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Effect of water in fabricating copper nanoparticles onto reduced graphene oxide nanosheets: application in catalytic Ullmann-coupling reactions

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Abstract

Copper nanoparticles fabricated onto reduced graphene oxide (Cu NPs/rGO) were successfully synthesized *via* a one-pot dimethylformamide (DMF) reduction approach with an addition of the nominal water. This small amount of water can significantly decrease the degree of GO reduction by DMF. As a result, the remaining oxygen-containing functionality on rGO can still interact with the copper cation precursor leading to the high Cu content fabricated onto the support material, which was evidenced by X-ray photoelectron spectroscopy (XPS). Moreover, small particle sizes and high dispersion of Cu NPs on rGO were confirmed by scanning transmission electron microscopy (STEM). In addition, our Cu NPs/rGO was competent to catalyze the Ullmann-coupling reaction (i.e., arylation of 3,5-dimethylphenol with 86% yield and turnover number of 2,642).

Keywords: Copper nanoparticles fabricated onto reduced graphene oxide, Effect of water, Ullmann-coupling reaction

1. Introduction

Copper (Cu) is an abundant and low-cost transition metal that also serves as an active site for various catalytic reactions. Among an extensive variety of chemical syntheses, Ullmann condensation for arylation of phenols is one of the attractive methods for organic transformations because of a wide range of substrate applicability in polymers, pharmaceutical molecules and life science industries.^{1.4} Further extending the advantages of Cu, copper cations can be fashioned into nanoparticles, which have unique properties and large surface areas. Nanoparticles typically exhibit high catalytic activity. However, they can easily aggregate into larger agglomerates and rapidly deactivate, especially under harsh reaction conditions.⁵ Recently, a wealth of interdependent research has focused on stabilizing nanoparticles (NPs) with functionalized polymers,⁶⁻⁹ dendrimers,¹⁰⁻¹³ inorganic solids (silica, alumina, zeolite, *etc.*),¹⁴⁻²⁰ redox metal (Au)²¹ and carbonaceous materials.²²⁻²⁶

Graphene oxide (GO) and graphene derivatives are a current fascinating class of carbon because of their remarkable and unique chemical, physical and mechanical properties e.g. high mechanical strength, fast 2D electron-transfer kinetics, promising chemical and thermal stability and large specific surface areas, which demonstrate promising use as supports for heterogonous catalytic systems.²⁷⁻³² Furthermore, GO and GO composites demonstrate high adsorption capacities with metal ions and have also found use in applications for metal removal owing to a number of surface functionalized groups and high specific surface areas.³³⁻³⁶ Hence, GOs are considered to easily interact with metals, presumably due to the presence of oxygen functionalities including hydroxyl and epoxide groups, and therefore, should allow for reasonable fabrication with metal NPs (M NPs). The syntheses of hybrid materials between M NPs and graphene-based materials are potentially applicable in numerous fields including energy storage,³⁷ sensors,³⁸⁻⁴² medical therapy,43, 44 and particularly in catalysis (electrocatalysis⁴⁵ and chemical catalysis⁴⁶⁻⁵⁰). Hybrid nanocatalysts are likely to offer combined properties of both homogeneous and heterogeneous catalytic systems-exhibiting high activity and selectivity of homogeneous catalysts, whilst being reusable like heterogeneous catalysts.²⁸

Typically, M NPs deposited on graphene sheets are synthesized *via* electrodeposition⁴⁰ or chemical reduction processes in the presence of a reducing agent.^{5, 41, 51} *N,N*-Dimethylformamide (DMF) is well-known for exhibiting high chemical and thermal stability and demonstrates reducing properties for the preparation of M NPs⁵²⁻⁵⁵ and M NPs/reduced GO (rGO).⁵⁶ In the approach herein, DMF can be substituted for strong reducing agents, which are hazardous reductants (*i.e.* hydrazine, NaBH4). Additionally, DMF enhances the stability of M NPs, which prevents the graphene nanosheets from aggregating and restacking as a result of π - π interactions.⁵⁶ Challenges associated with improved catalytic activity and reducing catalyst materials can be designed with high dispersion, precise particle size control and improved recyclability.

