-dependent catalysis in methanol at room temperature. Among the five different types of CuNi NPs studied, the G-Cu36Ni64 showed the best catalytic activity and recyclability toward the methanolyis of AB with superior initial turnover frequency (TOF) and lowest Arrhenius activation energy. In the same reaction environment, the G-CuNi64 also served as an efficient catalyst to catalyze the hydrogenation of R-NO2 or R-CN into the corresponding primary amines with the conversion yield >97%.

Monodisperse CuNi NPs were prepared by the co-reduction of nickel(II) acetylacetonate (Ni(acac)2) and copper(II) acetylacetonate (Cu(acac)2) with borane-t-butylamine (BBA) in oleylamine (OAm) and oleic acid (OA). BBA served as the reducing agent, while OAm functioned as both a solvent and a surfactant. OA was added as a cosurfactant for the CuNi NP stabilization. The metal contents of the CuNi NPs were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) at various reaction stages.31,32 Hydrogen is released via AB methanolyis, which is determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) at various reaction stages.31,32

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Cu$_{24}$Ni$_{76}$ NPs are 15.8 and 15.0 nm, respectively. Such a narrow Cu$_{36}$Ni$_{64}$ NPs was confirmed by the X-ray diffraction (XRD) pattern (see Figure S1 in the Supporting Information). The alloy structure was further characterized by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS). Figure 1C shows the HAADF-STEM image of the Cu$_{36}$Ni$_{64}$ NPs and the STEM-EELS elemental mapping of a selected NP to show Ni (green) and Cu (red) distribution within the NP. (D) TEM image of the BA-treated G-Cu$_{36}$Ni$_{64}$ NPs.

Figure 1. (A) TEM image of the as-prepared Cu$_{36}$Ni$_{64}$ NPs. (B) HRTEM image of a single Cu$_{36}$Ni$_{64}$ NP. (C) HAADF-STEM image of the Cu$_{36}$Ni$_{64}$ NPs (scale bar: 10 nm) and STEM-EELS elemental mapping of a selected NP to show Ni (green) and Cu (red) distribution within the NP. (D) TEM image of the BA-treated G-Cu$_{36}$Ni$_{64}$ NPs.

Cu$_{36}$Ni$_{64}$ NPs were obtained by reducing 0.26 mmol of Ni(acac)$_2$ and 0.14 mmol of Cu(acac)$_2$. Figure 1A is a representative TEM image of the as-synthesized Cu$_{36}$Ni$_{64}$ NPs. The NPs have an average diameter of 16.0 ± 1.0 nm. Figure 1B shows a high-resolution TEM (HRTEM) image of a single Cu$_{36}$Ni$_{64}$ NP, exhibiting the interfringe distance of 2.05 Å, which is smaller than the Cu(111) spacing (2.088 Å) but larger than the Ni(111) spacing (2.034 Å). The face-centered cubic (fcc) type solid-solution structure of the Cu$_{36}$Ni$_{64}$ NPs was confirmed by the STEM-EELS line scan across one 16 nm Cu$_{36}$Ni$_{64}$ NP, all of which indicate that Cu and Ni distribute evenly in the NP.

The Cu/Ni compositions of the final CuNi NPs were controlled by the initial molar ratios of Cu and Ni salts. Cu$_{36}$Ni$_{64}$, Cu$_{38}$Ni$_{62}$, Cu$_{39}$Ni$_{60}$, Cu$_{36}$Ni$_{64}$, and Cu$_{26}$Ni$_{78}$ NPs were obtained from the Cu/Ni molar ratios of 3:1, 2:1, 1:1, 1:2, and 1:3, respectively. Figure S3 in the Supporting Information shows more representative TEM images of the CuNi NPs with different compositions. They are all in the 15–16 nm size range; for example, the average sizes of the Cu$_{37}$Ni$_{63}$ and Cu$_{25}$Ni$_{75}$ NPs are 15.8 and 15.0 nm, respectively. Such a narrow size variation among different CuNi NPs allows us to study composition-dependent activities of the NPs.

