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Comparative Study on Morphological Changes of Copper Nanoparticles Synthesised in Different Non-Ionic Surfactant Series of Polysorbates

Suman Mandal
Department of Chemistry, Basirhat College, Basirhat North 24 Pargana -743412,
West Bengal, India

Corresponding Author's Email: sumanmandal83@gmail.com

ABSTRACT

Several techniques can be used to create metallic nanoparticles. The wet chemical technique is the most widely used of all. Coinage metal nanoparticles are highly appealing to novice researchers due to their versatility. Due to its low cost, copper has been utilized extensively as a precursor. A variety of surfactants are employed as capping agents to stop particle oxidation and agglomeration. Here, the nature and morphological alterations of Copper Nanoparticles (CuNPs) are examined using three distinct polysorbate surfactants at varied concentrations. Here concentrations are used on the basis of Critical Micellar Concentration (CMC) of each surfactant. The nature of the particles is compared using Transmission Electron Microscopy (TEM) examination, DLS research, and UV-visible spectroscopy. This research has successfully investigated the impact of various non-ionic polysorbate surfactant micelles on the morphological changes of CuNPs.

Keywords: *Copper Nanoparticles; Micelles; Non-Ionic Surfactants; Polysorbates*

Introduction

Research on metal nanoparticles with unique chemical, optical, and electrical properties has increased recently. The catalytic (Crooks *et al*., 2001; Vitulli *et al*., 2002; Dhas, Raj & Gedanken, 1998), optical, and electrical properties (Athanassiou, Grass & Stark, 2006 ; Chen & Sommers, 2001) of copper nanoparticles (CuNPs) make them appealing among metal nanoparticles. CuNPs are particularly significant because of their high catalytic activity and electrical conductivity, which make them a good substitute for more costly metals like silver and gold. There have been numerous attempts to precisely control the size and shape of CuNPs because their properties depend on their size and shape (Lisiecki, Billoudet & Pileni, 1996; Mott *et al.*, 2007; Zhu, Zhang & Yin, 2005). Controlling size, and especially shape, at the nanoscale level is still an unsolved issue, though. A layer of copper oxide invariably forms a surface covering over the CuNPs (Chen *et al.*, 2005; Gao *et al*., 2001) due to their high reactivity towards air oxygen, which makes it difficult to synthesise pure CuNPs in their metallic state. Pure CuNPs are typically stabilised in their metallic state by applying a protective covering. Polymers and surfactants are the most often used stabilisers (Dang *et al.*, 2011; Salkar *et al*., 2000; Pootawang, Saito & Lee, 2013; Nandi, Gupta, & Banthia, 2002; Pileni *et al.*, 1998). More recently, the surface of CuNPs has been shielded by a graphene multilayer (Wang *et al*., 2012).

Chemical reduction, thermal decomposition, radiation techniques (Joshi *et al*., 1998), laser ablation (Liu *et al*., 2012), sonochemical reduction (Kumar *et al*., 2001), and microwave heating (Tu & Liu, 2000) are common synthetic procedures for CuNPs. Because of its ease of use, affordability, and ease of reaction condition optimisation, wet chemical reduction is the most popular of these. This method's main flaw is that it frequently produces wide NP size distributions. However, with the right surfactants, NP growth can be controlled. Micelles, reverse micelles, microemulsions, and vesicles are examples of ordered assemblies (Barnickel & Wokaun, 1990; Schramm, Stasiuk & Marangoni, 2003; Zhang & Han, 2003; Evans & Needham, 1987) that surfactant molecules can produce. These assemblies can be used as templates or microreactors to control the formation of nanomaterials. Through steric factors, Van der Waals forces, electrostatic forces, and occasionally hydrophobic interactions, surfactant molecules can also increase the system's stability. Certain surfactants exhibit preferential adsorption along other lattice planes, which can result in unidirectional growth along those planes (Jana, Gearheart & Murphy, 2001).

Numerous successful attempts to synthesise stable CuNPs in surfactant media have been made in the past. Pileni *et al*. (1998) have synthesised stable CuNPs in AOT [sodium bis(2-ethylhexyl) sulfosuccinate] reverse micelles (Cason & Roberts, 2000) in supercritical solvents. Other workers have synthesised CuNPs in AOT reverse micelles in supercritical solvents (Qi, Ma & Shen, 1997). CuNPs have also been synthesised in micelles formed by cationic surfactants such as Cetyltrimethylammonium Bromide (CTAB) (Wu & Chen, 2004; De & Mandal, 2013). It has been discovered that Cu-nanorods can be produced by fine-tuning the surfactant concentration.

