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One pot synthesis of copper nanoparticles at room temperature and its catalytic activity



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Abstract A facile reduction approach with sodium borohydride as a reducing agent and starch as a stabilizing agent leads to monodispersed Cu nanoparticles in aqueous medium at an ambient condition. The synthesized nanoparticles are highly pure with no traces of CuO found on surface. They are uniform in size in the range of 40–80 nm. The Cu nanoparticles have a FCC structure as characterized by powder X-ray diffraction (XRD). Transmission electron microscopy (TEM) images show that they are arranged in a regular array which is separated by starch thin layer which controls the growth as well as stabilizes the Cu nanoparticles from air oxidation. The catalytic activity of prepared Cu nanomaterial was tested in Ullman reaction for the synthesis of biphenyl from iodobenzene. We have shown in this paper that the size as well as exposed surface area of the copper nanoparticles is responsible for the increase in yield of biphenyl up to 92%. This is higher compare to the 40% yield with the normal size copper powder under the same reaction condition.

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1. Introduction

The study of nanocrystal compounds brought about the creation of functional materials with desired physiochemical properties. With the development of nanomaterials and

nanotechnology, more and more efforts have been directed toward large scale synthesis of nanomaterials (Guo et al., 2006; liu et al., 2006). In past two decades, considerable attention has been devoted to the synthesis of metal nanoparticles because of their unusual properties and potential application in optical, electronic, catalytic, magnetic materials, and so on (Beecroft and Ober, 1997; Fendler, 1987; Gates, 1995; Kamat, 1993; Lewis, 1993; Schmid, 1992; Toshima and Yonezawa, 1998). Number of methods have been developed for the preparation of metal nanoparticles, such as photolytic reduction (Remita et al., 1996), radiolytic reduction (Hodak et al., 2000), sonochemical method (Mizukoshi et al., 1997), solvent extraction reduction (Brust et al., 1994), microemulsion technique (Osseo and Arrigenda, 1990), polyol process (Kurihara et al., 1995) and alcohol reduction (Huang et al., 1996). Recently, chemist, physicist and material scientists have shown

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great interest in the development of new methods for the synthesis of nanomaterials. Physical and chemical properties of these materials are highly size dependant therefore, it is important to develop novel techniques for the synthesis of smaller and monodispersed nanomaterials. Amongst many metals like Au, Ag, Pd, Pt toward which research is directed, copper and copper based compounds are the most important materials. Metallic Cu plays a significant role in modern electronic circuits due to its excellent electrical conductivity and low cost (Schaper et al., 2004). So Cu will gain increasing importance as is expected to be an essential component in the future nanodevices due to its excellent conductivity as well as good biocompatibility and surface enhanced Raman scattering activity (Pergolese et al., 2006). Metallic copper nanocrystals homogenously dispersed in silica layers have attracted great attention recently for the development of nonlinear optical devices (Flytzanis, 2005). Such composite materials offer exciting possibilities of potential thin film device applications with novel function arising from size quantization effect. In organic synthesis, the Cu nanoparticles were useful as a catalyst in the synthesis of Ullman reaction. The high surface area of small Cu nanoparticles is effective in order to improve the rate of reaction. In the light of fast and growing applications of metallic copper nanoparticles, a reproductive method of synthesis with a specific size, well defined surface composition, isolable and re-dispersible properties remains a challenging task to a synthetic chemist. The ability to scale up the synthesis to bulk scale will gain increasing importance as more applications are established. Synthesis of copper metal nanoparticles is often difficult due to the possibility of surface oxidation. Surface oxidation can be prevented by protecting the outer surface by the use of suitable stabilizing agent. The stabilizing agent would also control nucleation of particles and thus would act as a particle growth terminator. Thus the stabilizing agent has a dual role i.e. to prevent surface oxidation of the particles and control growth of particles (Khanna et al., 2008; Surmawar et al., 2011). Very little work has been carried out on the synthesis of copper nanoparticles. Synthesis of nano-Cu by use of oleic acid in aqueous solution via a two-stage reduction processes was reported, the two stage reduction process was necessary to avoid formation of copper oxide (Yang et al., 2006). Synthesis of copper nanoparticles of varied shapes by reverse micelles method has been described (Pileni et al., 1998). Copper colloids have been reported by electrolytic techniques at different electrode potential (Lu and Tanaka, 1997) and similarly alkanethiolate protected nano-particles of copper have been reported by electrolysis method (Chen and Sommers, 2001). Photochemical synthesis of nano Cu was found to generate excellent SPR band but the size was rather in the region of about 50–100 nm (Condorelli et al., 2003). Sono-chemical synthesis of copper particles has been reported by Dhas et al. (1998). In most of these synthetic methods to produce copper nanoparticles they used hazardous chemicals to give irregular shape with wide size distribution or prepared Cu nanomaterial contaminated with copper oxide. There are some reports in which the nitrogen gas was purged in reaction medium to avoid the surface oxidation of Cu nanoparticles but in this paper we have reported a one pot synthesis procedure to prepare pure copper nanomaterial with uniform size at ambient condition (air atmosphere and at room temperature) by using starch as a stabilizer which by itself a biomolecule and sodium borohydride as a reducing agent. We study its catalytic