Nonetheless, oxygen-derived GO functionalities can be directly reduced to rGO during dispersion in DMF,⁵⁷⁻⁵⁹ which may result in negatively-charged materials having low interactions with copper cations, which also negatively impacts Cu NP deposition onto rGO. Previous reports have attempted to enhance the interaction upon the addition of a base to deprotonate, to yield GOs having increased numbers of negatively-charged oxygen sites.^{5, 60} Similarly, efforts have been made to decrease the dosage of reducing agents by dividing the reduction processes into two steps to protect full GO reduction.⁶¹

Herein, we introduced a new approach to decrease the reducing power of DMF upon dispersion of GO during Cu NPs/rGO preparation by addition of a nominal amount of water (Scheme 1). This led to a significant enhancement of the Cu concentration on rGO. The increased number of Cu active sites retained on the support material resulted in enhanced catalytic activity and product yield. The correlation of Cu concentration on the rGO and catalytic activity toward the Ullmann-coupling reaction was also examined.



Scheme 1. Synthesis of copper nanoparticles fabricated onto reduced graphene oxide (Cu NPs/rGO) using a CuCl₂ precursor in *N*,*N*-Dimethylformamide (DMF)/H₂O (50/4 v/v).

2. Experimental

2.1 Materials and methods

All commercially available chemicals and solvents were purchased from Acros Organics, Wako Chemical Co., TCI and Sigma Aldrich, and used without further purification unless otherwise stated. For Cu NPs/rGO syntheses and catalytic activity studies, DMF of high purity grade was purchased from Wako Chemical Co. Catalytic activity was investigated by GC coupled to a flame ionization detector (FID) using a 0.22 mm \times 25 m capillary column (BP-5). GC-FID response factors for the products were compared with n-tridecane as an internal standard. For STEM (JEOL JEM-ARM200F), the Cu NPs/rGO was dispersed in EtOH and dropped onto a carbon-coated Mo grid, with imaging performed at an acceleration voltage of 200 kV. IR measurements were recorded using a Thermo Nicolet 6700 FT-IR spectrometer. ICP-AES data was determined using a Shimadzu ICPS-8100 spectrometer. XPS was recorded using a ULVAC-PHI PHI5000 VersaProbe instrument with Al K α radiation.

2.2 Preparation of GO

GO was synthesized according to a modified Hammers method,⁶², in which graphite powder was chemically oxidized by KMnO₄ in the presence of NaNO₃ and H₂SO₄. In brief, graphite powder (0.8 g) and NaNO₃ (0.4 g) were suspended in conc. H₂SO₄ (25 mL) at 0 °C. After being stirred in an ice bath for 20 min, KMnO₄ (2.45 g) was added to the reaction. The reaction was allowed to stir for 6 h prior to the addition of $KMnO_4$ (2.66 g). Subsequently, another portion of H_2SO_4 (10 mL) was added, and the reaction was further stirred for 18 h. The crude product was poured into the ice bath in the presence of H₂O₂ (30%, 5 mL) and continuously stirred for 1 h. The GO product was centrifuged at 4,000 rpm for 10 min and washed with de-ionized (DI) water, a K₂HPO₄/KH₂PO₄ buffer solution (pH ~7), and again with DI water (×2). The product was dried under vacuum for at least 6 h before further analysis was conducted.

2.3 Preparation of Cu NPs

DMF (50 mL) was pre-heated at 140 °C for 5 min before the addition of CuCl₂·2H₂O (0.1 M, 0.5 mL). Thereafter, the solution was vigorously stirred at 140 °C, 1,500 rpm for 24 h. The blue CuCl₂ solution turned yellow, which is indicative of Cu NP formation.

