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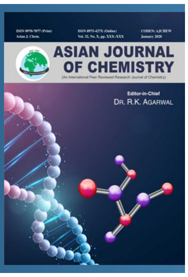

Synthesis and Characterization of Surfactant Assisted Copper Nanomaterials

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In this work, a simple and low cost synthetic method for four different copper nanomaterials having uniform shape and size using copper(II) acetate and *cis-bis*(glycinato)copper(II) complex in presence of non-ionic surfactants Tween-80 and Triton X-100 in the presence of ascorbic acid as reducing agent is described. The synthesized nanomaterials were characterized using FT-IR, UV-visible, powder XRD, EDX and SEM techniques. The characterization data reveals that all the copper nanomaterials formed are less than 30 nm size with spherical shape.

Keywords: Copper nanomaterials, Non-ionic surfactants, Tween-80, Triton X-100, Copper(II) acetate.

INTRODUCTION

In recent years, copper nanoparticles (CuNPs) have attracted attention of inorganic chemists in research field due to their significant optical and electrical properties and low cost [1,2]. In addition, copper nanoparticles show wide variety of applications such as conducting properties [3-9], printed circuit boards (PCBs), thermal, magnetic, antimicrobial, electronic [10-14], light emitting diodes (LED) [14], catalytic [15-18], and biocompatibility [19,20], lubricants [21], conductive inks [11,22], energy conversion [23], biosensors [24], antibiofouling agents [25] and cancer cell treatments [26]. Moreover, copper nanoparticles can be a good alternative candidate in comparison to expensive noble metal nanoparticles *viz*. silver and gold [27-29].

Literature review revealed that various methods [1,2,11, 13,30-39] are adotoped to synthesize the CuNPs. Among them, chemical reduction is one of the most convenient methods for the synthesis of CuNPs due to simple, faster, cleaner, economical and even can control the size and shape easily. As the copper nanoparticles are unstable in solution state, the reaction has been performed in non-aqueous medium [40]. In this context, ascorbic acid oftenly used as reducing agent and/or antioxidant of colloidal copper [41] and surfactants [35-38,42-44] were applied to the synthetic system as dispersant or modifier to control the morphology of the nanoparticles.

The synthesis of copper nanomaterial in the presence of non-ionic surfactants Tween-80 and Triton X-100 along with triphenyl phosphine as reducuing agent using bis(acetylacetonato)copper(II) was repoted in literature [45]. However, to the best of our knowledge no report has been found in the literature for the synthesis of copper nanomaterials from *cis-bis* (glycinato)copper(II) complex in presence of surfactants as a stabilizing agent and ascorbic acid as reducing agent. Thus, it is considered worthwhile to synthesize and characterize the copper nanomaterial obtained using copper substrate in the form of complex/salt in presence of surfactants and reducing agent ascorbic acid to achieve uniform shape and size.

EXPERIMENTAL

The analytical reagent grade chemicals *viz*. copper sulphate pentahydrate from Qualigens, copper(II) acetate monohydrate and L-ascorbic acid from Merck, Triton X-100 and Tween-80 from BDH, India were procured and used without further purification. Deionized water was used throughout the experiment for preparing the solutions.

Synthesis of *cis-bis*(glycinato)copper(II) complex [$Cu(gly)_2$]: To a 25 mL of hot aqueous solution of glycine (1.5 g), added 1:1 ethanolic solution of copper(II) acetate, then stirred for 5 min. The resulting solution was cooled on ice bath to get the precipitation, which was filtrated and washed with ethanol and dried in air. Yield: 1.16 g (62%).