properties by applying it as a catalyst in the Ullman reaction to synthesize biphenyl in improved reaction conditions which gave maximum yield with high purity.

2. Experimental method

2.1. Preparation of Cu nanoparticles

The entire reagent used in this Cu synthesis was of analytical grade and used without further purification. Nanoparticles were synthesized through a solution reduction process using sodium borohydride as a reducing agent. First the copper ammonia complex solution prepared by adding 1 g copper metal in 10 ml of (27%) ammonia solution forms the blue copper ammonia complex by consuming all the copper metal. To this blue solution of copper ammonia complex added dilute HCl (5%) under stirring until solution becomes neutral. After this added 100 ml of 0.25 M NaBH₄ solution having 4 g starch as a stabilizing agent slowly dropwise in half hour at room temperature, the color of solution changed to dark brown which confirmed the formation of Cu nanomaterial. The prepared nanomaterial is then separated out by centrifuge at 4000 rpm and washed with water. In most of the methods to produce Cu nanoparticles inert atmosphere was used in order to avoid oxidation of prepared Cu nanoparticles. But in our present method we did not pass nitrogen gas in the reaction medium in order to create inert atmosphere.

2.2. Sample characterization

The powder X-ray diffraction measurements of Cu nanomaterial were carried out on a PAN'ALYTICAL X'PERT PRO XRD system using Cu K α radiation. The absorption spectra were collected from Shimadzu UV-Visible Spectrophotometer. The morphology of the copper nanoparticles was investigated via transmission electron microscopy (TEM, Philips CM200). The size distribution of the copper nanoparticles was obtained by Nano-distribution and a zeta potential analyzer (SZ-100, Horiba).

2.3. Catalytic test

Iodobenzene (1.224 g, 6 mmol), CuO nanoparticles (0.210 g) and *N,N*-dimethyl formamide (10 ml) were taken in a round bottomed flask fitted with a reflux condenser. The resulting mixture was refluxed for 4 h and progress of the reaction was monitored by TLC. After completion of reaction, mixture cooled to room temperature, diluted with 10 ml of water and extracted with diethyl ether (2 \times 10 ml). The combined organic extracts were washed with brine and dried on anhydrous sodium sulfate. Solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel using ethyl acetate and petroleum ether (1:9) as eluent to yield analytically pure colorless crystal of biphenyl. The overall yield of the reaction is around 92%. We checked the melting point of the synthesized product which melts at temperature 68–70 °C. It matches well with the melting point of biphenyl given in the literature which was 69.8 °C; it shows the synthesized product was highly pure.

