

Self-assembly of copper succinate nanoparticles to form anisotropic mesostructures

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Uniform cylindrical rods of copper succinate dihydrate of several microns in length and 200 nm in diameter were obtained by the reverse micellar (microemulsion) method at room temperature using CTAB as the surfactant. The rod-like structures are formed by an ordered assembly of spherical particles of 4–5 nm, which is facilitated by water molecules. The copper succinate particles, in the absence of the microemulsion or surfactant, show only spherical geometry, while in the presence of the surfactant, thicker rods (compared to as obtained by reverse micellar method) of varying length were obtained. The formation of the rod-like structure is driven by the permanent dipole moment of the succinate ion, which leads to the oriented attachment of the nanoparticles in the presence of the surfactant. A new phase (anhydrous copper succinate) is obtained upon heating the dihydrate at 75 °C, which shows branched and corrugated rods assembled from a random arrangement of nanoparticles. The water molecules appear to control the morphology of the rods giving smooth rods (ordered arrangement of nanoparticles) for the dihydrate while branched or disrupted rods with random arrangement of nanoparticles are obtained for the anhydrous phase. The chain length of the dicarboxylic acid (ligand) appears to have a role in controlling the aspect ratio of these anisotropic mesostructures. The ability to generate suitable conditions for self assembly into ordered nanostructures and to control the anisotropy would lead us towards a proper design of nanodevices.

Introduction

Synthesis of nanostructured compounds with controlled size and shape is a challenge and several methodologies have been developed to realize them, such as chemical vapour deposition,^{1,2} ball milling,^{3,4} sol–gel^{5,6} and the microemulsion method using reverse micelles.^{7–11} The microemulsion method leads to uniform and homogenous nanomaterials and has been well adapted for the synthesis of metal and metal oxide nanoparticles.^{12,13} Recently, considerable interest has grown in the coordination chemistry of carboxylate ligands as their polymeric metal complexes are attractive for combining the properties of both organic and inorganic components. This has led to extensive studies on the synthesis of nanostructured transition metal oxalates by reverse micellar method.^{14–18} These metal oxalates having metal ions in the divalent state were found to crystallize with a rod-like morphology. The decomposition of these nanorods under specific conditions yields pure phases of metal and metal oxide nanoparticles.

Here, we discuss our results on the effect of change of the carboxylate ligand from the oxalate (used in previous studies) to the succinate ion, on the morphology of the rods of these metal succinates. The bidentate succinate anion has two additional CH₂ fragments compared to the oxalate anion and offers to create structural diversity attributed to its various binding sites and the conformational modes originating from its flexibility.¹⁹ The

objective of this investigation was to study the role of the chain length of the bidentate ligand on the aspect ratio of the succinate rods and also the texture of these nanorods. This study describes the oriented self assembly of copper succinate nanoparticles to form nanorods and a plausible mechanism for it.

Experimental

Commercially available Cetyltrimethylammoniumbromide (CTAB, Spectrochem, 99%), copper nitrate hydrate (BDH 97%), sodium succinate hexahydrate (CDH, 99%), 1-butanol (Qualigens, 99.5%), isooctane (Spectrochem, 99%), chloroform (SRL 99.5%), ethanol (Merck, 99.9%) and methanol (Qualigens, 99%) were used in the synthesis.

Microemulsions with CTAB as surfactant, 1-butanol as co-surfactant, isooctane as hydrocarbon phase and the aqueous phase were prepared. The constituents of the microemulsion were taken in the following weight fractions: 16.76% of CTAB, 13.90% of *n*-butanol, 59.29% of isooctane and 10.05% of the aqueous phase. 0.1 M metal nitrate (Cu²⁺) solution was used as the aqueous phase in one microemulsion and 0.1 M sodium succinate hexahydrate solution in the second one. The reaction was accomplished by mixing the two microemulsions and stirred overnight at room temperature. The coloured (turquoise blue) precipitate formed was separated from the apolar solvent and washed with 1 : 1 mixture of CHCl₃ and CH₃OH. The precipitate was dried at room temperature and heated under specific conditions to obtain the oxide or the metal nanoparticles. Similar synthesis using only the surfactant (CTAB) in aqueous medium (absence of reverse micelles) and by co-precipitation method was carried out.