Since $NaBH_4$ is a potent reducing agent and is frequently used in CuNP synthesis, the CuNPs produced in aqueous solution contain adherent negative charges. Consequently, both cationic and non-ionic surfactants will function as efficient growth controllers and stabilisers. It could be beneficial to carry out the synthesis in a non-ionic surfactant medium given the well-known cytotoxicity of several cationic surfactants, such as CTAB (Alkilany *et al.*, 2009). Non-ionic polymeric surfactants known as polysorbates or Tweens are frequently utilised in food and cosmetic products as well as in pharmaceutical formulations. Nontoxic surfactants known as polysorbates are frequently authorised pharmaceutical excipients for use in pharmaceutical formulations (O'Sullivan, Wood & O'Brien, 2004). The polysorbates for CuNP synthesis are a homologous non-ionic surfactant series that I have used in this work. In the food sector, polysorbate 60 is frequently used as an emulsifier (Dalgleish, Srinivasan & Sing, 1995). Noble metal nanoparticles have previously been synthesised using polysorbate 80 (Duy *et al.*, 2010; Premkumar *et al*., 2007; Habibi, Kamrani & Mokhtari, 2010; Koroleva *et al.*, 2011; Li *et al.*, 2012; Hormozi-Nezhad, Karami & Roberjazi, 2013). Other polysorbates are not used as frequently. The synthetic process described here is simple, affordable, environmentally friendly, and can be used in a range of biological and biomedical applications. This article has been written in a revised way on my published paper (Mandal & De, 2015).

Experiment

Materials

Analytical grade (AR) compounds were all utilised without additional purification. Polyoxyethylene Sorbitan Monolaurate (Tween 20), Polyoxyethylene Sorbitan Monopalmitate (Tween 40) and Polyoxyethylene sorbitan monostearate (Tween 60) are non-ionic surfactants that were acquired from E-Merck and utilised accordingly. To create the appropriate solutions, measured volumes of Tween 20, Tween 40, and Tween 60 were dissolved in water. E. Merck, Germany, was also the source of sodium borohydride ($NaBH_4$). Copper sulphate was the precursor salt utilised to create copper nanoparticles. All of the water used in the synthesis process was double-distilled and deionised.

Methodology

Freshly aqueous polysorbate solutions (Tween 20/polysorbate 20, Tween 40/polysorbate 40 and Tween 60/polysorbate 60) of different concentrations (maintaining CMC of all the polysorbates) were made and mixed with aliquots of $CuSO_4$ stock solution to synthesise copper nanoparticles (Lisiecki, Billoudet & Pileni, 1996) in an aqueous surfactant media of different polysorbates. After that, the necessary volume of ice-cold NaBH4 solution was added. Immediately a mild brownish colouration developed. After that, the mixture was sonicated for 30 minutes, which resulted in the formation of a clear, stable brown solution. All of the experiments were conducted using bubbling nitrogen gas in an inert atmosphere.

$CuSO_4 + 2NaBH_4 + 6H_2O \rightarrow Cu + 2H_3BO_3 + 7H_2\uparrow + Na_2SO_4$

Characterisation

A Shimadzu spectrophotometer, Model No. UV2401PC, was used to capture the absorption spectra of the resultant nanoparticles. Dynamic light scattering (DLS), performed in a Nano-ZS (Malvern) apparatus equipped with a 4 mW He-Ne laser (λ= 632 nm), was used to determine the size distribution and hydrodynamic radii. A 0.2 μm filter was used to filter the solutions to create the samples for this investigation. The nanoparticles were studied using Transmission Electron Microscopy (TEM) at a resolution of 1.9 using a Japanese JEOL, JEM-2100 electron microscope. Microdrops of solution were applied on a carbon sheet that was held up by a copper grid to create TEM specimens.