3. Results and discussion

3.1. Structural analysis of Cu nanoparticles

It is well known that strong intermolecular forces such as Van der Waals attraction, π - π interaction contribute to the aggregation of nanoparticles. As for the magnetic nanoparticles, magnetic dipole-dipole interaction makes this kind of attraction stronger. Different stabilizing agents are used to control particle size. In our experiment we used starch to control the particle size which stabilized nanoparticles dispersion and limited further oxidation on particle surface. Starch is an excellent stabilizing agent because of its coordination with metal. Colloidal dispersion of metal exhibits absorption band in the UV-visible region. This is due to the excitation of Plasmon resonance or interband transition and is a characteristic property of metallic nature of particle. The copper nanoparticles having size around 50 nm typically exhibit a surface Plasmon peak at around 560–570 nm (Creighton and Eadon, 1991). The synthesized Cu nanoparticles showed the characteristic absorption peak at 590 nm (Fig. 1), which indicated the copper nanoparticles have a size around 50 nm. This also confirmed by the XRD spectra (Fig. 2) which showed an intense peak at 43.30 which is having a plane (111) is the crystal plane of Cu which matched to FCC of bulk Copper. The low intensity peaks at 50.42 and 74.03 matched very well with the plane (200), (220). Some peaks were found at 89.79, 94.97 with plane (311) and (222) respectively. These are much close to those in the JCPDS File No. 5-0661. This indicated that the prepared Cu material was highly pure, crystalline and well arranged in specific orientation. No other peak was observed due to impurity. From the Debye-Scherrer equation we estimated the particle size. The crystal size of products as calculated by Scherrer formula is 55 nm. The results of size distribution analysis (Fig. 3) show that the products range from 40 to 90 nm. The morphology of prepared nanoparticles was investigated by TEM analysis which clearly shows the spherical morphology of prepared Cu nanomaterial having a size around 50 nm

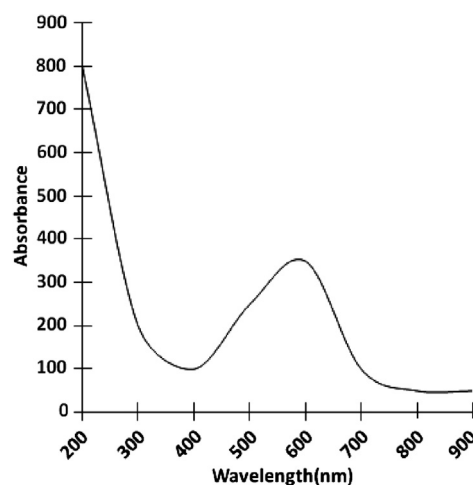


Figure 1 UV-visible spectra of colloidal solution of Cu nanoparticles.

(Fig. 4). The high resolution images show the aggregation of particles in such a way that they are arranged in a regular array which is separated by thin layer of starch responsible for controlling the growth of particle and also stabilized it toward further oxidation. The particle size found agrees well with the XRD results. It was well known that nanometer sized Cu particles get easily oxidized in air. However, after the sample was exposed in air for several months, no CuO phase was detected. This means that the starch layer on the surface of the Cu nanoparticles has strong ability to protect it from air oxidation. After confirming its stability toward oxidation we used the given nanoparticles as a catalyst in the synthesis of biphenyl.

3.2. Catalytic activity

Biphenyl is notable as a starting material for the production of polychlorinated biphenyls (PCBs), which were once widely