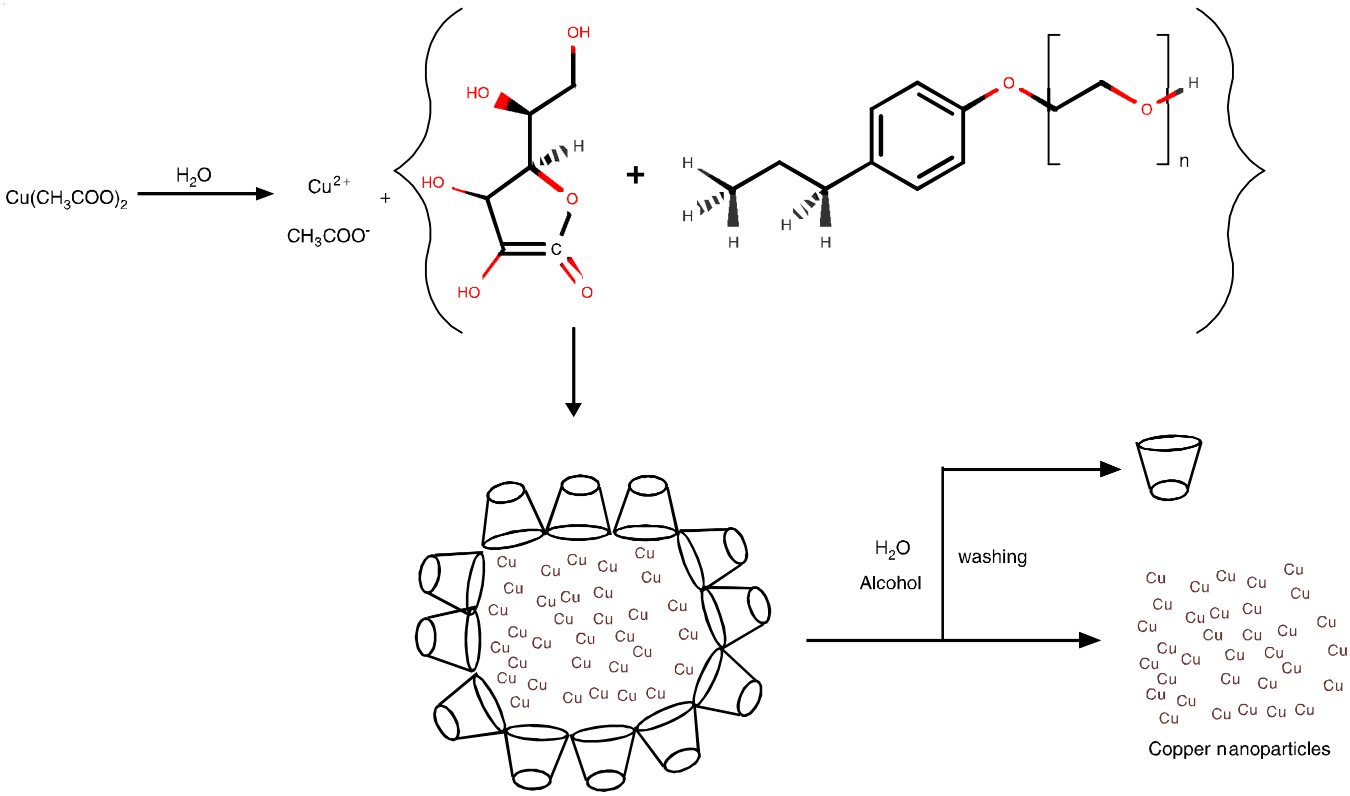
Synthesis of copper nanoparticles using *cis*-*bis*(glycinato)copper(II) complex/copper(II) acetate: Copper nanomaterials were synthesized using *bis*(glycine)copper(II) complex and copper(II) acetate in presence surfactants Tween-80/Triton-X 100 and ascorbic acid as reducing agent by following the nanoprecipitation method [46]. In brief, 2.3 g of *cis*-*bis*-(glycinato)copper(II) complex or cupric acetate mono hydrate dissolved in 40 mL of distilled water was added to 10 mL of 1:1 ethanolic solution of Tween-80/Triton-X 100 (surfactant), then contents were stirred for 5 min. Finally, ascorbic acid (1 g) dissolved in 15 mL distilled water was added to the solution of complex in the surfactant. The reaction mixture was heated on a hot plate at 80 ºC for 1 h. Brown coloured shiny solid particles were formed at the bottom of the beaker and collected in a sintered glass crucible. Metal particles were washed with distilled water and anhydrous ethanol (5 mL) to remove unreacted precursors. Finally, brown powder was dried at room temperature to obtain CuNPs. The CuNPs are sensitive to air and tend to from copper(II) oxide nanoparticles. Thus, the formation of CuNPs was achieved by using reducing and stabilizing agent. Yield: **CGT** (Cu(gly)$_2$ + Tween-80): 0.3 g (34% as CuO, 43% as Cu), **CAT** (copper(II) acetate + Tween-80): 0.65 g, (75% as CuO; 95% as Cu), **CGX** (Cu(gly)$_2$ + Triton-X 100): 0.24 g (27% as CuO, 35% as Cu), **CAX** (copper(II) acetate + Triton-X 100): 0.6 g (69% as CuO; 87 % as Cu).

