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Effect of fuel characteristics on synthesis of calcium hydroxyapatite by solution combustion route

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Abstract. The effect of fuel characteristics on the processing of nano sized calcium hydroxyapatite (HA) fine powders by the solution combustion technique is reported. Urea, glycine and glucose were used as fuels in this study. By using different combinations of urea and glycine fuels and occasional addition of small amounts of highly water-soluble glucose, the flame temperature (T_f) of the process as well as product characteristics could be controlled easily. The powders obtained by this modified solution combustion technique were characterized by XRD, FTIR spectroscopy, SEM, FESEM–EDX, particle size analyser (PSD) and specific surface area (SSA) measurements. The particle size of phase pure HA powder was found to be <20 nm in this investigation. The effects of glucose addition with stoichiometric ($\mu = 1$) and fuel excess ($\mu > 1$) urea and glycine precursor batches were investigated separately.

Keywords. Modified solution combustion; hydroxyapatite; fuel/oxidizer ratio; urea/glycine/glucose; nanocrystalline; SEM/FESEM.

1. Introduction

Calcium phosphates (CaP) are the most ubiquitous family of inorganic compounds well known for their use in biological applications. Variety of calcium phosphates phases offer excellent bio-active properties of which calcium hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ is most widely used as powders, particulate or porous and solid scaffold forms in various bone repair applications (Bauer *et al* 1991) and also as coatings for metallic prostheses to improve their biological properties (Liu *et al* 2001). HA being the most stable calcium phosphate ceramic compound at the pH, temperature and composition of the physiological fluid (Correia *et al* 1996) finds widespread application including matrices for controlled drug delivery (Itokazu *et al* 1998), fillers in periodontal bony defects, alveolar ridge augmentation and for filling in tooth extraction sites to preserve alveolar ridge contours (Jarcho 1981).

However, in spite of chemical and structural similarities, bio-activity as well as mechanical properties of synthetic HA is much on lower side in comparison to those of natural hard tissues. Many researchers (Suchanek and Yoshimura 1998) have observed that the mechanical strength and fracture toughness of HA ceramics can be improved by the formation of phase pure ultra-fine HA powder. HA in nano-size particle form has considered to have potential to revolutionize the field of biomedical science from bone regeneration to drug delivery and therefore, for last 20 years, considerable scientific activity was focused to develop nanostructured HA to improve the mechanical as well as biological properties (Yeong *et al* 1999).

Many routes, such as hydrothermal reaction (Liu H S *et al* 1997), sol–gel synthesis (Kivrak and Tas 1998; Weng and Baptista 1998; Liu *et al* 2001, 2002; Sarig and Kahana 2002; Bose and Saha 2003), micro-emulsion synthesis (Lim *et al* 1997) and mechanochemical synthesis (Yeong *et al* 2001; Suchanek *et al* 2002; Manuell *et al* 2003) were employed to synthesize HA powder. Currently, solution combustion processing of HA powder is being considered to be a promising method to obtain nano-sized powder because of its several advantages. The method involves a high level of molecular mixing of the components in solution leading to improved chemical homogeneity of the synthesized powder. Further, the process yields powder with high purity, better homogeneity and high surface area in a rapid, inexpensive single step operation (Fumo *et al* 1996; Adhikary *et al* 1998; Muthuraman and Patil 1998; Varma *et al* 1998; Sukumar *et al* 1999; Yue *et al* 2000; Ghosh *et al* 2004, 2008; Han *et al* 2004).

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Combustion synthesis technique involves the exothermic chemical reaction between metal nitrates and an organic fuel, typically urea (CH_4N_2O) (Kingsley and Patil 1988), carbohydrazide (CH_6N_4O) (Anuradha *et al* 2001), or glycine ($C_2H_5NO_2$) (Mimani and Patil 2001). The maximum reaction temperature generated in this process depends on fuel to oxidizer ratio (μ) (Jain *et al* 1981), initial furnace temperature, nature of the fuel and quantity of the initial precursor. Several researchers (Fumo *et al* 1996; Ye *et al* 1997; Purohit *et al* 2001a,b) have tried to control the combustion flame temperature (T_f) and scale up the synthesis process by adjusting the nature and content of the fuel, solution loading, volume of gases formed and the furnace temperature/environment. Although maximum reaction temperature of a solution combustion process depends strongly on nature and amount of fuel, surprisingly barring some sketchy reports no systematic study was undertaken on use of mixture of fuel on the process (Aruna and Rajam 2004; Sasikumar and Vijayaraghavan 2007). A novel idea would be to use an additional fuel having lower decomposition temperature with evolution of gases which may help generate sufficient local heating to enable decomposition of the primary fuel (urea and glycine) to complete the combustion synthesis and at the same time creating porosity within the mixture to prevent particle agglomeration. The objective of this work is to study the effect of combinations of urea–glycine (in stoichiometric and in fuel excess quantity) and glucose (a fuel decomposing at lower temperature ~180°C) on the combustion flame temperature as well as resultant powder characteristics of synthesized calcium phosphate through solution combustion process.