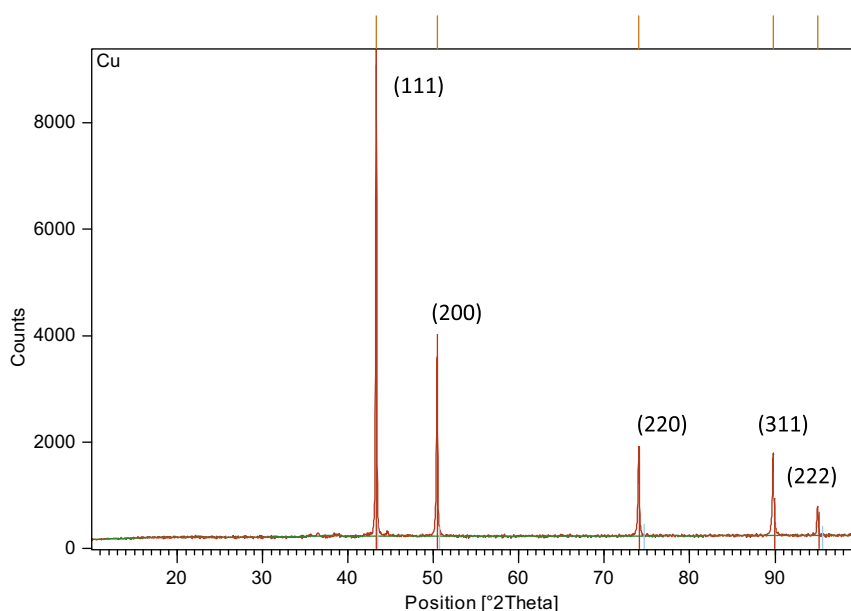


Figure 2 XRD spectra of Cu nanoparticles.

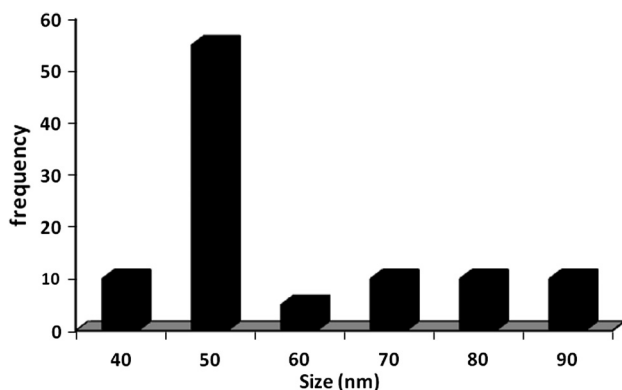
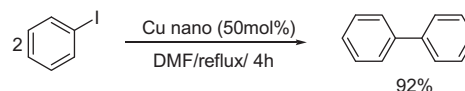


Figure 3 Size distribution of Cu nanoparticles.

used as dielectric fluids and heat transfer agents (Kumamaru et al., 1998). In history biphenyl derivatives can be prepared synthetically by various coupling reactions including the Suzuki reaction (Suzuki, 1999) and the Ullmann reaction (Fanta, 1974) and have many uses. In Suzuki cross-coupling, reaction between an aryl boronic acid and an aryl bromide was conducted in the presence of tetrakis (triphenylphosphine) palladium (0) and aqueous sodium carbonate in toluene/ethanol at 80 °C for 12 h. One drawback of the conventional Suzuki coupling is the tetrakis (triphenylphosphine) palladium (0) catalyst itself which, appears to be difficult to store over periods of several months and causes the formation of various side products (Lehmle and Robertson, 2001).



Scheme 1 Synthesis of biphenyl from condensation of iodobenzene.

The condensation of iodobenzene to biphenyl was chosen as the model reaction for catalytic activity due to its significant role in organic synthesis (Scheme 1).

There was report on the application of Cu nanomaterial on the biphenyl synthesis but the use of large amount of Cu nanoparticles (150 mol%) and the high temperature 200 °C limits the method (Samim et al., 2007). To find out the optimum reaction conditions for condensation process using Cu nanoparticles the variations in the parameters like solvent and the quantity of nano Cu catalyst were carried out and the results were summarized in Table 1.

The data of Table 1 show that the condensation of iodobenzene to biphenyl was effectively possible in various solvents. As the concentration of catalyst was increased from 15 mol% to 50 mol%, the yield of the product was increased from 50% to 92% (Table 1, entries 5 and 7). It is important to mention that condensation of iodobenzene did not take place in the absence of Cu nanoparticles (Table 1, entry 8) and there was no increase in the yield of the product after varying the reaction time (Table 1, entry 9). The combination of 50 mol% of Cu nanoparticles as the catalyst in DMF solvent with 4 h of reaction time was found to be the best choice to get maximum yield of the product (Table 1, entry 7). For further confirmation and significance of this work we carried out the biphenyl synthesis