Instrumentation: The X-ray diffraction (XRD) study was carried out to analyze the phase and the crystallite size of the samples using X-ray diffractometer (XRD, Smart Lab SE, Rigaku Corporation) with 0.15405 nm CuKα radiation source in the 2θ range from 5º to 90º (40 KV, 30 mA, step size 0.010, scan rate 10.00 min^{-1}). The surface morphology of the sample was obtained using scanning electron mocroscopy (JEOL, JSM-IT500 in TouchScope). Energy dispersive X-ray (EDX) analysis was carried out with JEOL JSM-IT500 for composition analysis. FT-IR spectra of present samples were recorded in the 4000-500 cm^{-1} region on a Perkin-Elmer spectrum 100 spectrometer. The UV-visible spectroscopy of the nanomaterials was recorded in the region of 200-500 nm on ELICO, SL 210 UV-visible spectro-photomter.

RESULTS AND DISCUSSION

In the synthesis of copper nanoparticles, controlling of the particle size, particle shape and morphology are the important features. Hence, in the present work, uniform size and shape of the particles controlled by using the different surfactants (Tween-80/Triton-X 100). The progress of the reaction was monitered by observing the changing of the colour from blue to brownish colour of the solution on addition of reagents.

Mechanism: The mechanism of copper nanomaterials formation is shown in **Scheme-I**. The copper acetate dissolved in water and dissociates in to Cu^{2+} and CH$_3$COO$^-$ ions. Then Cu(II) is reduced to Cu(0) by reduction action of ascorbic acid, forming metallic copper nuclei, which initiate the growth stage. Growing nanoparticles were stabilized by surfactant molecules such as Triton X-100/Tween 80 distributed around them. These agglomerates grow to certain size due to the difference in water solubility of surfactant, eventually precipitated. Finally, the surfactant



Scheme-I: Synthetic mechanism of copper nanomaterials molecules present in precipitate were removed by washing with water and ethanol, and thus obtained the pure CuNPs.

UV-visible studies: The UV-visible spectra of all CuNPs in ethanol are shown in Fig. 1. It is well known that the position and shape of plasmon absorption of metal nanoparticle are strongly dependent on the particle size, dielectric medium and surface adsorbed species. Hence, from the Mie′s theory [47], single SPR peak was expected for spherical nanoparticles whereas anisotropic shape particles could give two or more SPR peaks depending on the shape of the particle. The results of the present nanoparticles indicate to have anisotropic shapes.

IR studies: The FTIR spectra of the copper nanoparticles are shown in Fig. 2. In IR spectrum, Tween-80 bands at 3434, 2923, 2869, 1604 and 1100 cm^{-1} are may be due to the O-H stretching vibrations, asymmetric (ν_{as}) and symmetric (ν_{sym}) stretching vibrations of methylene (-CH$_2$), C=O stretching of the ester group, respectively. The nanoparticles derived from Tween-80 (CAT and CGT) also showed the less intense bands which indicate that nanoparticles are capped with surfactants for stability. Similarly, the IR spectrum of Triton X-100 also shown 3434, 2904, 1607, 1510, 1455 cm^{-1} indicates the presence of O-H stretching vibrations, asymmetric (ν_{as}) and symmetric (ν_{sym}) stretching vibrations of methylene (-CH$_2$), C=C skeletal vibration of phenyl group, respectively. The change in these stretching vibrations indicate that the nanoparticles derived from Triton X-100 (CAX, CGX) the change in these strectuing vibrations indicates the caping of some unreacted sufactants with nanoparticles.

XRD studies: Typical XRD patterns of CGT, CGX, CAT and CAX are shown in Fig. 3. The calculated peak indexing data by using simple indexing method and *d*-spaing method, corresponding data are given in Table-1. The 2θ values 43.32° and 50.53° correspond to hkl of (111) and (200) planes of copper (JCPDS copper file No. 04-0836) related to the face centered cubic (FCC) phase with Fm$\bar{3}$m (No. 225) space group (JCPDF card No. 85-1326). Similarly peaks at 2θ values of 36.66° and 63.50° corresponds to (100) and (211) to the body centered cubic (BCC) phase. Based on the XRD pattern, it may be inferred that the CGT copper nanoparticles are formed in mixed phases (*i.e.* BCC + FCC).