2.4 Synthesis of Cu NPs/rGO

In a typical procedure, GO (40 mg) was dispersed in DMF (25 mL) by sonication for 3 h. Prior addition of a metal precursor (CuCl₂ or Cu NPs), and additional DMF (25 mL) were added to the mixture solution and pre-heated at 140 °C for 5 min. The solution was vigorously stirred at 1,500 rpm for 24 h. Thereafter, the solvent was removed *in vacuo* and the product was washed with MeOH (×3).

To enhance Cu NP deposition onto rGO, the solvent mixture comprising DMF and a varying nominal amount of water was employed to study the effect of water in the synthetic process. First, GO (40 mg) was dispersed in DMF (25 mL) by sonication for 1 h prior to the addition of a nominal amount of water (0.5–8 mL). The solution was then sonicated for an additional 2 h. CuCl₂ (0.1 M, 0.5 mL) was then added to the pre-heated GO solution (5 min for pre-heating) and stirred at 1,500 rpm for 24 h. The solvent was removed *in vacuo* and the product was washed with MeOH (×3).

The copper loading on rGO was determined by ICP-AES. The Cu NPs/rGO samples were dispersed in a 3 M HNO₃ solution to extract the copper from the support material prior to ICP-AES analysis. The ICP-AES data for each sample were compared with a standard copper solution to obtain correct and reliable results.

2.5 Catalytic activity studies toward the Ullmann-coupling reaction

In a typical reaction, Cu NPs/rGO (1 mg), Cs₂CO₃ (2 mmol), iodobenzene (1.5 mmol) and 3,5-dimethylphenol (1 mmol) were added into a pressure tube and dispersed in DMF (1 mL) by sonication for 10 min. The mixture solution was deoxygenated under Ar for a 2-3 minutes and then stirred at 110, 120 or 130 °C for 24 h. For quantitative analysis, the products were extracted with ethyl acetate, hexane and n-tridecane as an internal standard prior to GC analysis. TON values were calculated from the number of moles of the obtained product per mole of copper active sites on the catalyst.

3. Results and Discussion

3.1 Fabrication of Cu NPs onto rGO

Initially, Cu NPs deposited on rGO were chemically synthesized using a one-pot reduction approach with DMF as a pure solvent. DMF is demonstrated to play three important functions including serving as solvent, a reducing agent and a stabilizer.53, 55, 56 To prepare the efficient fabrication of Cu NPs onto rGO, the influence of copper precursor types (CuCl2 and Cu NPs) on the Cu deposition onto rGO was examined. From the Cu concentration, analyzed by X-ray fluorescence (XRF), the use of CuCl₂ as a Cu precursor provided a significant enhancement of Cu on the rGO, when compared with the Cu NPs precursor (Fig. S2). However, from a naked-eye observation, the solution color after washing the Cu NPs/rGO product still retained an intense yellow color indicating a low Cu content fabricated onto the rGO leading to a yellow solution of free Cu (Cu NPs). Particularly in the case of the Cu NPs precursor, a more intense yellow color was observed after washing the product with MeOH, which is in agreement with XRF and ICP (vide infra) results. Thus, CuCl₂ was appropriate as a Cu precursor for the preparation of Cu NPs/rGO.

From this hypothesis, the higher number of active sites (Cu NPs), on the support materials are expected to enhance the catalytic activity and reduce catalyst consumption. The aforementioned design strategy led to a new idea to improve the fabrication method. The architecture, shape, size, properties and functionalization of NPs is influenced by several synthetic conditions including the starting materials, reaction time, temperature and solvent. Additionally, varying the ratio of a mixture of solvents (i.e. DMF/H₂O) influenced the nanostructure,⁶² however, there are no reports detailing the fabrication of active NPs onto support materials *via* this method. Herein, the influence of the solvent mixture ratio, between DMF and H₂O, on the synthesis of such hybrid materials was investigated. The rationale was that the addition of water may assist facile exfoliation of the graphite oxide to a monolayer of

GO,⁵⁹ and in addition, influence particle dispersion by improving the GO dispersion in the solvent. Markedly, it was demonstrated that oxygen functionality on GO can be directly reduced by DMF, especially, under heating.⁵⁷⁻⁵⁹ This could lead to an inefficient fabricating Cu NPs onto rGO since oxygen-containing functional groups on GO play an important role to absorb the transition metal *via* non-covalent interaction.^{63, 64} Therefore, we hypothesized that using a mixture of solvent (i.e. DMF/H₂O) may also help to decrease the degree of GO reduction by DMF, resulting in a higher copper content deposited on rGO.

