

## SYNTHESIS OF NANO HYDROXYAPATITE CERAMIC POWDERS USING DIFFERENT SURFACTANT TEMPLATES AND THEIR CHARACTERIZATION

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In the present study synthesis of nano hydroxyapatite; HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  using different surfactants as templates are exploited. Three surfactants such as Cetyl Trimethyl Ammonium Bromide; CTAB (cationic), Sodium Dodecyl Sulphate; SDS (anionic) and Polyoxyethylene sorbitane monolaurate; Tween 20 (nonionic) surfactants have been used as nano reactors for the synthesis of hydroxyapatite ceramic powders. Precipitation route has been used for synthesis with same calcium and phosphate precursors. The effect of different templates on the synthesis, morphology and particle size has been investigated. Considerable influence of templates on the morphology and particle size of the synthesized HA is observed. The samples are characterized using XRD, FTIR and SEM to evaluate the quality, morphology and particle size. The chemical and structural compositions of the products are examined by FTIR. SEM micrographs reveal a rod like structure of HA; possessing various thickness and length in nano range; vary in contrast of each template while the XRD spectra show some other minor phases alongwith HA.

**Keywords :** Nano hydroxyapatite, Ceramic powder, XRD, FTIR, CTAB, SDS and Tween 20

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### 1. Introduction

Hydroxyapatite; HA chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  has been successfully applied in the orthopedic and dentistry for several years due to its excellent biocompatibility and bioactivity [1,2]. Unfortunately the fracture toughness of HA ceramic is a major issue now a days for load bearing applications of implants.

It is well documented that the properties of inorganic materials depend strongly on their morphologies. Thus, it is an issue for science and technology to design and control the synthesis of nano or microstructured materials with different morphological configurations and size distributions on large scale. Calcium phosphate belongs to the group of bioactive synthetic and its most frequently used representative are the Hydroxyapatite and Hydroxyapatite- $\beta$  tricalcium phosphate due to their osteoconductive, crystallographic structure and chemical composition similar to the natural bone. Hence these materials show enormous applications in the medical, pharmaceutical and

dentistry areas [3,4].

Bone is a relatively hard and lightweight composite material, formed mostly of calcium phosphate in the chemical arrangement termed calcium Hydroxyapatite. Bone is a linear and brittle, yet anisotropic and viscoelastic material, whose mechanical properties are determined by its porosity, degree of mineralisation, collagen fiber orientation, and other structural details [5].

Surfactant or surface active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and thus altering to a marked degree the surface or interfacial free energies of those surfaces [6].

The presence of amphiphilic organic additive at low concentration strengthens hydrophobic bonding tendency in aqueous surfactant solution and causes the depression in CMC, the concentration at which surfactant molecules aggregate to form micelle [6-8]. The overall solubility of many

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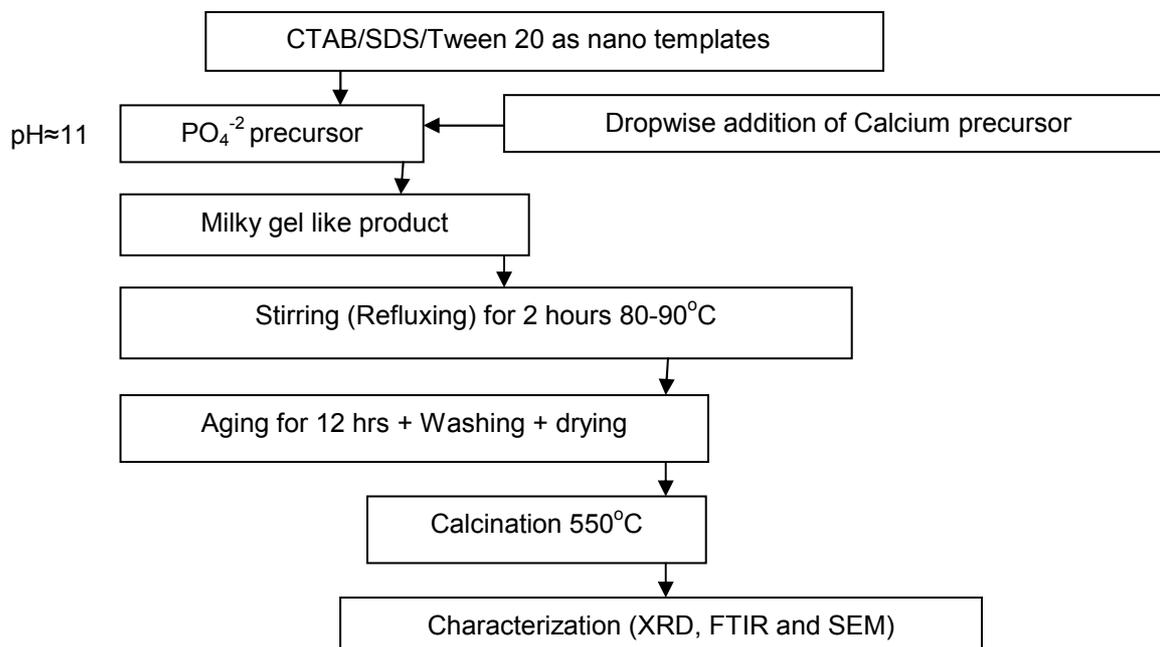