From XRD analysis, the average particle size has been calculated by using Debye-Scherrer formula [48-51]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is wavelength of X-ray (0.1541 nm), β is FWHM (full width at half maximum), θ is the diffraction angle and D is particle diameter size. The calculated particle size data are

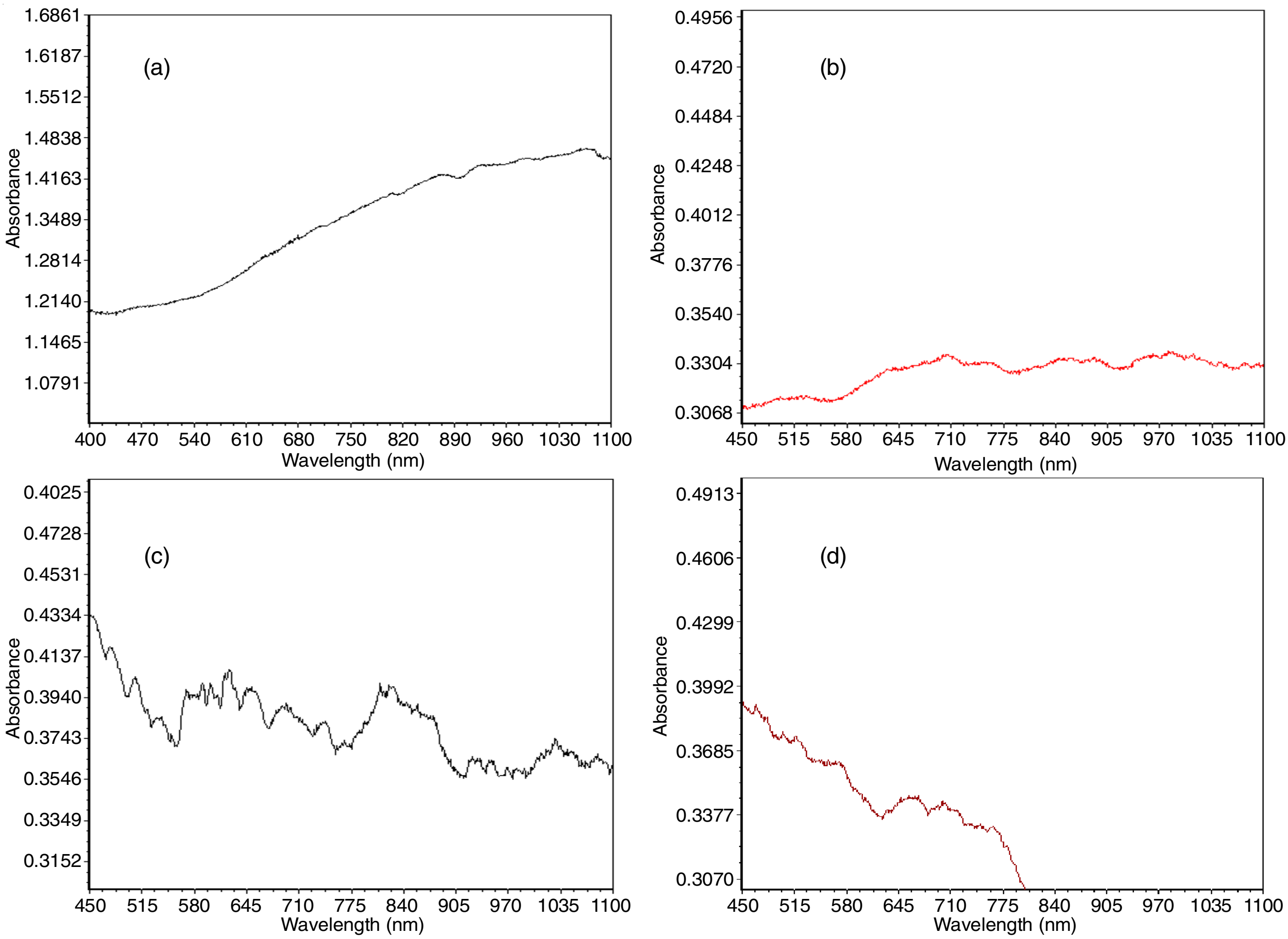


Fig. 1. UV-visible spectrum of (a) CGT (b) CGX (c) CAT (d) CAX nanomaterials

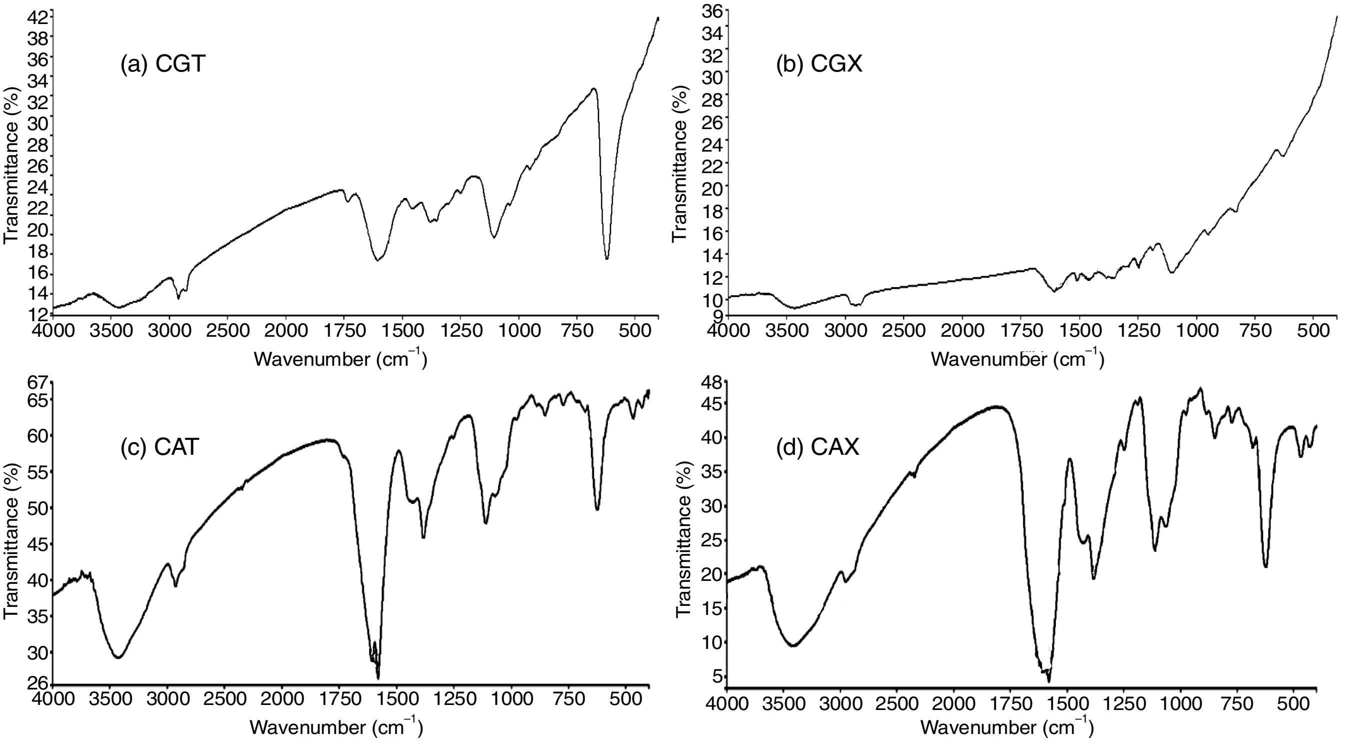


Fig. 2. FTIR spectrum of (a) CGT (b) CGX (c) CAT (d) CAX nanomaterials in KBr medium