2. Experimental

Analytical grade, calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$) (S.D. Fine-Chem. Ltd., India,), di-ammonium hydrogen ortho-phosphate (DAP), [$(NH_4)_2HPO_4$] (S.D. Fine-Chem. Ltd., India), urea [$CO(NH_2)_2$] (Glaxo, Qualigens, India) and glycine ($C_2H_5NO_2$) (Glaxo, Qualigens, India) were used as raw materials to prepare calcium phosphate powders. Commercially available glucose in various quantities (Glaxo, Qualigens, India) was also used with urea and glycine stoichiometric (for calcium hydroxyapatite) and fuel excess batches separately to control the nature of combustion reaction as well as powder characteristics. To synthesize, 8·80 g of stoichiometric HA (theoretical yield, Ca/P atomic ratio = 1·67), 32·20 ml of aqueous stock solutions of calcium nitrate tetrahydrate (2·72 M) and 25·10 ml of DAP (2·09 M) were first mixed slowly with continuous stirring till a white precipitate was formed. Subsequently 3·50 ml of concentrated nitric acid (14M, E-merck, India) was added dropwise to dissolve the resulting white precipitate. Pre-calculated amount of fuels or fuel–glucose mixture (F/O ratio = 1·0, for stoichiometric and 3·75, for fuel excess) were added to the clear solution which was homogenized by stirring with a magnetic stirrer for 30 min at room temperature. The experimental precursors made by different combinations of urea–glycine fuels and glucose is displayed in tables 1 and 2.

A glass ceramic-coated mild steel bowl (dia. ~80 mm, volume 130 c.c.) containing the solution was introduced into a muffle furnace preheated at 500°C. The reaction container was covered with a stainless steel wire mesh to reduce the particle loss through aerosol formation. A K-type (chromel–alumel) thermocouple was suitably placed just above the wire mesh to record temperature changes during reaction. Immediately after introduction in the furnace, the clear transparent solution started to boil ensued with evolution of a large volume of gases and finally it became viscous gel like mass. Afterwards the viscous mass frothed and swelled to yield foam, where a flame appeared and burned with incandescence. After initiation of the reaction, the furnace was switched off and the heat evolved during the combustion reaction sustained itself and proceeded to completion of the reaction without requiring any further heat from an external source. An electronic chart recorder (Z-trend, Honeywell, USA) was used to record the temperature profile during combustion. The entire process was over in <10 min with flame duration <2 min. The product was removed from the muffle immediately after the flame became invisible. The general flowchart of solution combustion process used in this work is schematically shown in figure 1.

The tap density of as-synthesized voluminous powder was measured conventionally and it was in the range of 0·076–0·07 g/cm^3. X-ray diffraction technique was employed on the as-synthesized powders for phase characterization, using Philips X-ray diffractometer (XRD) (Philips Analytical, X'Pert, 1830, The Netherlands) with Cu-$K_{\alpha 1}$ radiation and Ni-filter. The average crystallite size of the powders was determined by the line-broadening method by using the Scherrer formula, as given below

$$D = \frac{0{\cdot}9\lambda}{\beta\cos\theta},$$

where D is the average crystallite size in nm, λ (~ 0·154056 nm) the wavelength of the X-ray radiation, θ the Bragg's angle and β the full width at half maximum (FWHM) of the peak observed for the samples.

Scanning electron microscope (SEM) (Leo 430i, U.K.) and field emission scanning electron microscope (FESEM) (Supra-35 VP, Carl Zeiss, Germany) were used to investigate the particles size, shape and morphology, EDAX was done using Si–Li detector. The specific surface area (S_{BET}) of the as-formed powders was measured using multipoint BET (Brunauer–Emmett–Teller) method (SOPRTY-1750, Carlo Erba Strunetazione, Italy). The equivalent diameter (d_{BET}) of particle was calculated from

Table 1. Stoichiometric fuel to oxidizer precursor batches having different combinations of urea and glycine fuels.