Figure 1. Schematic diagram of Hydroxyapatite synthesis procedure.

hydrophobic molecules in water can be greatly increased by the presence of surfactants due to formation of spontaneous aggregates [9].

Morphologies of aggregates formed by surfactants in aqueous solution are micelles, vesicles, bicontinuous, or inverted structures [10, 11]. Aggregate morphology is mainly determined by a delicate balance between attractive hydrophobic interactions of surfactant alkyl tails and electrostatic repulsions of surfactant head groups [12]. The molecular architecture of a given surfactant determines the type of aggregate into which a surfactant associates in aqueous solution. The synthesis of mesoporous materials can be achieved using a supramolecular templating technique. A group of scientists successfully demonstrated that such a templating technique could be used to prepare silicon based mesoporous materials [13].

In the present work the mechanism of formation of nano HA using organic templates has been explored using precipitation instead of lengthy reflux procedure. Three surfactants of different charges were used as templates to produce the nano Hydroxyapatite ceramics. The self assembling mechanism of each surfactant is

compared on the basis of morphology, particle size of the ceramics produced.

## 2. Experimental

### 2.1. Chemicals and Reagents

Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), Calcium chloride ( $\text{CaCl}_2$ ), Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), Tween 20, Sodium Dodecyl Sulphate (SDS), Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ) from Merck, sodium hydroxide (NaOH) and Cetyl Trimethyl Ammonium Bromide (CTAB) from Fluka were used. All the chemicals were of AR grade and used as such without further purification. Doubly distilled deionised water of  $0.8 \mu\text{s/cm}$  conductivity was used for all set of experiments.

### 3. Instrumentation

The produced phases in all the samples were examined using X-ray diffraction using 3040/60 X'pert PRO system and the precursor's positions and stoichiometry was investigated by the FTIR using Perkin Elmer model spectrum GX spectral characterizations techniques. Scanning electron microscopy was used in order to study the morphology of formed HA particles using SEM model Jeol JSM 6340F.