Results and Discussion

Copper nanoparticles in aqueous solutions of three different concentrations of all the surfactants are made with the wet chemical reduction process. Different colorations of the sample indicates the distinct natures of the synthesised CuNPs. The different stability of the colorations tells the effect of the surfactants of varying concentration. To investigate the complete morphology of the CuNPs synthesised in the surfactants, UV-vis spectroscopy, DLS technique and transmission electron microscopy analysis are used here.

Metal nanoparticles with surface plasmon peaks in UV-vis spectroscopy are the common features. Copper nanoparticles show this peak in the visible region of 550 nm to 570 nm (Creighton & Eadon, 1991). Various research revealed that peak positions may change due to particle nature, which may depend on the surfactants. Here, a series of polysorbates (Tween 20, Tween 40, and Tween 60) are used as surfactants, and stable CuNPs were synthesised in different concentrations of aqueous solutions of the surfactants. Polysorbates with different hydrophobicity are used here, and Tween 60 is the most hydrophobic surfactant among all the polysorbates used. Hydrophobicity of the surfactant may affect the stability of the CuNPs and their sizes, which is reflected in the UV-vis spectra with different SPR peak positions of CuNPs.

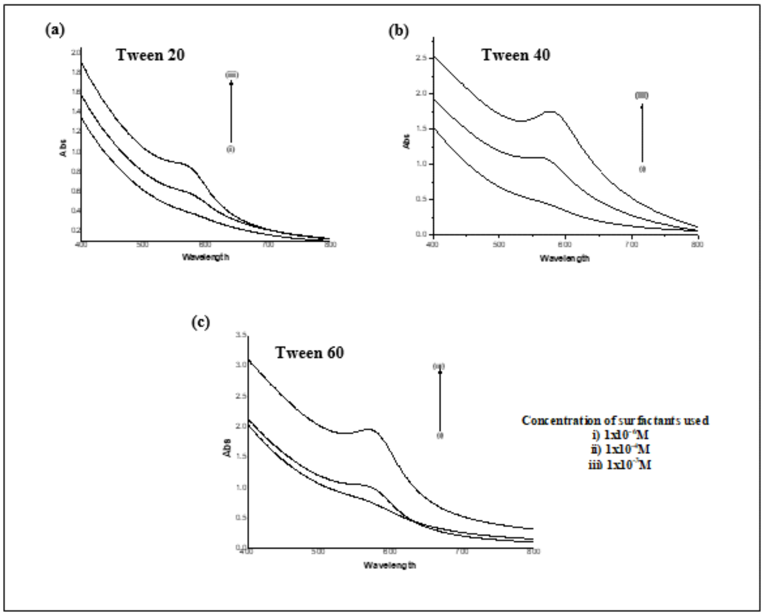


Figure 1: Absorption Spectra of CuNPs in Various Concentrations of Different Polysorbates (Mandal & De, 2015)

SPR peak position is related to the particle sizes. Particles with tiny diameters are produced in high concentrations of all the polysorbate surfactants (Creighton & Eadon, 1991). Figure 1 shows the temporal evolution of the SPR peak of CuNPs at various concentrations of polysorbates.

The dynamic light scattering (DLS) technique is the important technique for detecting the particle nature present in the aqueous medium. It helps to find out the hydrodynamic radius of the particles and their electronic charge. I.e., the technique can reveal the particle sizes and their environments in the aqueous medium. Capping agents like surfactants, polymers, proteins, and carbohydrates are used to restrict the particles' agglomeration and oxidation.

Here, different polysorbates (Scheme 1) of a homologous series are used to prevent the agglomeration of the synthesised CuNPs. High hydrodynamic sizes of the particles are due to agglomeration. Being less hydrophobic, the Tween 20 surfactants can form micelles in tiny sizes (Figure 2b) with respect to other polysorbates. Critical Micellar Concentration (CMC) is the important factor that measures the micelle formation in the aqueous medium. Below CMC, micelle formation is not possible, so it is expected there should be a lack of stability of the CuNPs; i.e., agglomeration (Figure 2a) may be the outcome of that. With two different concentrations of all the surfactants used to investigate the particle's nature in the DLS technique. The size distribution and number distribution curve show the different natures of the CUNPs in various concentrations of Tween 20, Tween 40, and Tween 60, respectively. From the DLS study, it has been observed that above the CMC of each surfactant helps to produce CuNPs of average size below 40 nm (except Tween 60) (Figures 2b, 2c, 2d), while in low concentrations of surfactant, approximately 100 nm (Figure 2a) of CuNPs are synthesised.