Fuel composition	Glucose addition (g)	Initial furnace temperature (°C)	Measured flame temperature (°C)
U	0	500	817
U	0·5	500	765
U	0·8	500	709
U	1·0	500	680
G	0	500	888
G	0·5	500	811
G	1·0	500	713
0·2U + 0·8G	0	500	867
0·3 + 0·7G	0	500	854
0·4U + 0·6G	0	500	847
0·5U + 0·5G	0	500	832
0·6U + 0·4G	0	500	830
0·7U + 0·3G	0	500	822
0·8U + 0·2G	0	500	819

#U: Stoichiometric urea ($\mu = 1$); G: stoichiometric glycine ($\mu = 1$).

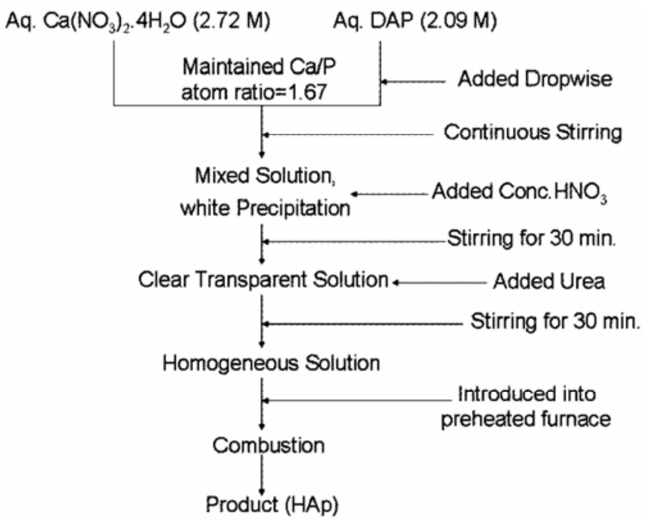

Figure 1. General flowchart of solution combustion synthesis.

the measured surface area (S_{BET}) values by using the following relationship:

$$d_{\text{BET}} = \frac{6}{\rho S_{\text{BET}}},$$

where ρ is the theoretical density of the powder. The median diameter of the powder particles and the particle size distribution were ascertained by photon correlation spectroscopy (Mastersizer 2000, Malvern, U.K.). Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer, Model 1615, USA) of very selective samples were performed for confirmation of the functional groups of the phases formed by combination of urea and glycine fuels using a typical KBr pellet technique in the wave number range of 4000–400 cm^{-1}.

3. Results and discussion

3.1 *Nature of combustion reaction*

The combustion reaction was carried out by using the fuels, urea and glycine, individually as also different combinations of these. Effects of addition of a small quantity of glucose to these batches on the combustion behaviour and resulting powder characteristics were studied. It has been shown that individual stoichiometric urea and glycine both produce vigorous combustion reaction with high flame temperature and duration (Li *et al* 2002). Adiabatic flame temperature (T_{f}) (McKittrick *et al* 1999) can be estimated for a combustion reaction using Hess' Law which is expressed as follows: where T_{f} is the adiabatic flame temperature, T_0 the ignition temperature, ΔH_{r} the enthalpy of the reactants, ΔH_{p} the enthalpy of the products, and C_{p} the heat capacity of products at constant pressure.

$$T_{\text{f}} = T_0 + \frac{\Delta H_{\text{r}} - \Delta H_{\text{p}}}{C_{\text{p}}}.$$

In identical reaction conditions, both urea and glycine systems at stoichiometry separately produce flame temperature, 817°C and 888°C, respectively. This is quite expected because heat of combustion of glycine is almost three times that of urea. Experimentally, it has been observed that fuel mixture combination reaction not only reduces the intensity of the combustion reaction it also reduces the particle size of as-synthesized powder. To make the stoichiometric fuel to oxidizer ratio ($\mu = 1$) with mixed fuel batch, urea and glycine are used in various percentages. With increase in the percentage of urea in urea–glycine stoichiometric mixture, combustion flame

Table 2. Fuel excess precursor batches having different combinations of urea and glycine fuels.