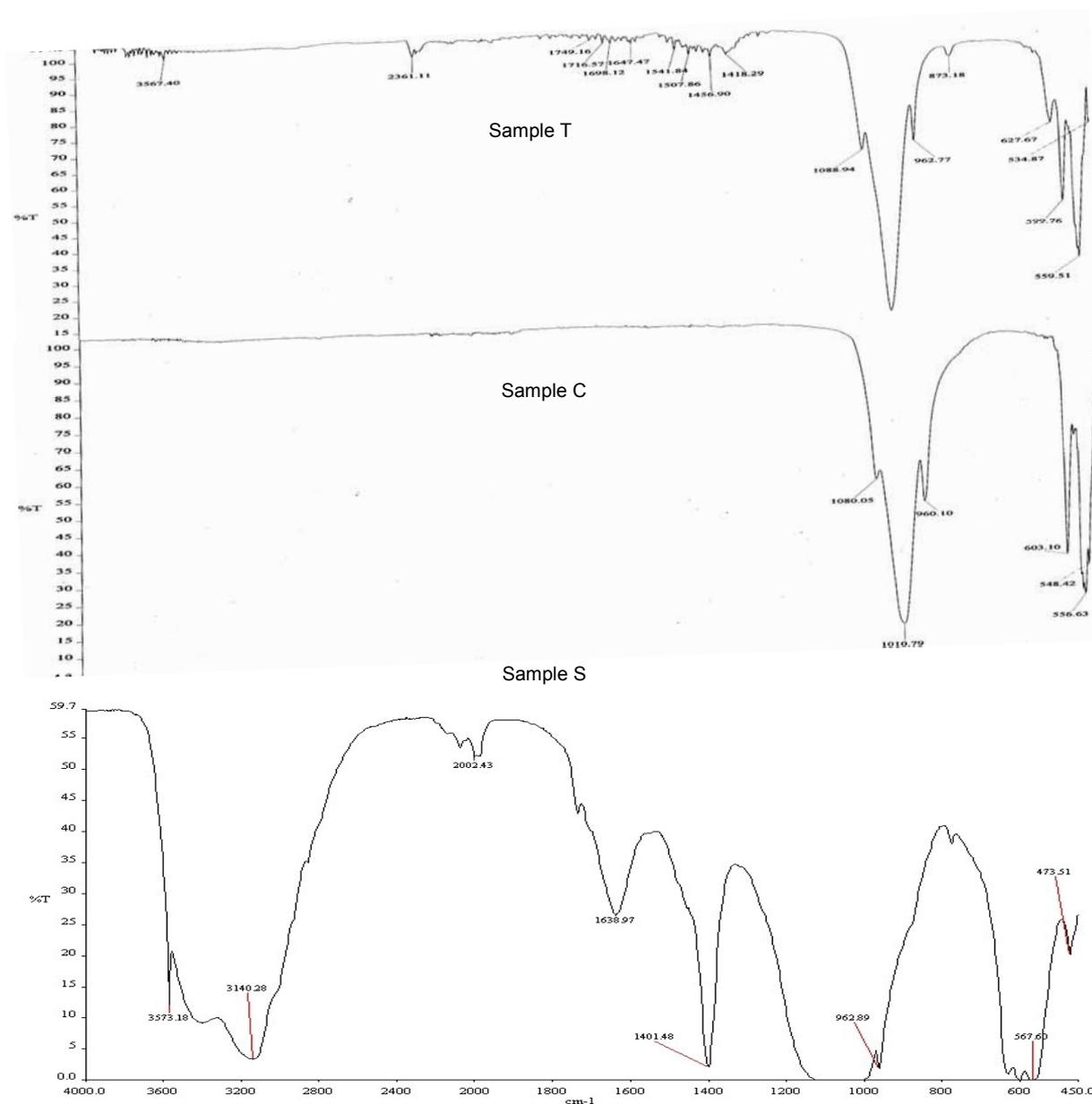


Figure 2. FTIR spectra of samples C, S and T using CTAB, SDS and Tween 20 templates respectively.

#### 4. Procedure

Required amount of  $\text{KH}_2\text{PO}_4\text{NH}_4\text{H}_2\text{PO}_4$  for 0.6 M was dissolved in 70 ml aqueous solution and added to 100 ml each of 0.4 M CTAB, 0.2 M SDS, 0.2M Tween 20 aqueous solutions. The pH of the mixture was maintained at 11 using NaOH or  $\text{NH}_4\text{OH}$  solution. After stirring mixture for 2 hours at 80-90°C, 100 ml of 1.0 M aqueous solution of  $\text{CaCl}_2\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was added dropwise and stirred again for 2 hours. After aging of 12 hours the precipitates were filtered, washed and then

dried at 80°C for 24 hours and finally dried at 110°C for 1 hour.

Calcination was performed at 550°C for 5 hours. White powder was obtained which was characterized by XRD, FTIR initially.

#### 5. Results and Discussion

The FTIR patterns in Fig. 2 show the peaks of phosphate group, OH group of HA and carbonate and/or hydrogen phosphate peaks are visible in the



contain HA as the only phase. Other phases are either absent or cannot be detected due to broad peaks in the XRD pattern. When the powder was heated to 550°C (sample T)  $\beta$ -TCP appeared as the minor phase, while the transformation of HA to  $\beta$ -TCP at relatively low temperature can be attributed to the high sensitivity of nano HA to temperature. Sample S represent the HA powders produced using SDS as shown in Fig.2 and Table 1. It is noted that the calcination temperature affects the morphology of HA prepared using different surfactants. In case of CTAB as template, the powder was prepared by the given procedure. X-ray diffraction patterns in Fig.3 showed that the synthesized powder (sample C) contains HA as major phase along with  $\beta$ -TCP as the minor phase. When this powder was heated upto 550°C the transformation of HA to other phases take place and the calcined powder also contains DCPA as minor phases along with  $\alpha$ -TCP and  $\beta$ -TCP.

The transformation of HA to these minor phases at relatively low temperature i.e. 550°C can be attributed to nano size of the powder particles. Obviously nano particles are more sensitive to temperature changes as compared to macro particles due to the materials properties at nano scale level. It is observed that after calcination the peaks become sharp which indicates high crystallinity or larger grain size.