Table 1: Tabular form of HBL and CMC Values of Different Polysorbates

Name of the surfactants	CMC Value	HLB Value	Used Concentration (bellow CMC)	UsedConcentration (above CMC)
Tween-20	5.9 x10^{-5}M	16.7	1x10^{-6}M	1x10^{-3}M
Tween-40	2.7x10^{-5}M	15.6	1x10^{-6}M	1x10^{-3}M
Tween-60	2.3x10^{-6} M	14.9	1x10^{-6}M	1x10^{-3}M

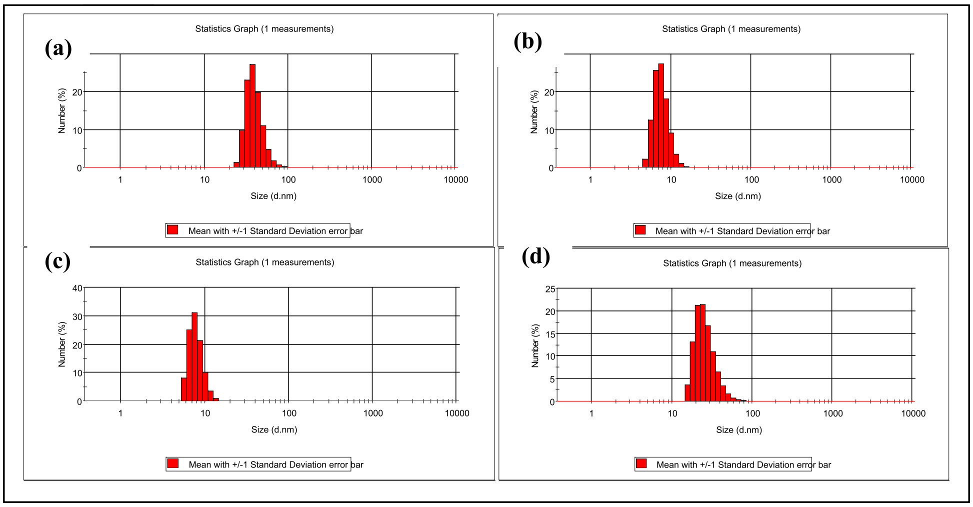
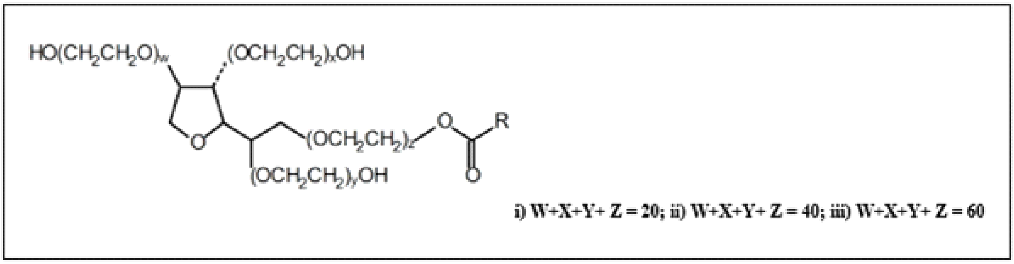


Figure 2: Size Distribution Plots of CuNPs Obtained from DLS Data at Surfactant Concentration 1x10-6M b) at 1x10-3M Tween 20; c) 1x10-3M Tween 40; c) 1x10-3M Tween 60 (Mandal & De, 2015)

In comparison to the surfactants of the polysorbate series, it has been found that Tween-60, being highly hydrophobic in nature and having a lower hydrophilic-lipophilic balance (HLB) value, can form micelles of greater size with respect to other surfactants



Scheme 1: Molecular structure of polysorbate) Tween 20 ii) Tween 40 iii) Tween 60

Transmission electron microscopy gives pictorial images of the CuNPs synthesised in various concentrations of aqueous solutions of polysorbates. The nature of the particles on the basis of crystallinity or amorphousness may be found out by this analysis. Crystal planes can be calculated from TEM. Two different concentrations of each polysorbate surfactant are used here. One is below CMC, and the other is above CMC for the corresponding surfactant. The concentration of Cu^{2+} ion used is $5x10^{-3}$ M, and $1x10^{-2}$ M $NaBH_4$ solution is used as a reducing agent.