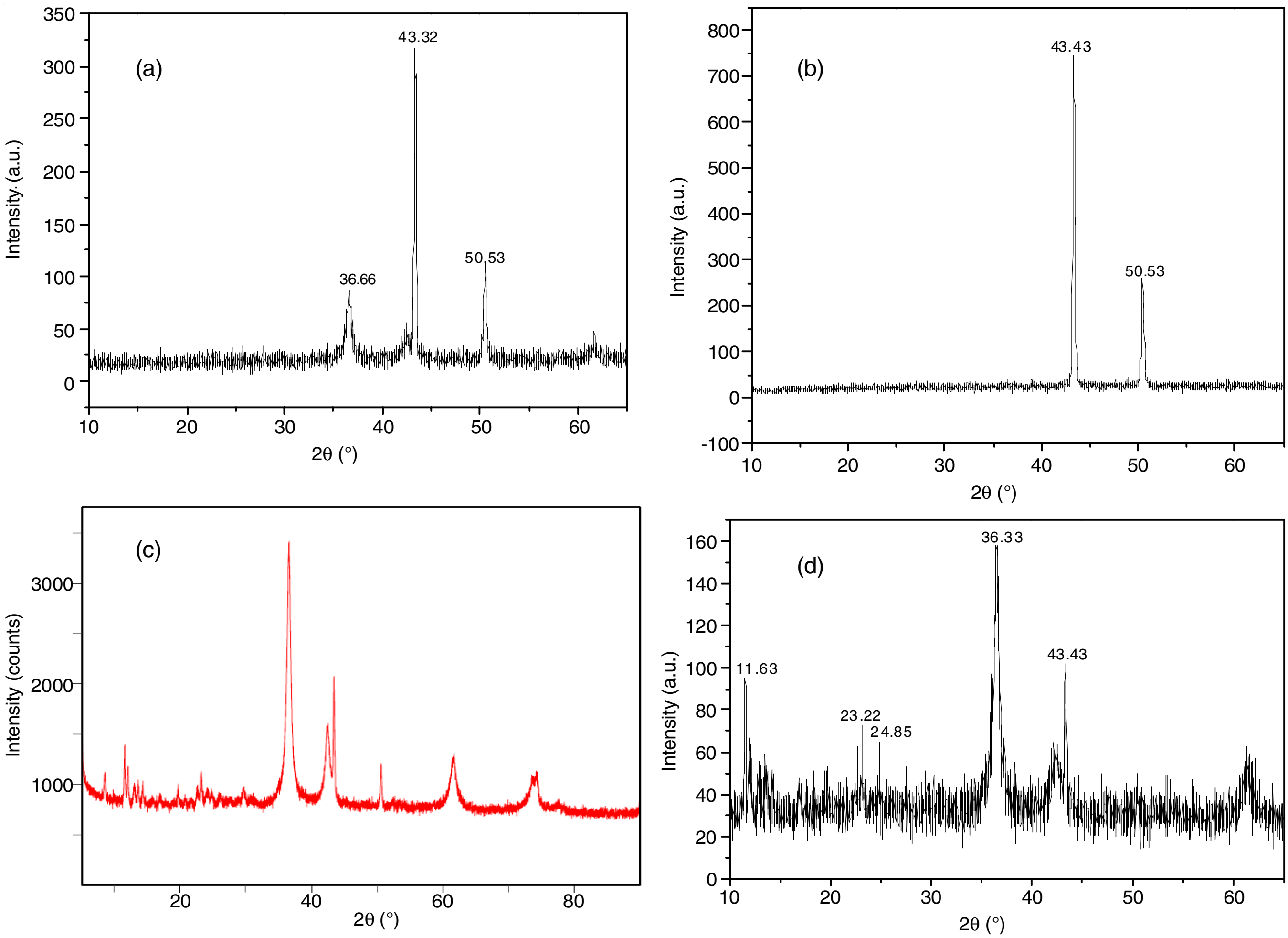


Fig. 3. Powder diffractogram of (a) CGT (b) CGX (c) CAT (d) CAX nanomaterials

TABLE-1
PEAK INDEXING A DATA OF COPPER NAOPARTICLES

Nanoparticle	Peak index method					d-spacing method			
	Peak position (2θ)	1000xSin²θ	1000xSin²θ/ 45.86	Reflection	Remarks	d	1000/d²	(1000/d²)/77.51	hkl
CGT	36.66	98.903	2.150	110	$1^2 + 1^2 + 0^2 = 2$	2.45	166.59	2.149	110
	43.32	136.233	2.970	111	$1^2 + 1^2 + 1^2 = 3$	2.08	231.13	2.982	111
	50.53	182.095	3.970	200	$2^2 + 0^2 + 0^2 = 4$	1.80	308.64	3.982	200
	63.50	276.900	6.030	211	$2^2 + 1^2 + 1^2 = 6$	1.46	469.13	6.052	211
CGX	43.43	136.832	3.020	111	$1^2 + 1^2 + 1^2 = 3$	2.08	231.13	2.982	111
	50.53	182.095	4.020	200	$2^2 + 0^2 + 0^2 = 4$	1.80	308.64	3.982	200
CAX	24.85	46.257	0.909	100	$1^2 + 0^2 + 0^2 = 1$	0.358	7791	0.909	100
	36.33	97.139	1.900	110	$1^2 + 1^2 + 0^2 = 2$	0.247	16362	1.909	110
	43.43	136.832	2.680	111	$1^2 + 1^2 + 1^2 = 3$	0.208	23048	2.689	111
CAT	36.51	98.123	2.154	(110)	$1^2 + 1^2 + 0^2 = 2$	2.45	166.59	1.888	110
	43.34	136.353	3.003	(111)	$1^2 + 1^2 + 1^2 = 3$	2.13	220.41	2.498	111
	50.49	181.893	3.994	(200)	$2^2 + 0^2 + 0^2 = 4$	1.80	308.64	3.498	200

given in Table-2, which indicates that the particle size is less than 30 nm. The results of XRD analysis for CGX, CAT and CAX also observed mixed FCC and BCC phases with Fm$\bar{3}$m space group [52,53].