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XRD studies were carried out on a Bruker D-8 Advance X-ray diffractometer using Ni filtered Cu K α radiation. Normal scans were recorded with a 2θ step of 0.02° and a residence time of 1 s. With the help of X-ray line broadening studies, the crystallite size could be obtained for the oxide particles. Thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out on a Perkin-Elmer TGA-DTA instrument. Well ground and dry samples were loaded under flowing nitrogen with a heating rate of 5°C min^{-1} . SEM investigations were carried out on a ZEISS EVO 50 scanning electron microscope. HRTEM was recorded on a Technai G² 20 (FEI) electron microscope operated at 200 kV. TEM specimens were prepared by loading a drop of the ultrasonically dispersed sample in ethanol on a carbon-coated copper grid and dried in air. Small angle X-ray scattering (SAXS) measurement was carried out on a Bruker AXS Nanostar instrument. Zeta potential measurements were done on a Malvern Zetasizer, ZS90 instrument. Magnetization studies of the metal succinate was measured at temperatures ranging from 5–300 K, in applied fields of up to 10 kOe with a quantumdesign physical properties measurement system.

Results and discussion

The powder X-ray diffraction pattern of copper succinate dihydrate obtained using the microemulsion method could be indexed on the basis of a triclinic cell (Fig. 1a; JCPDS: 261767), which matches with the simulated pattern obtained from the single crystal data²⁰ (fig. 1b). Transmission electron microscopy showed the formation of rods with length greater than $1\ \mu\text{m}$ and diameter of $\sim 200\ \text{nm}$ (Fig. 2a and b). The HRTEM image (Fig. 2c) shows that the rods are made up of an ordered assembly of spherical nanoparticles of size $\sim 4\text{--}5\ \text{nm}$. To compare the synthesis of metal succinates in the absence of reverse micelles, a control experiment was carried out where copper succinate dihydrate particles were synthesized by a simple precipitation method. Spherical particles of size $\sim 200\ \text{nm}$ were formed *instead of rods* as obtained using reverse micelles (Fig. 3). This clearly indicates that the surfactant acts as a structure directing agent and helps in the formation of the rod-like structure. However, when the reaction was carried out only in the presence of the surfactant (CTAB) and not the microemulsion (reverse micelles), rods made up of small ($4\text{--}5\ \text{nm}$) particles were again obtained (Fig. 4) but the diameter of these nanorods were almost twice ($500\ \text{nm}$) than the one obtained in the presence of reverse micelles ($200\ \text{nm}$). Apart from the diameter, the texture (smoothness) of the nanorod was affected by the use

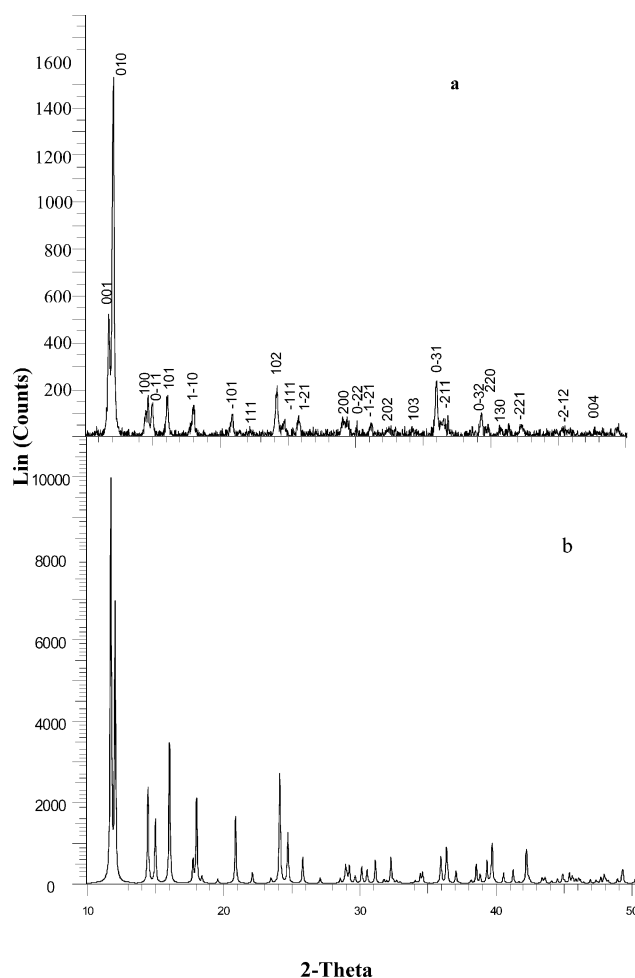


Fig. 1 (a) PXRD pattern for copper succinate dihydrate synthesized using reverse micellar (microemulsion) and (b) the simulated pattern from single crystal data.

