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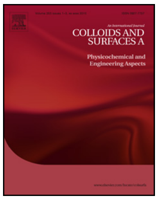

Preparation of stable sub 10 nm copper nanopowders redispersible in polar and non-polar solvents

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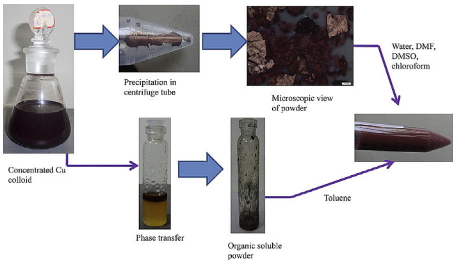
HIGHLIGHTS

- Sub 10 nm PVP–PEG protected copper nanoparticles have been prepared.
- Centrifugation and ethanol precipitation employed to prepare Cu nanopowder.
- Cu nanopowder was redispersed in water, DMF, DMSO, chloroform.
- Concentrated Cu colloid has been successfully phase transferred.
- Toluene soluble Cu nanopowders have been successfully produced.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we prepare 10 nm copper nanopowders redispersible in various polar and non-polar solvents. First, concentrated colloid of copper nanoparticles protected by PVP–PEG is synthesized by a simple wet chemical method using hydrazine hydrate as reducing agent. Extremely stable copper nano-powder containing sub 10 nm particles can be readily prepared by drying this colloid. This powder readily disperses in water, DMF, DMSO and choloroform and produces a stable colloid. To increase the copper content of the powder, washing of the colloid using (i) high speed centrifugation and (ii) ethanol addition and centrifugation at lower speed have been successfully conducted. The high speed centrifugation increases the size of the colloid to 50 nm after re-suspension while the size remains sub-10 nm when washing is conducted using ethanol. Particles were also phase transferred successfully from the aqueous polymeric solution to toluene using a protocol previously used for gold nano-rods. Many other simpler phase transfer techniques have also been tried but such methods failed to transfer particles from such polymer loaded colloid efficiently. Stable organic dispersible nanopowders have been produced from the organosol. The particle size is preserved after phase transfer and redispersion in organic solvent.

1. Introduction

Nanoparticles have become a popular product in the market for a variety of applications such as catalysis [1], biosensors [2], optoelectronics [3], absorbents [4] etc. Copper nanoparticles are of special interest because of its favourable properties and low cost. It has applications in various fields such as ink jet printing technology [5], catalysis [6], medicine [7], antimicrobial agents [8], etc. While a lot of other nanoparticles are available as nanopowder, copper nanoparticles are mostly obtained as colloidal solution. Literature on production of copper nanopowder is very sparse. The aim of this article is to demonstrate production of stable, re-dispersible sub-10 nm copper nano-powders.

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Nanopowders have been produced for a variety of materials using a number of techniques. Majority of the materials are oxide since they already have market for bulk applications. For example, TiO_2 nanopowder finds applications in solar cells and is produced in larger amount. Other oxide nanopowders such as ZnO, CdO and NiO are also produced in large amount. Mainly combustion [9], high energy ball milling [10] and sol–gel process [11] are used for production of such oxide nanopowders. RF plasma [12], laser ablation [13] and solution precipitation methods [14] are also employed for production of oxide nanopowders. Unlike oxide materials, production of metal nanopowders is not so common. Probably because many metals form oxide when in contact with air. Nevertheless, some metal nanopowder like gold [15], silver [16], copper [17,18] and aluminium [19] have been prepared.

In most cases nanopowders contain aggregates with primary particles in the range of 30–100 nm [12]. In some cases, however, well separated particles have been produced [16,20]. Even for such cases, mostly physical methods have been followed. One particular case that needs special mention here is the particles synthesized using Brust's method [15]. Here small 2–4 nm thiol coated very stable gold or silver nano-powder can be prepared using chemical method. Gautam et al. [21] also produced silver nanopowder using polyol process.

Although a large number of synthesis protocols exist for preparation of copper colloid containing a range of particle size, preparation of copper nanopowder is rarely reported. Song et al. [18] prepared organic solvent compatible thiol coated copper nanopowder of ~60 nm size using Brust's method [15]. Nekouei et al. [17] reported copper nanopowder using electrochemical method. In the later work, particles mostly exist in the form of agglomerates. Sub-10 nm well separate, re-dispersible copper nanopowder has not been reported so far.