From our experimental data, the presence of a nominal amount of water can improve the Cu deposition on the support materials. Both XRF and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) results revealed that the Cu concentration on the graphene sheets was obviously enhanced in the presence of a nominal amount of water in DMF. Notably, 28 ppm of Cu on rGO in pure DMF could be increased to 100 ppm in 4:50 (v/v) H_2O/DMF (Fig. 1).



Fig. 1 Quantitative analysis of Cu fabricated on rGO by inductively coupled plasma-atomic emission spectroscopy. The Cu NPs/rGO was prepared under various conditions (use of ■ Cu NPs precursor in DMF, ■ CuCl₂ precursor in DMF and ■ CuCl₂ precursor in 4:50 (v/v) H₂O/DMF.

3.2 Effect of water on the synthesis of hybrid CuNPs/rGO materials

To understand the key role of water, structural prediction of GO, after dispersion in pure DMF or H₂O/DMF (4:50 (v/v)), was elucidated from the x-ray photoelectron spectroscopy (XPS) binding energies. The findings determined that the GO oxygen functionalities (i.e. hydroxyl, epoxide, carbonyl and carboxyl) nearly disappeared in the case of pure DMF. Conversely, the H₂O/DMF (4:50 (v/v)) system exhibited enhanced oxygen functional groups despite a lesser starting GO content (Fig. 2). When comparing the carbon/oxygen (C/O) ratio, the GO dispersed in H₂O/DMF (4:50 (v/v)) exhibited a significantly lower ratio than pure DMF (GO C/O = 1.95 in H₂O/DMF; GO C/O = 5.37 in DMF) suggesting a higher degree of GO oxygen functional groups in H2O/DMF. The addition of a nominal amount of water appears to hinder DMF reduction leading to an enhanced concentration of oxygen functionalities. Increased negatively-charged oxygen functional groups are likely to interact more strongly with Cu(II) cations, therefore, enhancing the number of Cu NPs onto rGO. These findings are consistent with previous studies, which show that GO can be directly reduced to graphene sheets by DMF.⁵⁷⁻⁵⁹ The results also imply that the interaction between the Cu(II) ions and GO oxygen functional groups might be a key step to enhance the adhesion of Cu(II) onto GO prior to the DMF reduction process.



Fig. 2 X-ray photoelectron spectroscopy (XPS) survey spectrum in the C1s region of: (a) the GO starting material, (b) GO dispersed in DMF and (c) GO dispersed in 4:50 (v/v) H_2O/DMF . Intensity of XPS was reported in counts per second (CPS).

Although the role of water is important to protect the oxygen functionalities, an excessive amount inhibits the reduction of Cu(II) to Cu NPs, which can lead to aggregation of the Cu NPs to larger agglomerates or deactivation by oxidation. Varying the H₂O ratio in DMF supports this hypothesis (see XRF and ICP-AES results in supporting info). No H₂O, or a nominal amount, is observed to yield a yellow solution of Cu NPs after washing the Cu NPs/rGO product with MeOH, which thereafter, displays fluorescence properties (NP properties), while an excessive H₂O ratio yields a blue solution (Cu(II) ions).

3.3 Characterization of the hybrid Cu NPs/rGO materials

Above all, the addition of a suitable H_2O content in DMF (4:50 (v/v)) successfully improves the fabrication of the hybrid Cu NPs/rGO material *via* a one-pot DMF reduction approach. Next, Cu NPs/rGO was characterized by various techniques including IR, XPS and scanning transmission electron microscopy (STEM).