EDX studies: EDX analysis data indicate that all the nanoparticles were capped with surfactants or unreacted surfactant remains on surface of the copper nanoparticles (Fig. 4).

TABLE-2
GRAIN SIZE DATA OF COPPER NANOPARTICLE

Nanoparticle	Peak position, 2θ	Hkl	Theta of the intense peak	FWHM of intense peak (θ) radians	Size of particle (nm)
CGT	36.66	110	18.330	0.012	12.17
	43.32	111	21.660	0.005	29.80
	50.53	200	25.260	0.006	21.90
CGX	43.43	111	21.665	0.00593	25.17
	50.53	200	25.265	0.00594	25.81
CAX	24.85	100	12.425	0.012	71.00
	36.33	110	18.165	0.005	16.77
	43.43	111	21.715	0.006	71.08
CAT	36.51	110	18.255	0.0059	24.76
	43.34	111	21.670	0.0052	26.67
	50.49	200	25.245	0.0133	11.55

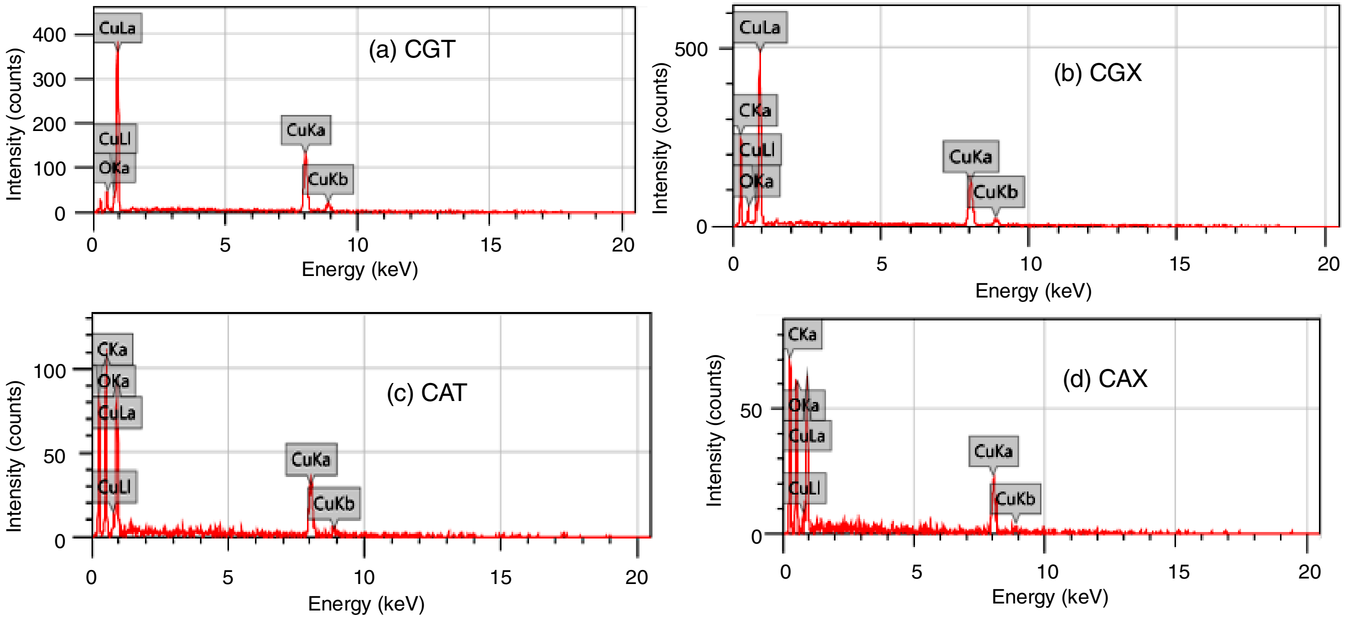


Fig. 4. EDAX images of (a) CGT (b) CGX (c) CAT (d) CAX nanomaterials

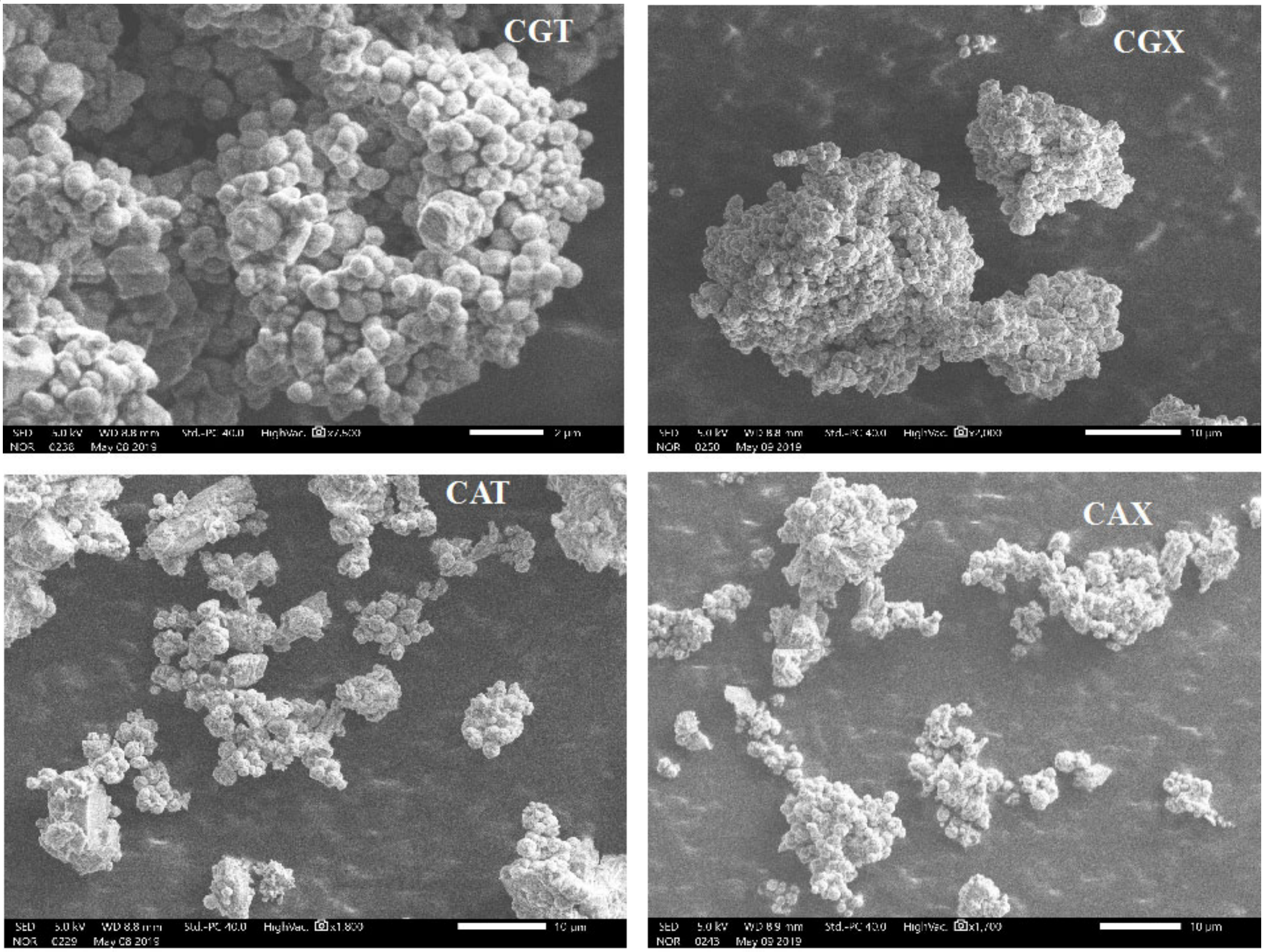


Fig. 5. SEM images of (a) CGT (b) CGX (c) CAT (d) CAX nanomaterials

SEM studies: Based on the SEM micrographs the actual size of the nanoparticles are around less than 30-70 nm which is correlated with the particle grain size data of XRD analysis. The SEM micrographs (Fig. 5) indicates that all the synthesized copper nanoparticles are in spherical in shape.

Conclusion

The present paper illustrates a simple, convenient and low cost method for the synthesis of copper nanoparticles through chemical reduction of copper(II) compounds with ascorbic acid in the presence of two non-ionic surfactants (Tween-80/ Triton-X 100). The characterization results indicated that all the nanoparticles were capped with surfactant molecules. The materials are found to have spherical shape with size from 30-70 nm.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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