The sample 'S' represents the Hydroxyapatite powders produced using SDS templates and it is observed from Fig.3(S) that all the peaks relate to the standard HA peaks where as Fig.3(C) represents CTAB templates and shows the similar behavior like SDS. The XRD patterns also show very minute peaks of  $\beta$ -TCP and DCPC phases. These phases either may be due the conversion of HA phase during calcination or it may be obtained as the intermediaries during apatite crystallization. Another contributing factor may be that residual carbon which retained after burning off surfactant templates and during calcination for 5 to 6 hours in oxygen resulted in the formation of amorphous carbonate phase.

Fig. 4 shows the morphologies and the particle sizes of the synthesized HA powders and clearly describe the nano scale structure of HA powders. It is observed that the different surfactant templates reveal different morphologies as well as the particles sizes. In Fig. 4 C the needle like structure is produced with lowest agglomeration using CTAB

templates having positive charge head groups while the spherical or low aspect ratio as compared to CTAB templates were observed with SDS templates having negative charge on the head group. Fig.4T elaborates the morphology of the HA particles which were produced using non ionic Tween 20 templates. It is noted that the particles agglomerated in bunches of nano scale flowery structures with different aspect ratios. From SEM characterization, the agglomeration is graded in the order of CTAB<SDS<Tween 20.

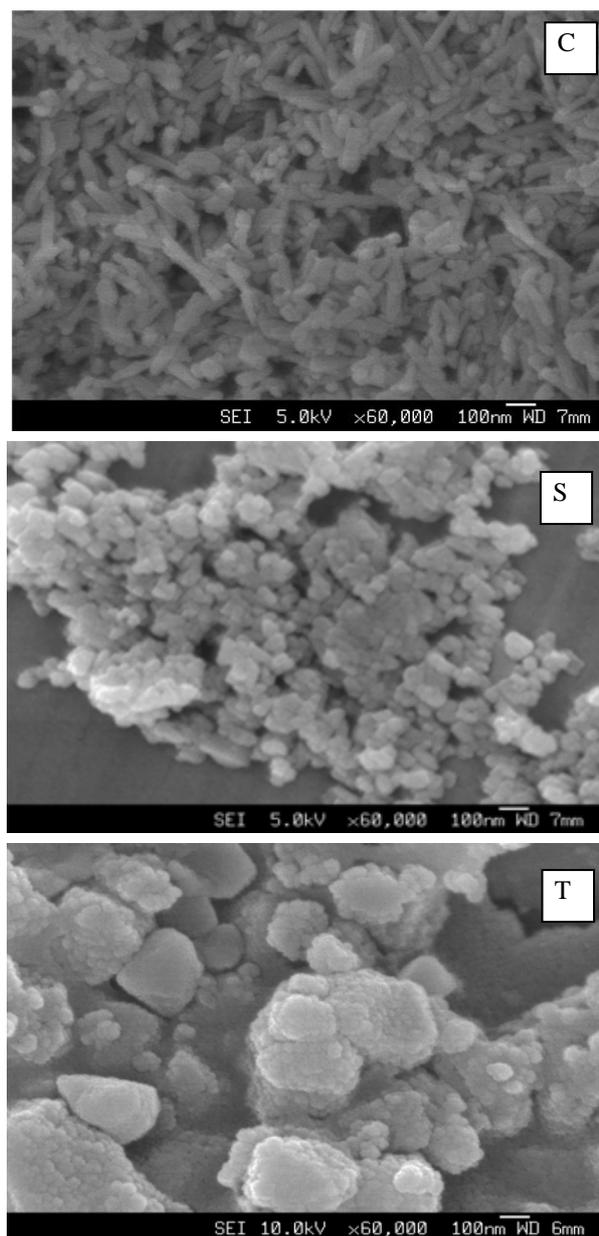


Figure 4. SEM micrographs of HA samples C, S and T for CTAB, SDS and Tween 20 templates respectively.

## 6. Conclusion

Novel biomaterial Hydroxyapatite based on calcium phosphate were synthesized and extensively characterized through structural and morphological features. The low cost precursors via low cost route were adopted to produce different morphological ceramic powders. Surfactant templates have been used successfully to control the morphology and particle size of the synthesized HA powders.  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions when used with calcium precursor as counter ions, results in the formation of different morphologies of HA particles.  $\text{Cl}^-$  ions formed plate like particles where  $\text{NO}_3^-$  results in the formation of rod shaped particles. Anionic counter ions affect the properties of formed HA.  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  were applied with phosphate precursors.  $\text{NH}_4^+$  being the largest of all does not affect the stoichiometry of formed powder while  $\text{Na}^+$  interacts most of them resulting in the formation of other phases of calcium phosphate. The presented research has shown the technology for potential use in several fields of medicine, materials and biomaterials for the applications in orthopedic and dentistry.

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