of reverse micelles as in the absence of the microemulsion, but only in the presence of surfactant, rods were obtained that were not uniform. The aqueous reactor (core) in the reverse micelles wherein the metal ions and the dicarboxylate ions are allowed to react is small and the presence of organic phase outside the reactor restricts the growth leading to smaller diameter of the rods. While in the presence of only the surfactant (CTAB), not the microemulsion, the aqueous media does not offer any restriction on its growth and thus affects the aspect ratio of the metal

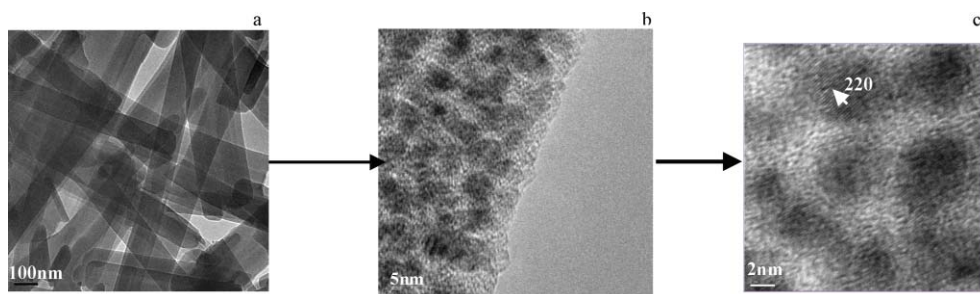


Fig. 2 (a) TEM micrographs for copper succinate dihydrate, (b) HRTEM shows the formation of rod from spherical particles and (c) HRTEM micrographs at high magnification showing the lattice fringes.

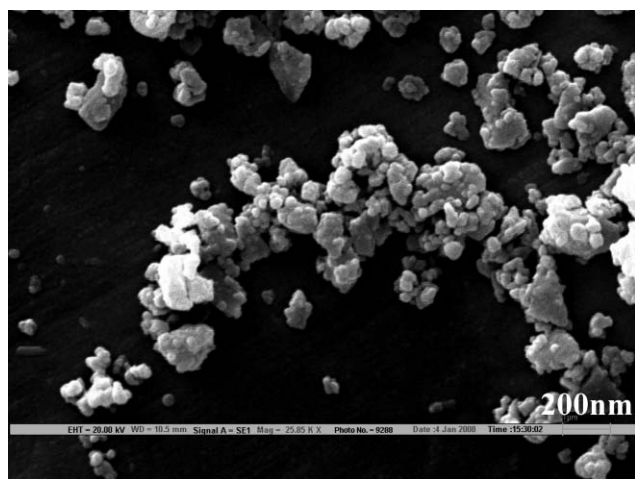


Fig. 3 SEM of copper succinate dihydrate obtained by precipitation method.

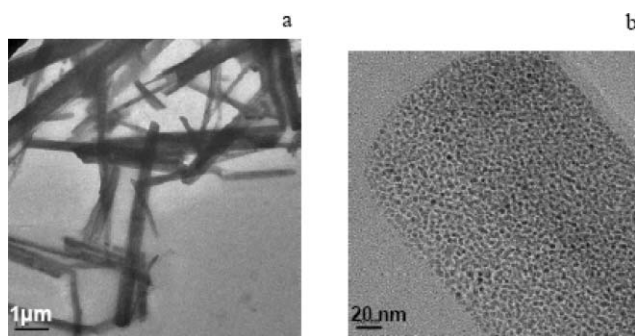


Fig. 4 TEM micrographs for copper succinate dihydrate synthesized only in presence of CTAB and (b) HRTEM micrograph for copper succinate dihydrate.