Fuel composition	Glucose addition (g)	Initial furnace temperature (°C)	Nature of combustion	Flame characteristics	Crystallite size from XRD (nm)
3·75U	0	500	Smouldering	Mild, short duration	61
3·75U	0·5	500	Voluminous	Flameless	–
3·75G	0	500	Smouldering	Moderate, higher duration	48·3
3·75G	0·5	500	Voluminous	Flameless	38·0
0·9375U + 2·8125G	0	500	Smouldering	Moderate, higher duration	48·3
1·3125U + 2·4375G	0	500	Smouldering	Nearly flameless	34·5
1·875U + 1·875G	0	500	Smouldering	Mild, short duration	46·9
2·4375U + 1·3125G	0	500	Smouldering	Mild, short duration	50
2·8125U + 0·9375G	0	500	Smouldering	Mild, short duration	61·2
0·9375U + 2·8125G	0·5	500	Voluminous	Flameless	36·0
1·875U + 1·875G	0·5	500	Voluminous	Flameless	36·0
2·8125U + 0·9375G	0·5	500	Voluminous	Flameless	35·0

#U: Stoichiometric urea ($\mu = 1$); G: stoichiometric glycine ($\mu = 1$).

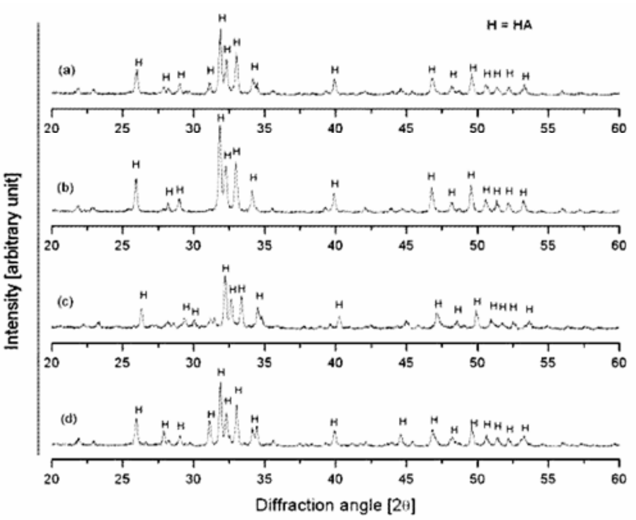

Figure 2. X-ray diffraction patterns of as synthesized powders using (a) U, (b) G, (c) 0·6U + 0·4G and (d) 0·4U + 0·6G stoichiometric mixture.

temperature and intensity of the reaction reduces gradually. Table 1 shows the measured flame temperature of various experimental batches.

Keeping all other parameters constant, fuel excess ($\mu = 3{\cdot}75$) combustion reactions are, as expected, less vigorous (smouldering) and prolonged in comparison to stoichiometric fuel mixture systems. The mixed fuel batches behave similarly to stoichiometric fuel ($\mu = 1$) ones at lower flame intensity. Table 2 shows the nature of combustion and calculated crystallite size of a very few selective samples obtained from mixed fuel excess conditions.

Various investigators (Manoharan and Patil 1992; Zhang and Stangle 1997; Patro *et al* 2003) have reported that combustion reaction using stoichiometric amount of urea produces lower flame temperature and higher number of gas molecules than those of stoichiometric amount of glycine. The probable reasons of lower flame temperature in higher urea containing batches are lower enthalpy of urea along with higher gaseous volume released from the reaction. Heat of combustion of urea is –333·19 kJ/mole, about one third of that for glycine, –973·49 kJ/mole, and as a consequence releases much less heat to the system. Further, the higher volume of gaseous molecules removes more heat from the system by convection and further lowers the flame temperature. The effects of glucose addition with stoichiometric and fuel excess urea and glycine mixed fuel batches were investigated. It has been observed that small quantity of glucose reduces the flame temperature tremendously and vigorous reaction almost becomes smouldering in nature. The glucose molecules decomposes at much lower temperature (<200°C) and generates large volume of gases that dissipates heat quickly from the system and causes lowering of the temperature. The glucose molecules decompose at the first instance releasing large volumes of gases and separates the whole reaction mass to porous agglomerates which subsequently decompose in small individual lumps by using heat from fuel oxidation and avoids self-propagating vigorous reaction resulting in smouldering combustion. The smouldering combustion mode was characterized by relatively slow, essentially flameless reaction, with formation of large voluminous powder compared to the self-propagating reactions with flame.