To test the NPs as the catalyst for the methanolysis of AB, we first assembled the preweighed CuNi NPs on 18 mg G through the sonication of the ethanol dispersion of G and the hexane dispersion of NPs to produce G-CuNi (see the Supporting Information). The CuNi NPs were then activated by immersing the NPs in t-butylamine (BA). The mixture in the flask was prepurged with N$_2$ sealed with septa rubber and stirred for 3 days. The solid product was separated by centrifugation and washed with ethanol. This process could also be applied to prepare C-NPs and SiO$_2$-NPs. Infrared (IR) spectroscopy was used to characterize the OA/MeOH removal. To avoid the G- or C-hydrocarbon background interference with the spectra, the SiO$_2$–CuNi was specifically selected for the characterization purpose. IR spectra of the SiO$_2$–Cu$_{36}$Ni$_{64}$ NPs (Figure S4 in the Supporting Information) show that the pretreated NP sample has the characteristic −C=C (1658 cm$^{-1}$), −C−H (3010 cm$^{-1}$) bond signals, as well as the NH$_2$ symmetric (3372 cm$^{-1}$) and asymmetric vibrations (3296 cm$^{-1}$), while the BA-treated sample shows no such peaks. The TEM image analysis on the BA-treated G-Cu$_{36}$Ni$_{64}$ further suggests that this BA-treatment procedure did not affect the size and morphology of the NPs (Figure 1D). The NPs remain 16 ± 1 nm in size and are still well-dispersed on the G surface.

Figure 2. (A) Plot of time versus volume of H$_2$ generated from AB methanolysis catalyzed by G-CuNi with different Cu/Ni compositions (CuNPs = 9.8 mM, [AB] = 300 mM, T = 298 K). (B) Stoichiometric hydrogen evolution from AB methanolysis catalyzed by G-Cu$_{36}$Ni$_{64}$ at different catalyst concentrations ([AB] = 300 mM, T = 298 K). (Inset shows logarithmic plots of reaction rate vs [AB]). (C) Stoichiometric hydrogen evolution at different AB concentrations ([CuNi] = 9.8 mM, T = 298 K). (Inset shows logarithmic plots of rate vs [AB]). (D) Plot of time versus volume of hydrogen generated at different temperatures ([AB] = 300 mM, [CuNi] = 9.8 mM). (Inset shows an Arrhenius plot of ln k vs (1000/T).)

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CuNi composition-dependent methanolysis of AB was studied in methanol at room temperature with catalyst and AB concentrations being kept constant, as reported in the AB methanolysis$^{50–52}$ for easy comparisons between the new CuNi and other NP systems. Figure 2A shows the methanolysis data from G-CuNi with different Cu/Ni compositions from which we can see that G-Cu$_{36}$Ni$_{64}$ is the most active catalyst in the current test condition. As a control, we also prepared G-Cu and G-Ni NPs for the methanolysis of AB. As shown in Figure S5 in the Supporting Information, the Ni catalyst is much more active than either the Cu or Ni NPs. This catalytic
enhancement should result from the alloy effect that is often observed to show a certain degree of enhancement in catalysis, compared to the elemental counterparts. The calculated d-band centers of Cu and Ni are −2.67 eV and −1.29 eV, respectively. Once the CuNi alloy is formed, the d-band center position of the alloy should shift to a location between Cu and Ni. This d-band shift may further optimize the bonding between bimetallic surface and reacting species for catalysis. Using the reported solution-phase synthesis, we are able to control the CuNi alloy compositions and engineer the electronic structure of the alloy to optimize the NP catalysis.

In addition, we also tested the support effect. CuNi NPs without any support are less active than the G-CuNi NPs but show the same Cu/Ni composition-dependent activity trend as the G-CuNi NPs with the Cu36Ni64 NPs being the most active (Figure S6 in the Supporting Information). Similar tests showed that C=Cu36Ni64 NPs and SiO2−Cu36Ni64 NPs were less active than the G-Cu36Ni64 NPs (Figure S7 in the Supporting Information), demonstrating the effect of G on promoting the NP catalysis.

The reaction kinetics of the G-Cu36Ni64 catalyst was further studied. In one group of tests, AB concentration was kept at 300 mM but the CuNi NP concentrations were varied to be 3.8–9.8 mM. The methanolysis kinetic plots are given in Figure 2B and the corresponding inset. In another group of tests, the NP loading was fixed at 9.8 mM but the AB concentrations were varied from 200 mM to 350 mM (see Figure 2C and inset). We can see that, in these two groups of tests, H2 is fast-released within minutes and the H2 volume released from the reaction is linearly related to the concentration of AB or Cu36Ni64. The reaction is first-order, with respect to the NP concentration (Figure 2B) and half-order with respect to the AB concentration (Figure 2C), which is different from the zero-order dependence to AB on Pd, or the non-BA-treated G-Cu36Ni64 (blue) in successive reaction cycles ([Cu36Ni64] = 9.8 mM, [AB] = 300 mM, T = 298 K).

Figure 3. Initial catalytic activity change of the BA-treated (black) and non-BA-treated G-Cu36Ni64 (blue) in successive reaction cycles ([Cu36Ni64] = 9.8 mM, [AB] = 300 mM, T = 298 K).