Polysorbate 20 at a lower concentration of 1x10-6M, i.e., below its CMC, is not so helpful to produce stable micelles and so allow CuNPs in aerial oxidation. Oxides of CuNPs are attached to each other due to static electric forces, and agglomeration (Figure 3a) occurred. At the high concentration of 1x10-3M (> CMC), the polysorbate 20 forms stable micelles of small size that allow for the formation of 10 nm spherical CuNPs (Figure 3b) by a favourable reduction process with $NaBH_4$ in colloidal solution.

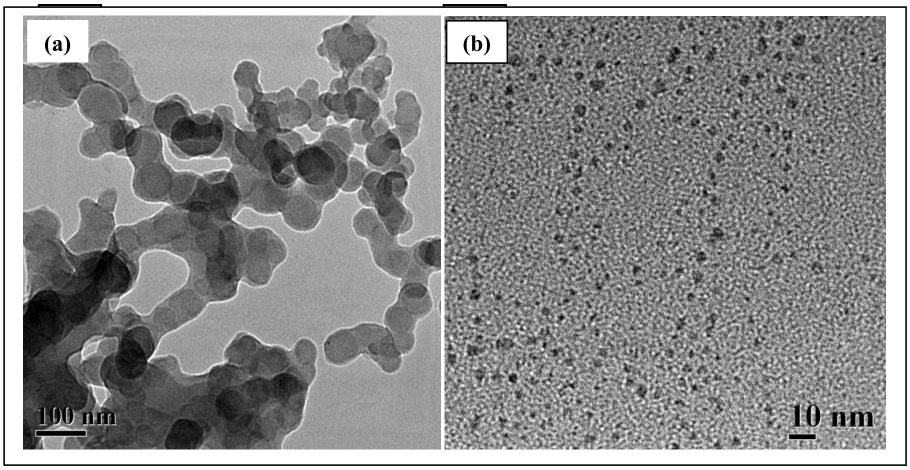


Figure 3: TEM Images of CuNPs in Different Concentrations of Polysorbate 20; a) 1x10-6M b) $1x10^{-3}$M (Mandal & De, 2015)

Like polysorbate 20, polysorbate 40 at its lower concentration of 1x10-6M shows the tendency of oxide formation, but from the TEM image, a honeycomb pattern (Figure 4a) of CuNPs is observed. Further increasing the concentration of the surfactant solution may form micelles of uniform spherical size that can help to build up the crystallinity of those synthesised spherical CuNPs (Figure 4b) in the micelles. The SAED pattern (Figure 4c) of the sample shows the metallic CuNPs feature a face-centred cubic lattice. The fringe patterns correspond to the (200), (222), (311) and (333) planes of metallic copper. i.e., polysorbate 40 is very helpful to produce well-shaped spherical CuNPs.

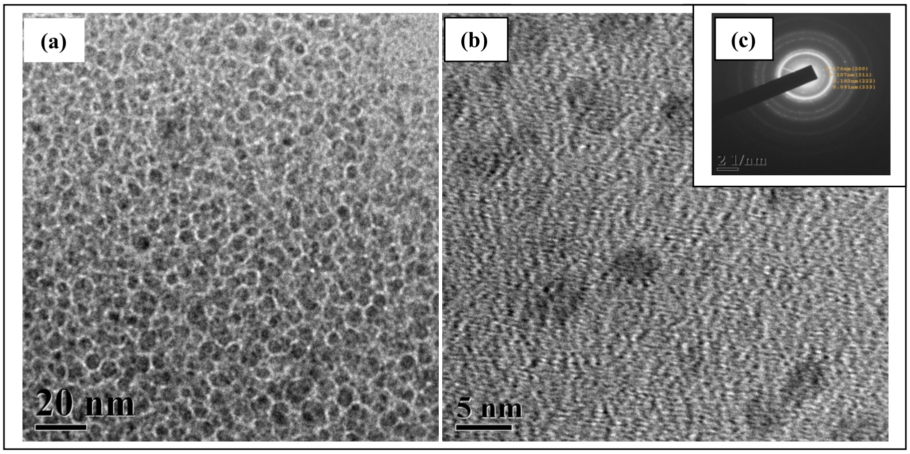


Figure 4: TEM Images of CuNPs in Different Concentrations of Polysorbate 40; a) 1x10-6M b) 1x10-^{3}M (Mandal & De, 2015)

