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Catalytic and fluorescence studies with copper nanoparticles synthesized in polysorbates of varying hydrophobicity

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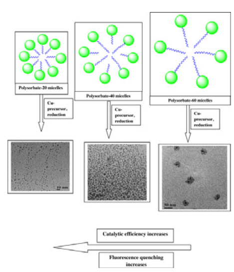
HIGHLIGHTS

- CuNPs synthesized in non-ionic polysorbates.
- CuNPs characteristics depend on HLB value.
- Metallic or oxide nanoparticle formation guided by polysorbate concentration.
- Catalytic efficiency and fluorescence quenching by CuNPs is correlated.

GRAPHICAL ABSTRACT



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ABSTRACT

Nonionic polysorbate surfactants used in pharmaceutical formulations have been used for synthesizing stable and highly crystalline copper nanoparticles. Polysorbate concentration, chain length and hydrophile:lipophile balance (HLB) are important parameters determining nanoparticle characteristics. At low polysorbate concentrations, amorphous copper oxide nanoparticles are formed. Highly crystalline and well-dispersed metallic copper nanoparticles are formed only at micellar concentrations. The more hydrophobic polysorbate-60 forming large, loosely packed micelles is not suitable for metallic nanoparticle formation. However, HLB is not the sole factor guiding nanoparticle formation. Polysorbate-40 with intermediate HLB value promotes the formation of good quality, perfectly hexagonal and crystalline metallic nanoparticles with uniform size distribution. Catalytic efficiency of the nanoparticles depends on their size and structural organization. In this respect, the discrete and spherical metallic nanoparticles formed in the more hydrophilic polysorbate-20 micelles perform best. Additionally, the fluorescence quenching ability of the nanoparticles can be directly correlated to their catalytic behaviour. Summarizing, this work shows how one can modulate the size, shape, structural organization and quality of the copper nanoparticles by fine-tuning polysorbate concentration and HLB value.

1. Introduction

Recent years have witnessed an upsurge in research on metal nanoparticles which exhibit novel chemical, optical and electronic properties. Among metal nanoparticles, copper nanoparticles (CuNPs) are attractive due to their catalytic [1–3], optical and electrical properties [4,5]. CuNPs are especially important because of their high electrical conductivity and catalytic activity thus providing a viable alternative to the more expensive metals like gold and silver. As the properties of CuNPs are size and shape dependent, therefore there have been extensive attempts to gain precise control over the size and shape of CuNPs [6–8]. However, the control of size and particularly shape at the nanometre level remains an unresolved problem till date. Another problem with CuNPs is their high reactivity towards atmospheric oxygen, so pure CuNPs in the metallic state are not easy to synthesize, a layer of copper

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oxide inevitably forms a surface covering over the CuNPs [9,10]. To stabilize pure CuNPs in the metallic state, usually a protective coating is applied. The most popular stabilizers used are surfactants and polymers [11–15]. More recently, a multilayer of graphene has been used to protect the surface of CuNPs [16].

Common synthetic protocols for CuNPs include chemical reduction [1,8,12,14], laser ablation [17], radiation method [18], sonochemical reduction [19] and microwave heating [20]. Among these, the wet chemical reduction is preferred due to its simplicity, low cost and easy optimization of reaction conditions. The basic drawback of this method is that it often results in broad NP size distributions. However, NP growth can be confined using appropriate surfactants. Surfactant molecules can form organized assemblies such as micelles, reverse micelles, microemulsions and vesicles which can serve either as microreactors or templates for the controlled growth of nanomaterials [21–24]. Surfactant molecules can also improve the stability of the system through electrostatic forces, steric factors, Vander Waals forces and sometimes via hydrophobic interactions. Some surfactants can lead to unidirectional growth along certain lattice planes by preferential adsorption along other planes [25].

In the past, there have been many successful attempts for the synthesis of stable CuNPs in surfactant media. Pileni et al. have widely used microemulsions formed by the anionic surfactant Aerosol OT (AOT) to synthesize stable CuNPs [12,26]. Other workers have synthesized CuNPs in AOT reverse micelles in supercritical solvents [27]. Microemulsions formed by TritonX-100 have also been used [28]. CuNPs have also been synthesized in micelles formed by cationic surfactants like cetyltrimethylammonium bromide (CTAB) [29,30]. It has been found that Cu-nanorods can be synthesized by fine tuning the surfactant concentration [30]. Pileni et al. [8] have also synthesized copper nanoparticles and nanorods via reduction of copper dodecylsulfate, $Cu(DS)_2$. Liu et al. [31] used sodium dodecylbenzene sulfonate (SDBS) to prepare size-controlled copper nanowires.