Fig. 3 shows the IR spectra of the starting GO and Cu NPs/rGO synthesized under 4:50 (v/v) H₂O/DMF. The GO revealed IR vibrations related to oxygen functionalities including C-O (1106 cm⁻¹), O-H (1231 cm⁻¹), C=O (1699 cm⁻¹) as well as sp²-hybridized C=C at ~1500–1600 cm⁻¹, which are consistent with previous works^{47, 60, 65-69}. Conversely, the intense oxygen vibrational bands at ~1,000 - 1,800 cm⁻¹ are weakened in Cu NPs/rGO indicating the incomplete reduction of GO (reduced graphene oxide form, rGO). Some oxygen functionalities retained their structures because of the inhibition for GO to be fabricated with Cu NPs.



Fig. 3 Comparison of the FT-IR spectra of GO (red line) and Cu NPs/rGO (black line).

The chemical structure of Cu NPs/rGO was further explored using XPS by identifying the signals from carbon, oxygen and copper. The narrow XPS spectra (Fig. 4) in the C1s region exhibited C-C/C=C, C-OH/C-O, C=O and (C=O)-OH peaks at 284.8, 286.0, 288.1 and 290.0 eV, respectively. Likewise, the binding energies in the O1s region at 532.3 and 532.6 eV, corresponding to oxygen-carbon bonds, were also observed. The findings may infer that the Cu NPs/rGO structure still comprises oxygen functionalities despite a lesser starting GO content. Additionally, data fitting of the Cu 2p_{3/2} and Cu 2p1/2 regions showed Cu⁰ and Cu(II) signals at 932.5 and 952.4 eV, and 934.1 and 954.0 eV, respectively. Nonetheless, both valence states can serve as efficient active species toward catalytic processes. Furthermore, Cu NPs/rGO prepared under 4:50 (v/v) H2O/DMF is observed to exhibit higher catalytic activity than Cu NPs/rGO prepared under pure DMF regardless of the presence of a lower Cu⁰/Cu(II) ratio (vide infra). Consideration should also be given to the possibility that the number of Cu active sites on the support material influences the catalysis more than the oxidation state of Cu.



Fig. 4 XPS survey spectra of Cu NPs/rGO (synthesized under 4:50 (v/v) H_2O/DMF) in the (a) C1s, (b) O1s and (c) Cu $2p_{1/2}$ and Cu $2p_{3/2}$ regions.



Fig. 5 Scanning transmission electron microscopy image of Cu NPs/rGO exhibiting a high degree of Cu NP dispersion on rGO. Inset: size distribution histogram indicating an average particle size of \sim 3–5 nm.

Additionally, STEM observations revealed a narrow and precise nano-sized distribution of Cu on rGO (~3–5 nm), Fig. 5. The small particle diameter implied a high specific surface area, which is a prerequisite for improved catalytic activity. The results also suggest that the Cu NPs are highly dispersed on rGO and are not aggregated to larger sizes, resulting in stabilizing of the Cu NPs with the support material (rGO) and DMF.

3.4 Catalytic activity of copper nanoparticles fabricated onto reduced graphene oxide (Cu NPs/rGO) toward the Ullmann-coupling reaction.

	+	HO	Cs ₂ CO ₃ (2 mmol), DMF	
			110–130 °C, 24 h	

iodobenzene 3,5-dimethylphenol (1.5 mmol) (1 mmol)

Table 1 Cu NPs/rGO-catalyzed arylation of phenol¹

Entry	Catalyst	Temp.(°C)	Yield ³ (%)	TON^4
1	-	130	1	-
2	GO	110	1	-
3	GO	130	1	-
4	Cu NPs	110	17	1662
5	Cu NPs	130	40	3866
6	Cu NPs/rGO ^a	110	49	237
7	Cu NPs/rGO ^a	120	57	353
8	Cu NPs/rGO ^a	130	89	549
9	Cu NPs/rGO ^{a,2}	130	86	2642
10	Cu NPs/rGO ^b	110	8	47
11	Cu NPs/rGO ^b	130	21	135
12	Cu NPs/rGO ^c	110	33	214
13	Cu NPs/rGO ^c	130	68	428

