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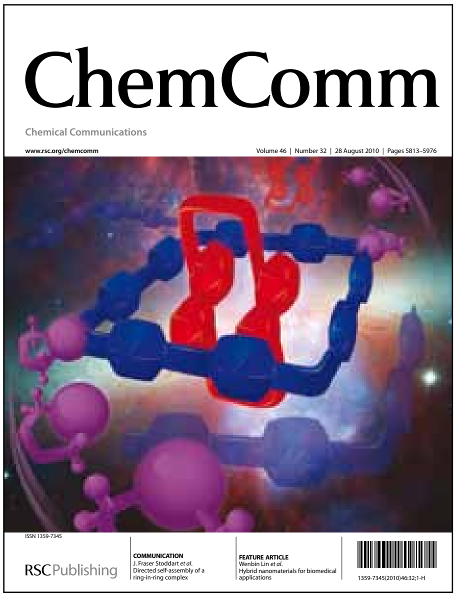

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ARTICLE TYPE

Gold-Carbon Nanoparticle Composite as Efficient Catalyst for Homocoupling Reaction

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Carbon nanoparticle supported Au nanoparticle could be synthesized starting with Au nanoparticle-chitosan composite. The composite nanoparticle efficiently converted phehylboronic acid to biphenyl through homocoupling.

Progress in catalytic chemical reactions – the mainstay of chemistry of new molecules or pathways of reactions – depends on development of efficient, environmentally friendly and cost-effective catalysts.[1a] Although the tremendous growth that has taken place in this regard for the last one hundred years or so seems to overwhelm any new attempt in this regard, there is still plenty of opportunity for finding new catalysts, relook at old catalysts in a modified form or for developing combination of catalysts in order to have the best of all worlds.

For example, charcoal-supported Pd or Pt metal catalysts have contributed greatly in catalytic organic transformations.[1] Recent reports suggest that carbon nanoparticles (CNPs) could provide better option, owing to their stability, sizes, ease of dispersion in liquid medium and facile formation of composites – especially with catalytic metal nanoparticles (NPs).[2] In addition, carbon NP supported metal NPs have been used for photocatalysis[2d] and surface enhanced Raman spectroscopy (SERS).[3] Further, porous carbon supported metal NPs have been used extensively for reduction of nitroaromarotics.[4]

Among the metal NPs, catalytic activity of Au NP, supported on the surfaces of various organic and inorganic substrates, has made Au an alternative choice.[5, 8a-c] For example, carbon supported Au NPs have been used for performing reduction and oxidation reactions.[6] However, it is also important to develop newer methods for pursuing coupling reactions on supported Au NPs. A case could be the production of biaryls, which are an important class of compounds being present as active moiety in pharmaceutically important molecules, natural products and in advanced functional materials.[7] Transition metal catalysed oxidative homocoupling of the arylboronic acid is a major pathway to achieve the homomeric biaryls synthetically.[8-10] In this context, palladium based catalysis has dominated the field.[10] However, several other metal catalysts as well as the reaction conditions were varied to minimize the limitation and increase the efficiency of the parent palladium catalysed coupling reaction. In one such case, cationic Au either supported on metal oxides and polysaccharides or complexed with organic ligands is shown to serve as efficient catalyst for self-coupling of arylboronic acid.[8a, d, 11] However, higher loading of 2.25 to 30 mole percent of the catalyst was required for high conversion and selectivity. It has also been demonstrated - although only in two instances - that Au NPs are efficient in catalyzing oxidative coupling of aryl boronic acid. For example, PVP-stabilized Au NP catalyzes homocoupling reaction under aerial condition.[8c] Even though high conversion of starting material was achieved, poor selectivity towards desired biaryl was observed. On the other hand, Mg-Al mixed oxide supported Au NPs require high pressure of oxygen and higher temperature for higher conversion and better selectivity.[8b] Therefore, developing novel catalyst, in order to bridge the gap between ambient reaction conditions and reactivity-selectivity, is desirable so that the application potential of the reaction could be expanded further.