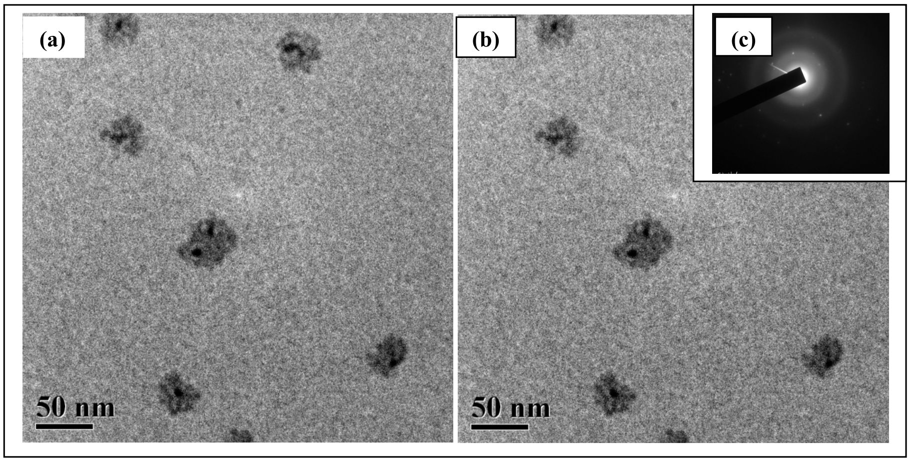
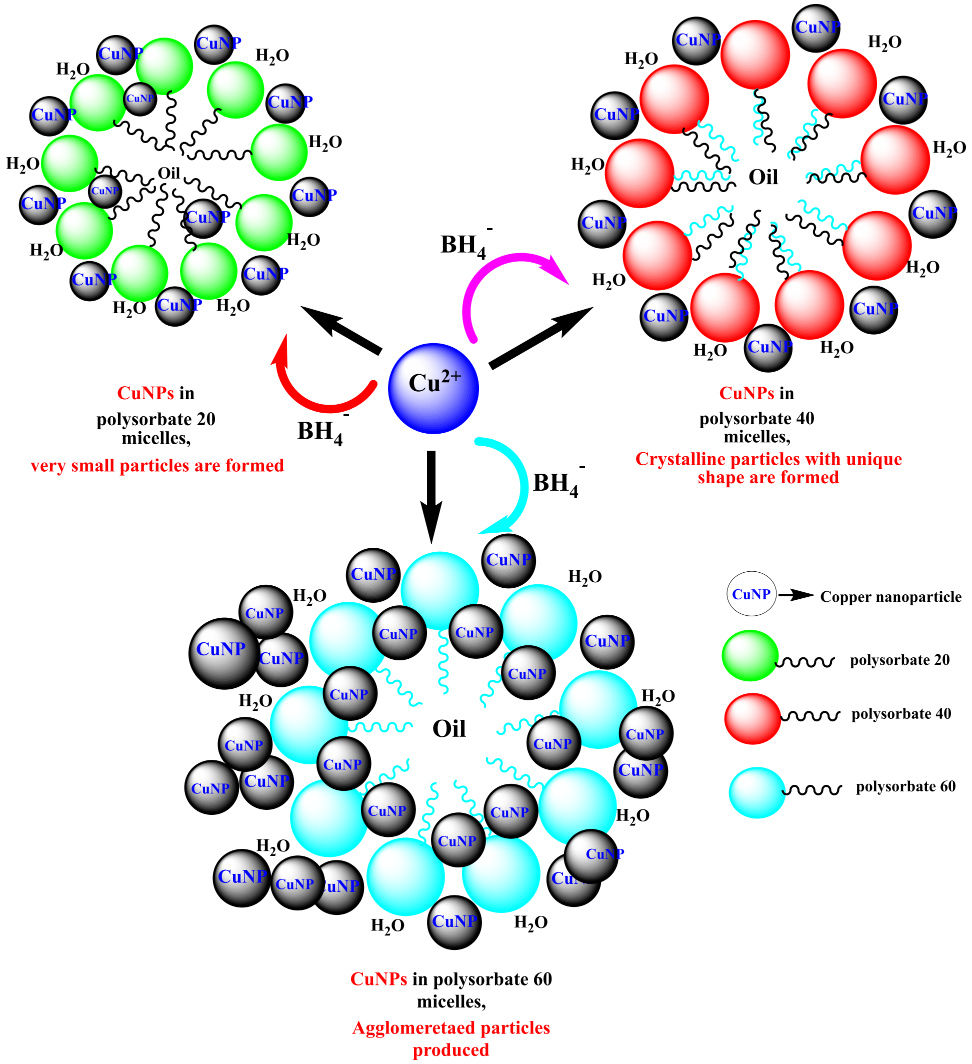