dicarboxylates. The anisotropy in the growth of the nanorod is purely due to the cationic surfactant which is inferred from the fact that simple co-precipitation method leads to the formation of spherical nanoparticles. In earlier studies of the synthesis of metal carboxylates,¹⁶ where the oxalate ion was used as the ligand, corrugated rods with low aspect ratio (130 nm by 480 nm) were obtained, compared to smooth and much longer rods in case of succinates (this study). We have carried out zeta potential measurement for all the samples in water at neutral pH to see the effect of the surfactant on the surface of the nanomaterials. The sample prepared by simple co-precipitation method showed a zeta potential of ~ 4.4 mV while in the presence of the surfactant (CTAB) the zeta potential was found to be ~ 11.7 mV. The sample prepared by the reverse micellar route showed the maximum stability as reflected by its high zeta potential of 47 mV. The higher zeta potential is due to the surfactant molecules adhering to the surface. In the case of reverse micelles, the aggregation of the surfactants is thermodynamically favoured as opposed to the random surfactant molecules present in the aqueous solution; as a result the adherence of surfactant molecules providing the stability to the rods is much higher for the reverse micellar synthesis. Another point to note is that the particles with high zeta potential have much smaller average size due to less aggregation of these highly charged nanostructures.

The Cu^{2+} succinate complexes show a high degree of ionic character in the metal–ligand bond and are considered to have a planar arrangement with each carboxylate group on each molecule of the succinate ion bonded to two different metal centers to give a chain-like structure.²¹ Also, the metal ions in adjacent layers are bonded by the carboxylate groups of the bridging succinate molecules to give a six-coordinated environment. The water molecules (dihydrate) have been suggested to be involved in hydrogen bonding in each compound.^{21,22} Another report shows the formation of a succinato-bridged copper complex, $[\{\text{Cu}(\text{L})(\text{H}_2\text{O})_2\}(\text{H}_2\text{O})]_n$, which shows the one dimensional coordination chain of $\text{Cu}(\text{II})\text{--L--Cu}(\text{II})$ extended to a supramolecular 3D network through H-bonding.²³ In the chain, each $\text{Cu}(\text{II})$ ion is bonded to two bridging succinate ligands and two water molecules in square planar arrangement with the CuO_4 chromophore. The XRD pattern for this tetrahydrate metal carboxylate does not match with our copper succinates (dihydrate or anhydrous form). Number of studies have been done on the structure elucidation of copper(II) oxalate, $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ ($0 < n \leq 1$) and it is found that it differs from the other 3d-oxalates $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Zn) in several aspects. It is not isostructural to the dihydrates of Mn, Fe, Co, Ni or Zn oxalates. It is known from earlier studies,^{16,17} that other transition metal carboxylates ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$) crystallize as a *dihydrate* and the rods show a smooth texture while for copper oxalate the water content varies between *0–1 moles* per molecular formula and shows a corrugated rod like morphology. The number of water molecules depends on the nature of the complex structure and also on the drying procedure.²¹ For the $\text{Cu}(\text{II})$ oxalate, a ribbon-like structure is established in which, according to Schmittler,²⁴ each copper atom is bound with four oxygen atoms in the same ribbon and with two oxygen atoms of the upper and lower ribbons to complete the octahedral coordination, while in the case of other $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ type phases the octahedral coordination of the 3d-cation is completed with the oxygen atoms from the water molecules. Similar to this, we propose a 7-membered ring structure for the copper succinate dihydrate in an octahedral environment (Fig. 5a) while with the oxalate ion it would form five-membered rings with Cu-ion in a square-planar arrangement (Fig. 5b). This structural change will cause differences in the strain in the microstructure which would bring changes in the texture, morphology and aspect ratio of the rods.

The formation of the mesostructure by the assembly of nanoparticles in solution is mainly due to the permanent dipole moment of the copper succinate nanoparticles. The very small size ($\sim 4\text{--}5$ nm), of these particles allow Brownian collision and thus *via* oriented attachment it aggregates to form highly oriented linear chains.²⁵ Though the long range ordering of the nanoparticles within the rods is not conclusive from the SAXS data (Fig. 6), there appears to be some short range ordering of the spherical particles in the sub micron rods as observed in the HRTEM image. Thus, it seems that two mechanisms play an important role in the formation of these rods: (1) small spherical particles aggregate to form the anisotropic rod and (2) the structure of the planar succinate ligand acts as a structure-directing agent and templates the anisotropic growth.