We report herein an easy and bio-friendly method of preparation of composite of Au NPs and CNPs, which was used for carrying out facile homocoupling reaction of phenylboronic acid to provide excellent conversion with high selectivity under aerial reaction conditions. In the composite, the size of Au NPs was 4.9±1.4 nm, while that of CNPs varied from 50 nm to 350 nm. In addition, a mechanistic proposal relying on the role of Au-NP as the active site is described, which rationalizes the solvent dependent reactivity and selectivity of the reaction.

Chitosan-stabilized Au NPs were synthesized by reduction of $HAuCl_4$ in the presence of $NaBH_4$ and chitosan at room temperature. This was followed by heating the mixture at 200 ^{0}C for 2 h which led to formation of a paste. The mixture was heated additionally for 1 min, during which carbonization took place. The details of the procedure are included in ESI†. The final dried powder was black in colour, which could easily be dispersed in water by mild sonication. Photographs of the powder and the dispersion are shown in Fig. 1 (A and B). UV-vis spectrum of the dispersion (Fig. 1C) consisted of three peaks at 267 nm, 345 nm and at 522 nm. The peak at 267 nm and 345 nm are characteristic of CNPs (imputed to the π–π^* transition), whereas that at 522 nm is due to Au NPs.[2a-c] On the other hand, as prepared chitosan –Au NP composite exhibited a single peak at 510 nm, indicating the presence of Au NPs only. Further, photoluminescence property of the composite resembled that of carbon dots. For example, as shown in Fig. S1, (ESI†), the excitation-tuneable emission peaks in the range of 325 nm to 500 nm of the composite resembled those of CNPs. However, the quantum yield of luminescence was higher for the composite (0.54%) in comparison to that of the CNPs (0.36%). Transmission electron microscopy (TEM) measurements indicated the presence of distinct particles of

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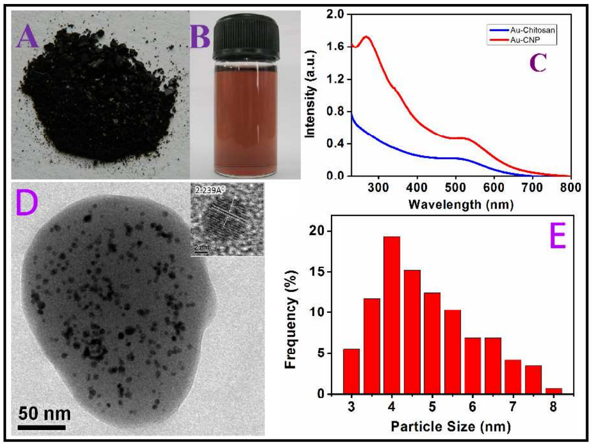


Fig. 1 Photographs of (A) dry composite and (B) that of the composite dispersed in water. (C) Absorption spectra of Au-CNP composite and Au NP-chitosan. (D) TEM image of Au-CNP composite with HRTEM image in the inset. (E) Size distribution of Au NP present in the composite as calculated from TEM images.

average size 4.9 ± 1.4 nm, embedded in larger particles of sizes in the range of 50 nm to 350 nm (Fig. 1D, 1E and Fig. S3, S5; ESI†). Also, a large number of Au NPs were embedded in each of the larger particles, as is evident from TEM measurements. That the smaller particles were due to Au was confirmed from selected area electron diffraction (SAED) measurement (Fig. S4, ESI†). Further, high resolution TEM (HRTEM) measurements indicated the presence of planes owing to lattice spacing of 0.224 nm, which is due to (111) planes of metallic Au. On the other hand, the larger particles could be CNPs. X-ray diffraction (XRD) measurements indicated the presence of four planes of Au, namely, (111), (200), (220) and (311) leading to diffractions at 38.3^0, 44.6^0, 64.8^0, and 77.8^o (JCPDS 4-0783) ,respectively (Fig. S4, ESI†). A broad peak at 24.8 ^{o} is assigned to amorphous CNPs.

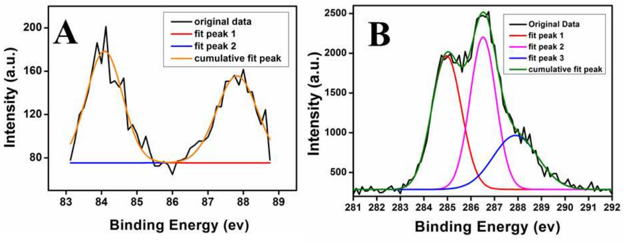
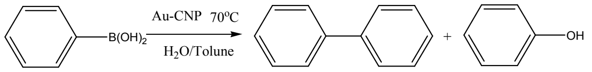


Fig. 2 X-ray photoelectron spectra of Au-CNP composite. (A) is for Au 4f and (B) is for C 1s.