As the CuNP synthesis is often performed using $NaBH_4$ as reductant (it is a strong reducing agent), the CuNPs synthesized in aqueous solution have adhering negative charges. Therefore cationic and non-ionic surfactants will act as effective stabilizers/growth controllers. Keeping in mind the well-known cytotoxicity of some of the cationic surfactants like CTAB [32], it seemed useful to perform the synthesis in non-ionic surfactant media. Polysorbates or Tweens are non-ionic polymeric surfactants that are commonly used in the cosmetic and food industries and also in pharmaceutical formulations. Polysorbates are nontoxic surfactants that have been widely approved as pharmaceutical excipients for use in medicinal formulations [33]. In this work, we have used a homologous non-ionic surfactant series i.e. the polysorbates for CuNP synthesis. Polysorbate 60 is widely used as an emulsifier in the food industry [34]. Polysorbate 80 has been used for the synthesis of nobel metal nanoparticles in the past [35–40]. Use of other polysorbates is not so common. The synthetic procedure reported here is easy, inexpensive and green and may be integrated into a variety of biological and biomedical applications.

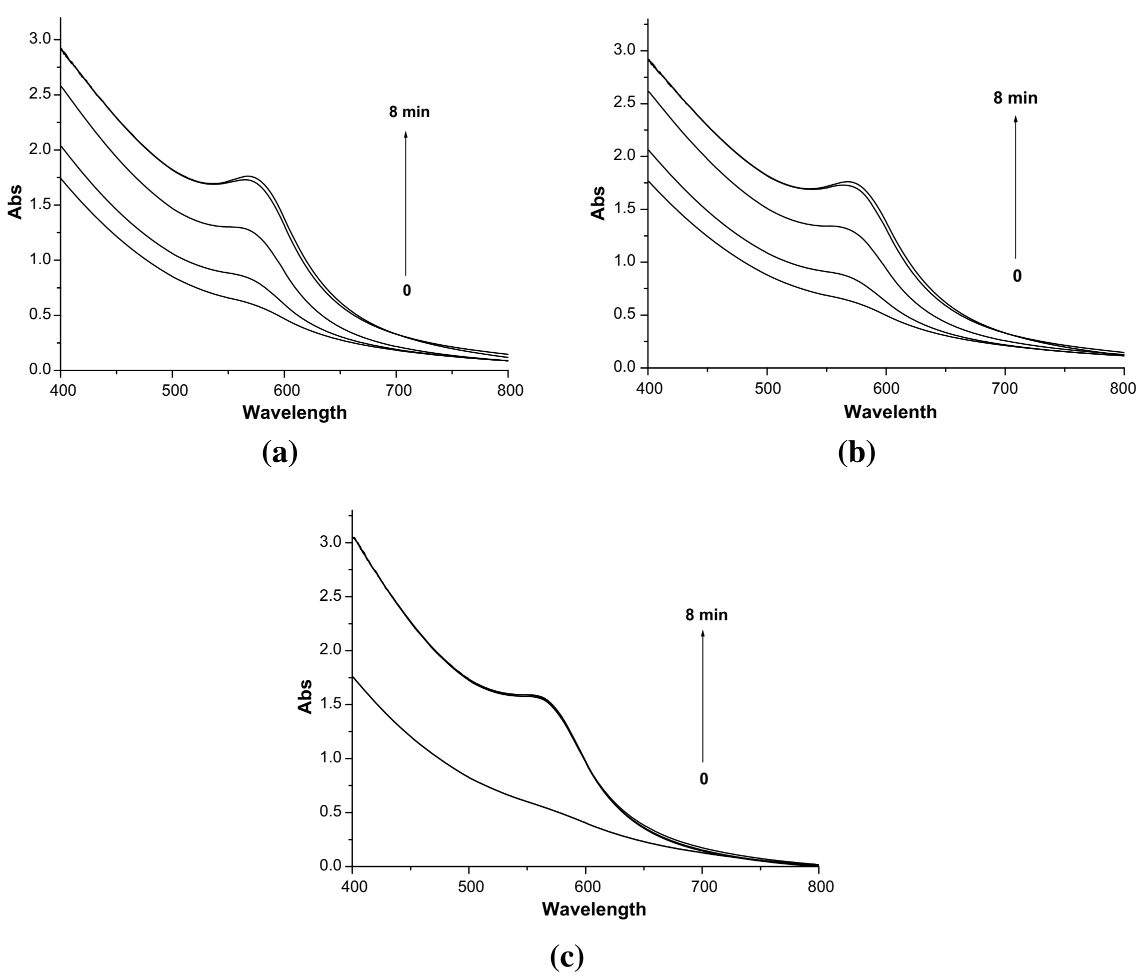

Fig. 1. Time evolution of CuNPs in polysorbate-20 micelles: (a) 1×10^{-4} M surfactant, (b) 5×10^{-4} M surfactant and (c) 5×10^{-3} M surfactant.