Thermal studies show that copper succinate dihydrate undergoes three decompositions at 75, 330 and 370 °C under nitrogen atmosphere Fig. 7. The first weight loss at 75 °C accounts for loss of 2 molecules of water leading to possibly the anhydrous

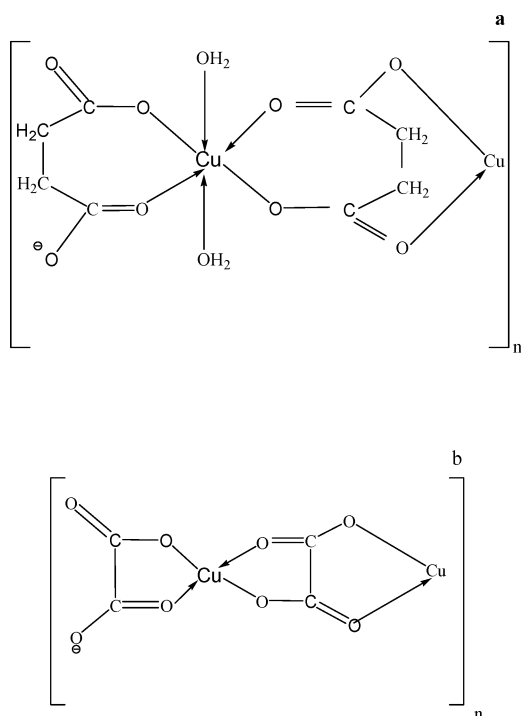


Fig. 5 Tentative structure of (a) copper succinate dihydrate and (b) copper oxalate monohydrate.

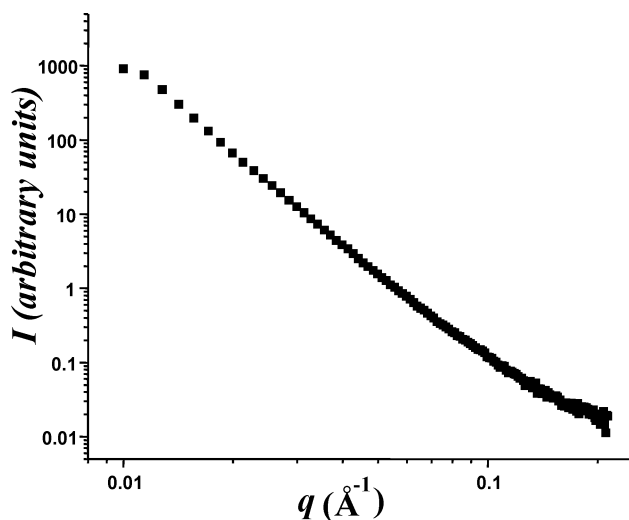


Fig. 6 SAXS pattern of copper succinate dihydrate.

copper succinate. The weight loss (subsequent two decomposition steps) corresponds to the conversion of anhydrous succinate to elemental copper (at 390 °C). The decomposition of the metal dicarboxylate probably proceeds with stepwise cation reduction, from Cu^{2+} to Cu^+ to Cu^0 . To investigate the structure of the intermediate phase obtained at 75 °C (as shown by TGA studies), the succinate precursor was heated in an oven at 75 °C for 6 h. The X-ray pattern (Fig. 8a) of this sample does not match either with the hydrated copper succinate ($\text{CuC}_4\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$) or with that of the anhydrous copper succinate reported in JCPDS file: 512293. Note that the X-ray powder pattern of the anhydrous succinate reported in JCPDS files does not appear to be a careful study since no description of cell parameters or the crystal

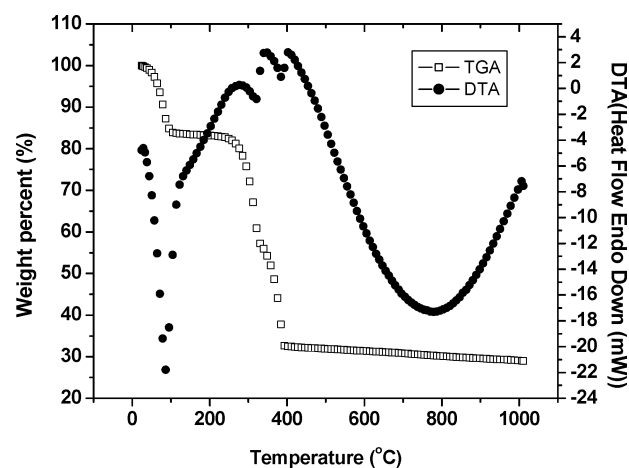


Fig. 7 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) plots for the nanorods of copper succinate dihydrate.