Figure 5: TEM Images of CuNPs in Different Concentrations of Polysorbate 60; a) 1x10^{-6}M b) 1x10^{-3}M (Mandal & De, 2015)

From the UV-visible spectra and DLS data, it was expected that particles synthesised in polysorbate 60 would not be so attractive. The nature of the particles in both concentrations is bigger and clumsier (Figures 5a & 5b). The SAED pattern (Figure 5c) also shows the amorphous nature of the particles. Here, the concentrations of $1x10^{-6}$M and $1x10^{-3}$M are used for TEM analysis. The agglomerated particles may be produced due to the labile and bigger micelle formation, which is not so useful for capping the CuNPs in the aqueous medium; i.e., in polysorbate 60, the CuNPs get oxidised, and so the particle size increases to 60 nm.



Scheme 2: Schematic Diagram of Synthetic Protocol of CuNPs

In this experiment, three different types of polysorbates are used on the basis of HLB value; polysorbate 60 is highly hydrophobic, and polysorbate 20 is the least hydrophobic in nature. Micelle formation is related to HLB values and CMC values.

Micelles allow the Cu^{2+} ions into their core and help to form CuNPs by $BH4^{-}$ ions. Below CMC, all surfactants are unable to form micelles, so CuNPs do not get any help from surfactants, i.e., at very low concentrations, synthesised CuNPs become agglomerated and oxidised to form copper oxides. Above CMC, polysorbate molecules can form micelles that can form a framework for producing stable nanoparticles (Scheme 2). Due to different HBL values, the types of the micelles will be different, and their intermolecular interactions will also be different. It may be expected that due to the greater hydrophobicity of polysorbate 60, it can form micelles with a lower density of surfactant molecules. So synthesised CuNPs are not so much capped by micelles; i.e., in this circumstance, agglomerated CuNPs are formed. On the other hand, polysorbate 20, being less hydrophobic (HLB value 16.7), can form close-packed, small-sized micelles in which CuNPs can form with uniform shapes and sizes. No agglomeration can be seen above the CMC concentration (1x10-3M) of the polysorbate 20. Absorption spectra (Figure 1) of CuNPs in various concentrations of different polysorbates gave the idea initially. With increasing the concentration of all the surfactants, the nature of the plot of CuNPs changes in a similar fashion. The tendency of agglomeration in low concentrations of polysorbate 20 (Figure 1(a)-i) is there. This is very much similar to Figure 1(b) & Figure 1(c). i.e., broad spectra. In the case of high concentration, the nature of the plasmon peaks is different; that may be due to the change of particle nature. It has been clearly seen with the resemblance of DLS data and TEM images of CuNPs. Below 10 nm of particles are formed in a $1x10^{-3}$ M concentration of polysorbate 20 solution. The polysorbate 40 with an intermediate HLB value can form stable micelles with a uniform size that can allow for the formation of CuNPs with unique crystallinity (Figures 4b & 4c).

Conclusion

This work is a simple work in which a comparative study on different polysorbates of the same homologous series has been done successfully. The comparison is on the basis of copper nanoparticle synthesis in different concentrations of polysorbate surfactant micelles. The morphological changes of the CuNPs have been investigated successfully. It has been revealed that at very low concentrations of polysorbate surfactants, i.e., below CMC, CuNPs get agglomerated and oxidised. Among all the polysorbates (Tween 20, Tween 40 & Tween 60), Tween 40 is very helpful to produce stable micelles of unique shape that help to synthesise spherical and crystalline CuNPs.

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