¹Reaction conditions: 3,5-dimethylphenol (1 mmol), iodobenzene (1.5 mmol), Cs_2CO_3 (2 mmol), catalysts: Cu NPs/rGO or GO (1 mg/1 mL DMF) or Cu NPs (0.1 mM, 1mL), reactions were performed under heating for 24 h.

 $^2 Reaction conditions: 3,5-dimethylphenol (5 mmol), iodobenzene (7.5 mmol), Cs₂CO₃ (10 mmol), catalysts: Cu NPs/rGO (1 mg/1 mL DMF), reactions were performed under heating for 24 h.$

³Quantitative product analysis by GC.

⁴TON = turnover number.

 $^a\mathrm{Cu}$ NPs were fabricated onto rGO under 4:50 (v/v) H_2O/DMF utilizing the CuCl_2 precursor.

^bCu NPs were fabricated onto rGO under DMF utilizing the Cu NPs precursor.

^eCu NPs were fabricated onto rGO under DMF utilizing the CuCl₂ precursor.

In addition to the observed high dispersion, precise narrow size distribution and high stability, the number of Cu active sites (Cu NPs) fabricated onto the support material was also important to improve catalytic activity. All of the Cu NPs/rGO materials prepared in 4:50 (v/v) H2O/DMF exhibited a higher Cu loading on rGO when compared with the other reaction conditions, and in addition, provided higher activity toward the Ullmann-coupling reaction. First, the optimal catalytic conditions were studied as a function of temperature (110-130 °C), Entries 6-8. The results show that product yield increased at higher reaction temperatures with the optimum temperature at 130 °C. As shown in Table 1, the catalytic activity data are in good agreement with the hypothesis that Cu NPs/rGO prepared in 4:50 (v/v) H2O/DMF exhibited significantly higher efficiency for the catalytic arylation of phenols than for Cu NPs/rGO prepared in pure DMF in the presence of the same precursor or the Cu NPs precursor. Additionally, the data show that the desired product was not obtained in the absence of any catalyst or in the presence of GO only, implying an insignificant number of any active sites (Cu), Entries 1-3.

To further increase the turn over number (TON) and test the robustness of the Cu NPs/rGO catalyst, the substrate (3,5-dimethylphenol and iodobenzene) was increased up to 5-fold under the same amount of the Cu NPs/rGO catalysts prepared in 4:50 (v/v) H₂O/DMF. The findings show that 86% of the product was still obtained, with TON increased to 2,642 implying the degree of robustness of the Cu NPs/rGO catalysts prepared in 4:50 (v/v) H₂O/DMF toward the Ullmann-coupling reaction.

4. Conclusion

Herein, a new approach is presented to improve the fabrication of Cu NPs/rGO upon addition of a nominal amount of water in DMF via a one-pot DMF reduction approach. Water decreases the reducing properties of DMF and further protects the GO oxygen functional groups, which are important for the adhesion of Cu on rGO. The influence of water content on the fabrication of Cu NPs on rGO was examined by XRF and ICP-AES analyses of the Cu concentrations. XPS elucidates the structural properties of the functional groups of the support and hybrid materials and provides an explanation for the synthetic mechanism. Furthermore, Cu NPs/rGO exhibited a narrow and precise nano-sized distribution (3-5 nm) with highly dispersed Cu on rGO, as observed by STEM. The analytical data reported herein demonstrates the successful synthetic approach for Cu NPs/rGO. Finally, to show an example for practical application toward Ullmann-coupling reaction, Cu NPs/rGO was demonstrated to catalyze arylation of 3,5-dimethylphenol with high yield (86% yield and turnover number = 2,642).

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