In this paper, we demonstrate for the first time preparation of polymer (PVP–PEG) stabilized copper nanopowders that can be redispersed in various solvents. The relative role of the polymers in the stability and the threshold concentration required has also been explored. Washing of the hydrosol has also been studied using various methods and the re-dispersibility and size of the redispersed sol has been investigated. The excess polymer has been recycled to produce fresh copper hydrosol.

Another important aspect explored in this work is the phase transfer of polymer stabilized copper hydrosol. Although phase transfer of copper nanoparticles have been studied recently [22,23], phase transfer of polymer stabilized particles has not been studied. Such phase transfer is challenging because of higher particle and polymer loading of the aqueous system. In this work we demonstrate phase transfer of polymer stabilized concentrated hydrosol to organic phase and also produce organic phase compatible copper nanopowder of sub 10 nm size.

2. Experimental

2.1. Materials required

Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$), hydrazine hydrate (80%) ($N_2H_4{\cdot}H_2O$), polyethylene glycol (MW-6000), ammonia solution (25% pure), dimethyl sulfoxide (DMSO) and toluene were purchased from Merck Chemicals, India. Polyvinylpyrrolidone (K30, MW-40000) was bought from SRL Chemicals, India. Mercaptosuccnic acid (MSA) was purchased from LOBA Chemicals, India. Tetraoctylammoniumbromide (TOAB) was purchased from Sigma–Aldrich, USA. 1-Dodecanethiol (DDT) was obtained from SD Fine Chemicals, India. Ethanol (AR 99.9%) was purchased from Jiangsu Huaxi International, China. All the chemicals were used as received. Nitrogen/argon gas with less than 50 ppm impurity was used for degassing the solvents.

2.2. Deoxygenation of solvents

Solvents used in the synthesis were deoxygenated by purging with argon or nitrogen in a conical flask for 30 min.

2.3. Synthesis of copper nanoparticles in aqueous phase

Copper nanoparticles were prepared by modifying a protocol given by Tian et al. [24]. In a typical synthesis, 4.8 g PEG and 3.6 g PVP were added to 40 ml of double distilled water (deoxygenation was not required) under vigorous stirring until complete dissolution. Then 0.136 g $CuCl_2{\cdot}2H_2O$ was added to the solution. This solution showed a pale blue colour. Next, ammonia solution was added to the above solution drop wise under vigorous stirring until the pH of the solution reached 11. The colour of the solution changed to inkish blue after this step. Then the solution was heated to 50 °C in a water bath and maintained at that temperature for 2 h under continuous stirring. The colour of the solution turned muddy brown gradually. Then 20 ml of 0.3 M hydrazine hydrate was added for reduction. The solution turned colourless immediately and then became yellowish orange. Later the temperature was changed to 60 °C after hydrazine hydrate addition. The stirring was continued for another 20 min during which the solution turned light reddish and finally became deep wine red colour indicating the formation of copper nanoparticles.

2.4. Washing and redispersion of copper nanoparticles

The colloid with surfactant can be dried by evaporating the water either by mild heating or inert gas bubbling. To wash the surfactant, the colloids were centrifuged at a speed of 11,500 rpm for 30 min. After centrifugation, a clear supernatant was obtained that was removed by decanting. Fresh degassed water was added to the precipitate deposited at the bottom of the centrifuge tube and redispersed using ultrasonication. This step was repeated twice to obtain a shining copper coloured solid. This solid readily re-disperse in deoxygenated water to form hydrosol.

Washing was also conducted using ethanol. Equal volumes of colloid and ethanol were mixed and the mixture was allowed to stand overnight. Then it was centrifuged at a speed of 7000 rpm for 30 min. This also produced shining copper coloured solid which readily re-disperse in to deoxygenated water.

2.5. Recycling of polymers

The supernatant obtained from centrifugation step contains excess of ammonium hydroxide and hydrazine hydrate. The liquid was first aerated to decompose excess hydrazine hydrate. The presence of hydrazine hydrate was judged by its reducing action on copper salt. After sufficient aeration, the solution is poured on a petri dish and kept in hot air oven for a day at 80 °C until the evaporation of solvent. A uniform coating of polymer was formed in the petri dish. This polymer was considered to be a mixture of PVP and PEG at the proportion they were fed to the synthesis mixture. This polymer was used in synthesis along with a make-up of fresh polymer to account for the mass loss in reaction-purification steps.

2.6. Phase transfer of PVP–PEG stabilized copper nanoparticles to toluene and formation of organic dispersible nanopowder

2 ml of 26 mM aqueous solution of mercaptosuccinic acid (MSA) was added to 2 ml Cu hydrosol in a glass vial and the vial was