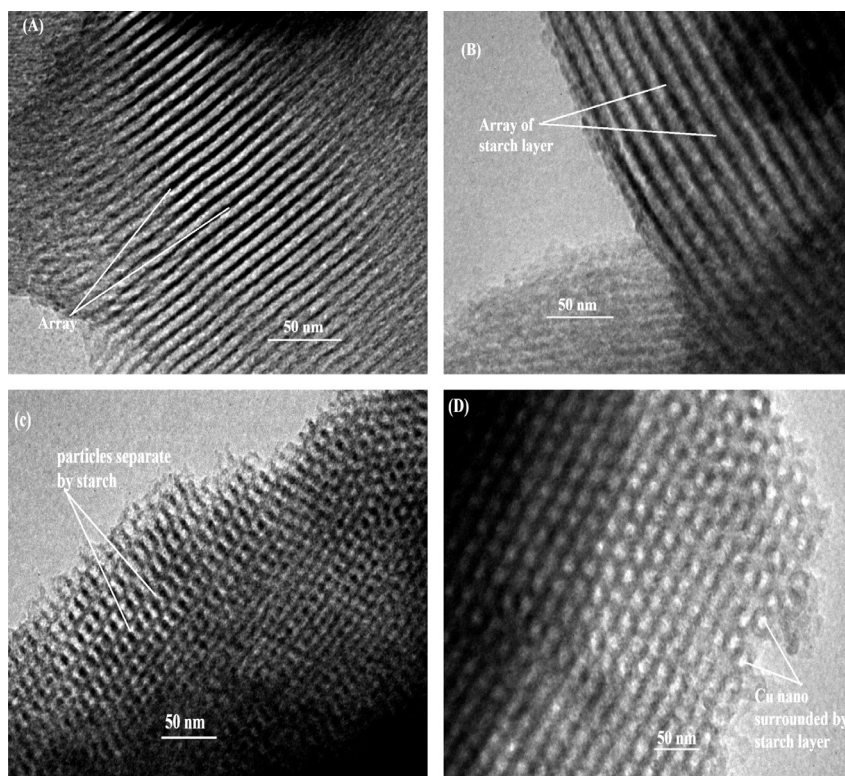


Figure 4 (A–D): TEM images of Cu nanoparticles.

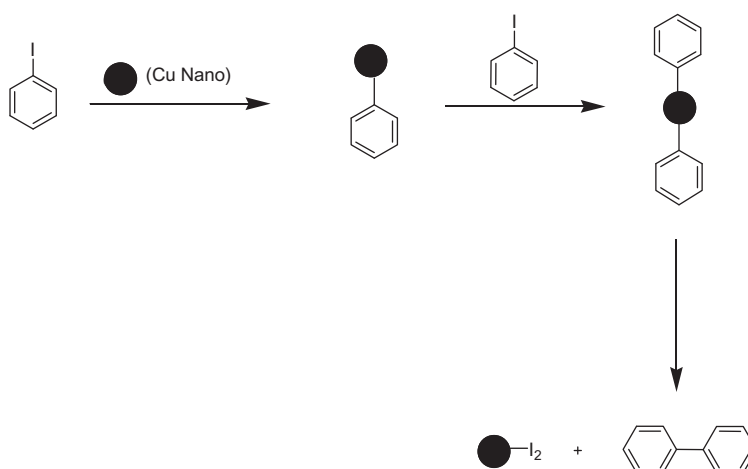
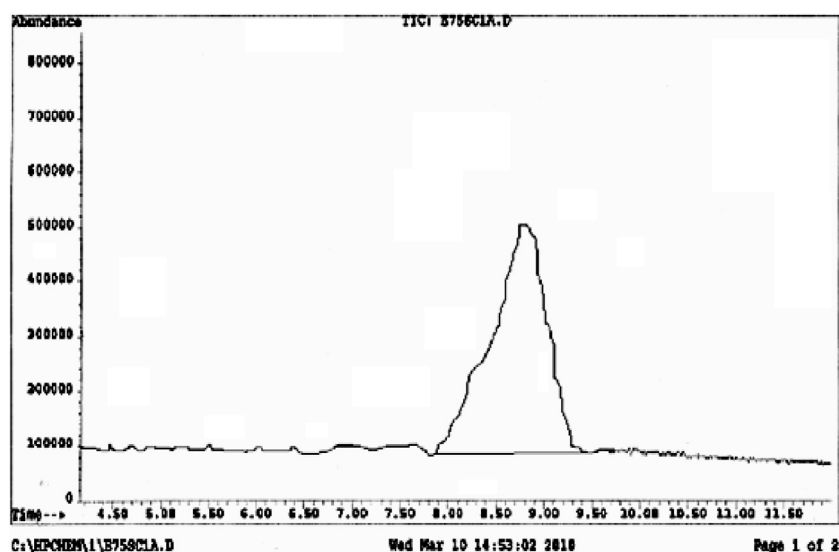
Table 1 Optimization of reaction condition for the condensation of iodobenzene to biphenyl.