X-ray photoelectron spectroscopy analysis of the composite evidenced the presence of peaks at 84.1 eV and 87.8 eV (Fig. 2), where the binding energies correspond to the $4f_{7/2}$ and $4f_{5/2}$ states of metallic gold i.e. Au^0. Thus the presence of Au^+ or Au^{3+} species could be ruled out. Further, analysis of peaks due to carbon species indicated the presence of C-C (284.9 ev), C-OH or C-O-C (286.5 ev) and C=O (287.9 ev) functional groups. On the other hand, inductive coupled plasma (ICP) spectroscopy indicated 1.95% of Au loading in the composite. Additionally, Raman spectroscopy measurements indicated the presence of broad peaks at 1341 cm^{-1} and 1581 cm^{-1}, corresponding to D and G bands of sp^2 carbon, signifying the formation of CNPs (Fig. S6, ESI†).

The above results indicated the formation of smaller Au NPs embedded in the larger amorphous CNPs. Also, the absence of any oxidation states other than Au(0) makes the Au-CNP composite ideal for studying the efficacy of Au NP catalyzed coupling reactions. It may be mentioned here that the smallness of the sizes of the CNPs (in the composite), as compared to traditional charcoal support makes, the composite an ideal platform for microheterogeneous reactions. It is important to mention here that catalytic reactions in microheterogeneous medium is inherently advantageous over its heterogeneous counterpart, owing to the ease of product diffusion, in addition to availability of large surface area for reactions.

Table 1. Au-CNP catalysed homocoupling of phenylboronic acid[a]



Entry	Solvent	Catalyst	Oxygen	Ph-Ph[b]	Ph-OH[b]	Conversion
1[c]	Toluene/H_2O	Au-CNP	atm.	86%	12%	98%
2	Toluene/H_2O	---------	atm.	--------	--------	--------
3	Toluene/H_2O	Chitosan	atm.	--------	--------	--------
4	Toluene/H_2O	CNP	atm.	--------	--------	--------
5	Toluene	Au-CNP	atm.	--------	--------	--------
6	Toluene	Au-CNP	balloon	--------	--------	--------
7	H_2O	Au-CNP	atm.	68%	18.3%	86.3%
8	Toluene/H_2O	Au-CNP	free	--------	--------	19% (24%)
9	Toluene/H_2O	Au-CNP	balloon	74%	26%	100%

[a]Reaction Condition: 0.3 mmol phenylboronic acid, 1mL toluene, 0.5 mL water, 10 mg catalyst (Au loading 0.66 mol%), 70 ^{0}C in open flask and 7h. [b]Isolated yields. [c]Gas-chromatographic analysis showed the yield to be 88% (ESI).

In order to investigate the catalytic activity of the composite, the well-known C-C bond forming homocoupling reaction of phenylboronic acid was pursued. Thus, phenylboronic acid in a binary solvent mixture (2:1 V/V ratio of toluene and water) was allowed to react in the presence of catalytic amount of the composite, under the aerial conditions at 70 ^{0}C, which was found to be the best reaction temperature (ESI, Table S2). A conversion of 98% of the phenylboronic acid in 7 h, in the presence of only 0.66 mol% of the gold leading to the TOF (turn over frequency) of 19 was observed. Biphenyl was isolated with yield of 86%, along with 12% of phenol, a by-product of oxidation of phenylboronic acid, presumably by the H_2O_2 generated in the reaction. Control experiments (Table 1) carried out in absence of catalyst and in the presence of CNP or chitosan did not result in the product formation. Thus Au NPs in the composite played key role in the catalytic conversion of phenylboronic acid to biphenyl. Further, reaction involving chitosan-stabilized Au NPs lacked selectivity and had lower conversion efficiency (ESI, Table S1, entry 3). Interestingly, when the reaction was carried out in toluene only medium there was no product formation (entry 5), even when gaseous O_2 was passed through the reaction mixture. On the other hand, in the water (only) medium 86% conversion – although with reduced selectivity – was observed. Interestingly, the extent of conversion was reduced when deaerated water was used instead. Additionally, externally added oxygen facilitated the reaction (entry 9), where the reaction was completed in 3.5 h with a TOF of 32. However, more amount of phenol was formed