The stability of the G-Cu36Ni64 was tested by the repeated use of the same catalyst for the new run of methanolysis reaction. After every 30 min when H2 generation was completed, another equivalent of AB (3 mmol) was added to the reaction system and the results were recorded, as shown in Figure 3. The catalyst shows almost no activity change in the first four runs. After the 10th cycle, the catalyst still remains the alloy structure (Figure S9 in the Supporting Information) and the activity remains at 80% of the initial catalytic activity. We attribute this degradation to the CuNi NP change (see Table S1 and Figure S8) and to the weak G-NP interaction, which competes with the NH1–NP interaction during the reaction. This is further supported by the catalysis of the as-synthesized, non-BA-treated G-Cu36Ni64 NPs, which show even poorer stability (Figure 3 and Figure S10 in the Supporting Information), despite the fact that they are as active as the BA-treated ones initially. This indicates that the OAm/OA coating does not reduce the NP catalysis, but it does make the NPs less stable on the G surface. We expect that the stability of these CuNi NPs should be further improved once the G-NP interactions are enhanced by introducing, for example, N-doping in the G network.

The excellent performance of the G-Cu36Ni64 for the AB methanolysis motivated us to use the catalyst and the reaction to reduce R-NO2/R-CN into primary amines in methanol. We should note that the use of methanol as the solvent in this work is different from what has been published, where methanol + water was used as the mixed solvent for the hydrogenation reaction. Our initial tests, shown in Table S6 in the Supporting Information, indicated that the presence of water in the reaction system degraded the NP catalytic activity. In the current hydrogenation reaction test in methanol, R-NO2 or R-CN/AB was set at 1:3 mol/mol at room temperature and the reaction was sealed by a balloon to prevent hydrogen from escaping from the reaction system. Thin layer chromatography (TLC) was used to monitor the reaction process and gas chromatography—mass spectrometry (GC-MS) was used to quantify the reaction mixture changes. Table 1 summarizes the results obtained from the G-Cu36Ni64 catalyzed hydrogenation of a few representative R-NO2/R-CN compounds. It is noteworthy that the mono-NO2 and CN compounds are hydrogenated into the corresponding amines with the reaction conversion yield reaching >97% within 30 min. Hydrogenation of di-NO2 to di-NH1 required 120 min for complete conversion. When CN and NO2 coexist, NO2 is selectively reduced to NH2 while CN is intact. This selective reduction is consistent with that reported on the MPd catalyst, indicating
that the π-donor conjuration raises the CN activation energy barrier, making it impossible to reduce CN under the current reaction conditions.\textsuperscript{24} The new G-Cu\textsubscript{36}Ni\textsubscript{64} catalyst can be compared favorably to MPd or other catalysts reported for the same reaction, as shown in Table S7 in the Supporting Information. After the fifth consecutive reaction cycle, the catalyst still showed a conversion yield of >97% in the same reaction time (see Figure S11 in the Supporting Information).

We further tested the reaction in an open (to air) system or under a gentle flow of N\textsubscript{2}. In both cases, the reaction led to a low conversion yield (<20%). Moreover, if only 1 equiv of AB was present in the reaction mixture, the conversion yield decreased to 34%. These indicate that H\textsubscript{2} generated in situ plays an important role in the hydrogenation reaction and excess of H\textsubscript{2} is needed to complete the conversion under the current reaction conditions. The reaction without the presence of the catalyst showed no sign of the conversion.

In summary, 16 nm CuNi NPs with controlled size, shape and composition were synthesized and assembled on G. The NPs are activated by washing with t-butylamine and ethanol at room temperature. The G-CuNi NPs show the Cu/NI composition-dependent AB methanolysis. Among different G-CuNi NPs studied in this work, the G-Cu\textsubscript{36}Ni\textsubscript{64} NPs represent the most active catalyst, with TOF = 49.1 mol H\textsubscript{2} mol CuNi\textsuperscript{-1} min\textsuperscript{-1} and \( E_\text{a} \) = 24.4 kJ/mol. The catalyst shows the desired durability, retaining 80% of its initial activity after the 10th cycle. The G-Cu\textsubscript{36}Ni\textsubscript{64} catalyst is also active for Ar-NO\textsubscript{2} (or Ar−CN) hydrogenation to Ar-NH\textsubscript{2} (or Ar−CH\textsubscript{2}NH\textsubscript{2}) in the AB methanolysis condition with excellent conversion yield (>97%). Therefore, the G-Cu\textsubscript{36}Ni\textsubscript{64} NPs act as a dual catalyst for both AB methanolysis to H\textsubscript{2} and Ar-NO\textsubscript{2} (or Ar−CN) hydrogenation to primary amines. The G-CuNi represents a unique noble-metal-free catalyst for hydrogenation reactions in a green environment without using the pure hydrogen. Studies of its catalysis on other important chemical reactions involving carbon−carbon coupling are underway.


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