Entry	Cu quantity (mol%)	Solvent	Reaction time (h)	Yield ^a (%)
1	50	CH ₂ Cl ₂	6	31
2	50	CH ₃ CN	6	20
3	50	DMSO	6	80
4	50	Toluene	6	45
5	15	DMF	6	50
6	25	DMF	4	70
7	50	DMF	4	92
8	00	DMF	8	00
9	50	DMF	8	92

^a Isolated yield.

under similar reaction conditions with normal size Cu powder purchased commercially from Merck. We performed the similar reaction as given in (Scheme 1) with normal size Cu powder

as a catalyst and found only 40 % conversion after 6 h of reflux. Unfortunately the yield of the reaction was mostly affected by large size and coating of copper metal by hard material like copper oxide or other strongly adsorbed compounds (Fransisco and Jorge, 1983). As a result, the total exposed surface area of the catalyst was significantly reduced. This was true when the nanoparticles were prepared in surfactant solution under high temperature heating. This creates additional complication of converting the catalyst surface into irremovable metal oxide which drastically reduced the catalytic efficiency. In the present context, we synthesized highly pure Cu nanoparticles at room temperature with higher catalytic activity toward the condensation of iodobenzene which could be due to the higher catalytic surface area of small nanoparticles. It was presumed that the electrophilic nature of the catalyst surface renders a weak bond between the π -system of benzene ring and vacant d-system of copper atoms which gives slightly positive charge over iodine atom. The whole complex reacts with another molecule of iodobenzene to produce biphenyl

**Figure 5** Possible mechanism of biphenyl formation.**Figure 6** GC spectra of biphenyl.

and copper iodide (Fig. 5). The electrophilic nature of copper surface obviates that when the particle is extremely small in size, the electrons are pumped into copper by the benzene π system, which usually reduces the band gap between Fermi level and conduction band considerably so that the catalytic activity is also expected to be reduced (Huynh et al., 2003), however, copper has d-bands well below the Fermi level and filled (Sharma et al., 2003). As a result, the catalytic activity did not decrease rather it remains constant. The high surface to volume ratio of Cu nanoparticles played a useful role in the synthesis of biphenyl as Cu nanomaterial acted as a heterogeneous catalyst in the given reaction. GC spectrum (Fig. 6) of the final product was taken and compared with the spectra of the standard sample which shows the intense peak at retention time 8.9 min indicates that synthesized product is having purity of 100%.

4. Conclusion

We have developed a facile route to synthesized size controlled Cu nanoparticles. Nanoparticles were successfully synthesized by solution reduction method in aqueous media at an ambient condition. The synthesized Cu nanoparticles were highly pure and uniform in size. Starch which is used as a stabilizing agent controls the particle growth, and stabilizes the nanoparticles toward air oxidation. The synthesized nanoparticles were successfully used for catalytic activity in the synthesis of biphenyl with high yield up to 92%.

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