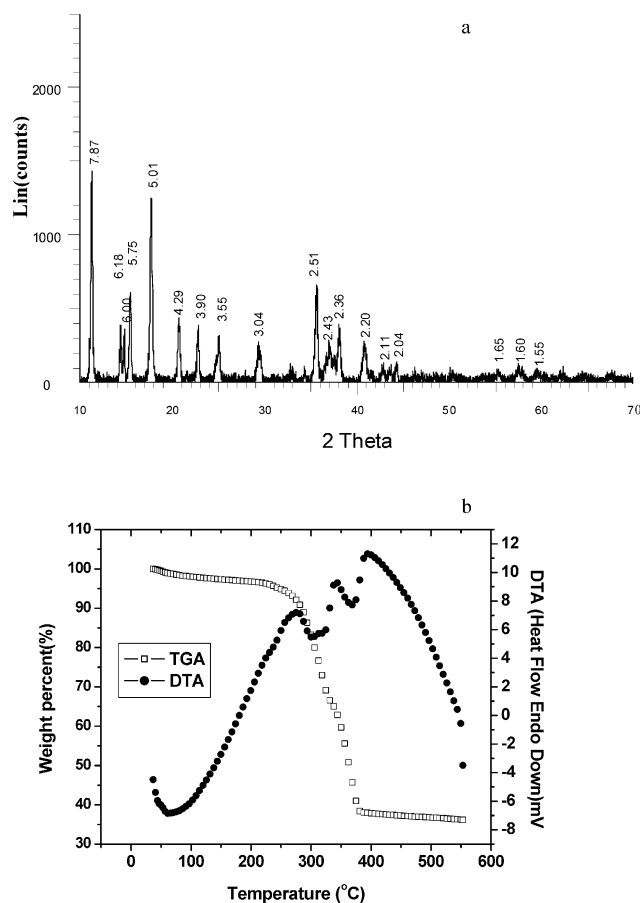


Fig. 8 (a) PXRD pattern of copper succinate dihydrate heated at 75 °C for 6 h and (b) TGA of copper succinate dihydrate heated at 75 °C.

system is mentioned. It may be noted that the reflections for the anhydrous succinate appear to have shifted non-uniformly to higher d-values compared to the reflections observed for the dihydrate. The TGA (Fig 8b) for this anhydrous sample shows no water loss, which affirms our designation of this compound to be an anhydrous form of copper succinate. The final weight loss for the anhydrous copper succinate to form the final product corresponds to the formation of elemental Cu. TEM studies

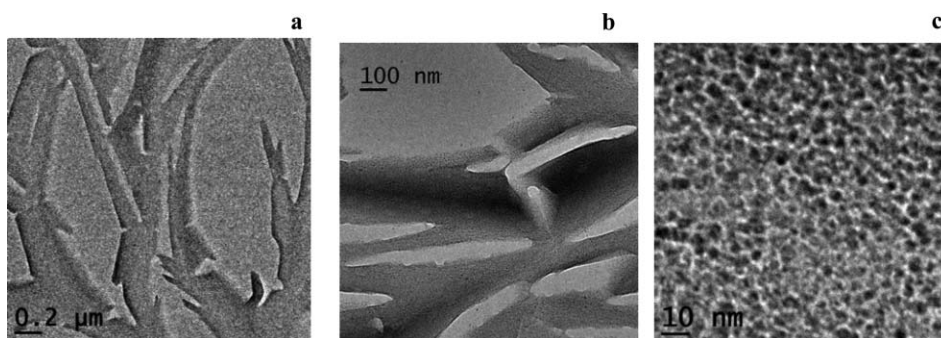


Fig. 9 (a and b) TEM micrographs of copper succinate heated at 75 °C for 6 h and (c) HRTEM images for the copper succinate heated at 75 °C.

carried out on the 75 °C heated succinate powders show poorly crystalline rods with branching (Fig 9a and b). HRTEM of the above rods show assemblage of spherical particles to form the rod-like structures (Fig 9c). Compared to our observation in the dihydrate where we had smooth ordered superstructure, here in the anhydrous succinate we find that the rods show significant branching. These studies show that the presence of water molecules in the nanostructure plays an important role in the formation of the rod-like shape. At 75 °C, when the water molecules are lost (as evident from the TGA), we obtain corrugated and branched rods as seen by TEM. It seems that the loss of water molecules disrupts the smooth morphology of the dihydrate rods and the planar arrangement of the succinate ligand bonded to the copper ion along with the water molecules.