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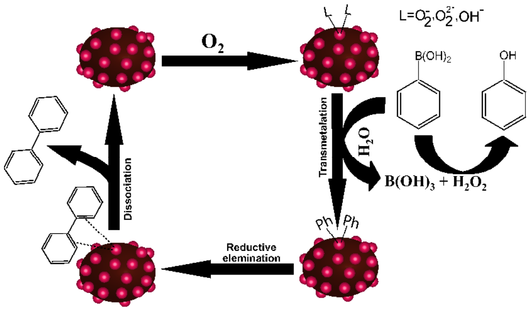
reducing the biphenyl to phenol selectivity to ~3:1 from 7:1 (entry 1).

Based on these experimental findings and the literature reports, a plausible mechanism of Au-CNP catalyzed homocoupling reaction is depicted in scheme 1.[8a-c, 11] The surface of the Au-NP is oxidized, by dissolved molecular oxygen,[8b-c,12] to positively charged species being associated with oxygenated ligands (e.g. O_2^{2-}, O_2^- or OH^-), in the first step of the catalytic cycle. The electron rich nature of CNP probably facilitates the aerial oxidation of Au NP, which is reflected in the enhanced catalytic activity of Au-CNP compared to Au-chitosan.[13] The base-mediated activation of phenylboronic acid occurred, prior to the double transmetallation on the charged Au surface. However, the ligand (coordinated to Au) induced transmetallation could also be possible. In parallel, H_2O_2 generated in situ from reduced oxygen (super oxide and/or peroxide) could have oxidized phenyl boronic acid to phenol.[12b] Finally, the reductive elimination with consequent product dissociation provided desired biphenyl, returning the Au-nanoparticle in to the catalytic cycle for the next turn over.



Scheme 1. Proposed mechanism of aerobic homocoupling reaction of phenylboronic acid catalyzed by Au-CNP composite.

The increase in the percentage of the phenol in the reaction in only water compared to that in toluene-water mixture can be rationalized with the help of proposed mechanism, by considering the comparative rate of transmetallation and oxidation of starting material. In contrast to the reaction in water, for the case of toluene-water mixture, biphenyl being hydrophobic diffuses immediately after its formation to toluene and thus the catalytic sites become ready for another cycle. However, due to higher amount of dissolved O_2 in only water or in toluene-water medium with externally added oxygen, the formation of higher amount of oxidizing species may lead to the larger amount of phenol formation. In contrast to the mechanism proposed by Carrettin et al. using Au-CeO$_2$, [8a] our mechanistic proposal relies on the positively charged Au NP as the active catalyst for the homocoupling reaction of phenylboronic acid. Furthermore, solvent dependent reactivity and the selectivity observed experimentally are in accordance with the proposed mechanism.

The stability and the ability to recycle the catalyst were also investigated. Firstly, the supernatant of the reaction mixture showed no significant absorbance above 300 nm (Fig. S7, ESI†), thus excluding the presence of ionic Au species in the medium and at the same time indicating the stability of the NPs. Moreover, TEM and XRD studies of the recovered catalyst indicated the stability of the Au NPs in terms of their shape and size (Fig. S8 & S9 ESI†). Accordingly, the catalyst was successfully recycled twice without compromising the conversion (98%) of the starting material as well as the yield (89%) of the desired product.

In summary, we have developed a simple method to synthesize Au-CNP composite, which was used for homocoupling reaction of phenylboronic acid. Importantly, selectivity of the reaction in the presence of H_2O and dissolved oxygen indicated the exceptional role played by Au NPs being supported on CNP. That the catalyst was stable and could be recycled is important for its practical application. This reaction may open new doors of metal-CNP composite towards coupling reaction and production of fine chemicals and pharmaceuticals of industrial importance.

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† Electronic Supplementary Information (ESI) available: Experimental section and Fig. S1-S11. See DOI: 10.1039/b000000x/

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