On heating copper succinate dihydrate under flowing nitrogen at 800 °C, pure elemental copper is obtained (Fig 10a), which show spherical particles of various sizes (~100–300 nm) (Fig 10b).

Temperature dependent magnetic studies were carried out on the copper succinate precursor. The nanorods of copper succinate dihydrate show a diamagnetic behaviour as is expected for copper^{II} dicarboxylates involving two Cu(II) ions in close proximity.^{20,22,26}

Summary

Sub-micron rods of copper succinate dihydrate having a very smooth texture have been obtained using the reverse micellar route. The length of the bidentate ligand modifies the ring size of the chelate formed and this seems to affect the morphology and aspect ratio of the succinate nanorods as compared to the oxalate rods studied earlier. The importance of surfactant in the synthesis was evident since simple co-precipitation yielded spherical particles while both the reverse micellar and surfactant-mediated routes led to rod-shaped nanostructures. The loss of water at 75 °C disrupts the ordered array of nanoparticles. Branched rods assembled from 5 nm sized particles without any particular order is obtained. In nitrogen atmosphere, the metal succinate rods decompose to give pure Cu nanoparticles.

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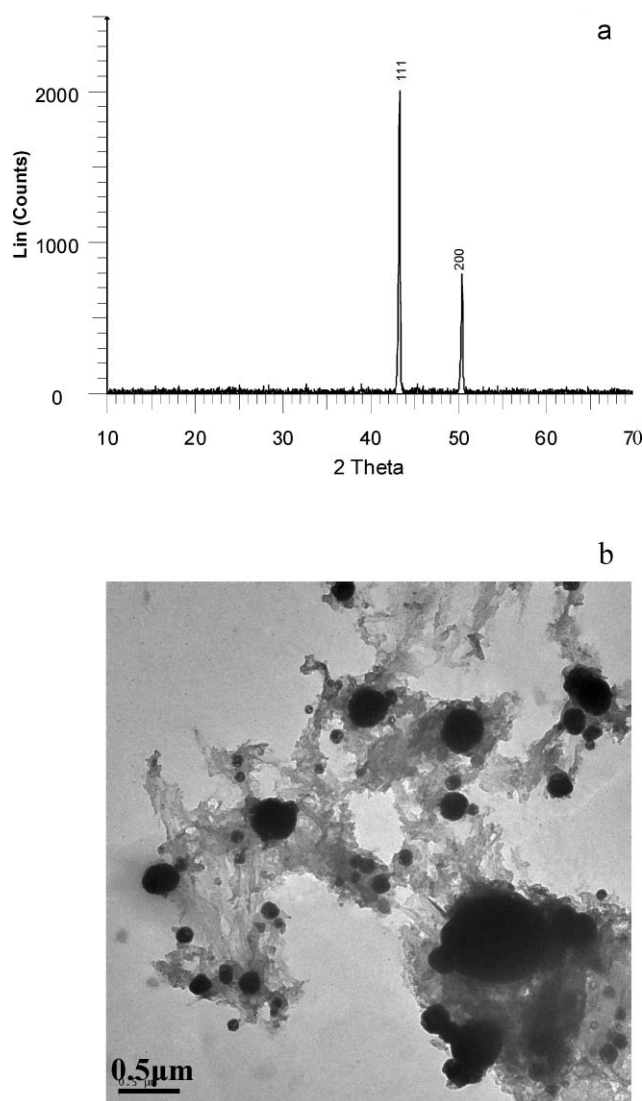


Fig. 10 (a) PXRD pattern of elemental copper obtained from the succinate precursor by heating it at 800 °C under flowing nitrogen and (b) TEM micrographs of nanosized copper particles.

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