3.2 *Powder characteristics*

3.2a *XRD of powders obtained with stoichiometric fuel to oxidizer ratio ($\mu = 1$)*: All combinations of urea–glycine stoichiometric batches produced well crystalline phase pure hydroxyapatite powder. Figure 2 (a, b, c, d) shows the X-ray diffraction patterns of as synthesized powders using urea–glycine stoichiometric mixture. The as-synthesized HA powders were identified by using JCPDS file 9-432. This result indicates that the well crystalline HA is directly formed after the combustion reaction. The combustion reaction generated large quantities of heat from the exothermic chemical reaction of nitrates and fuels and results in HA crystal phase formation (Tas 2000). Addition of small quantity of glucose (<1 g) with experimental batch size (to yield 8·80 g of HA) was able to produce crystalline HA powder and further increase of glucose quantity (~1·0 g) leads to carbon contaminated amorphous powder (figure 3b) which needs an additional heat treatment to convert to crystalline HA (figure 3a). Figure 3(a, b, c, d) represents the X-ray diffraction patterns of as-synthesized powder prepared by glucose addition along with heat treated powders.

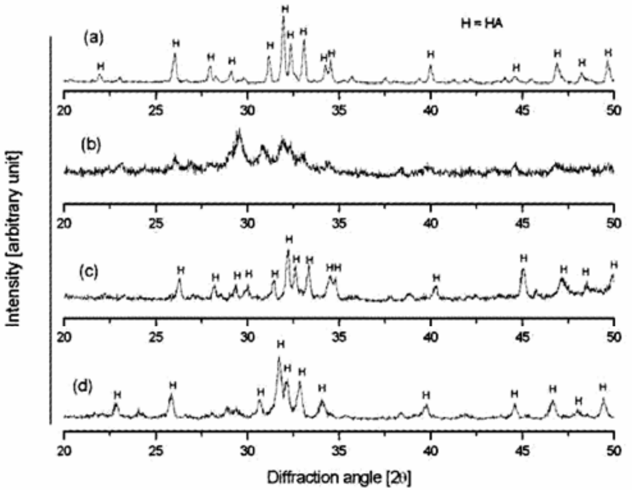

Figure 3. X-ray diffraction patterns of as-synthesized powder prepared by (a) U + 1·0 g glucose addition (heat treated at 800°C/1 h), (b) U + 1·0 g glucose addition, (c) U + 0·8 g glucose addition and (d) U + 0·5 g glucose addition.

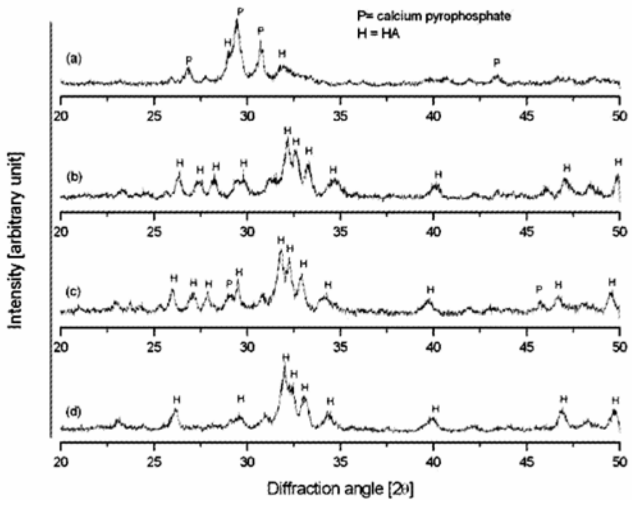

Figure 4. X-ray diffraction patterns of as-formed powder prepared by (a) addition of excess glycine alone ($\mu = 3{\cdot}75$), (b) combination of glycine, urea and glucose [1·875U + 1·875G + 0·5 g glucose], (c) combination of both fuels [2·4375U + 1·3125G] and (d) addition of excess urea alone ($\mu = 3{\cdot}75$).

The crystallite size of as-synthesized powder were measured from the X-ray peak broadening of the (211) diffraction peak of HA by using standard Scherrer's formula. Table 3 shows the crystallite size of as-synthesized powders. It was found that crystallite size of as-formed powder significantly decreases with increase in the glucose addition with the precursor batch. Precursors with 0·5, 0·8 and 1·0 g (heat treated) glucose produced HA powder having the crystallite size 33, 28 and 23 nm, respectively. It was evident that the crystallite size of the as-formed HA powder depends on the flame temperature as well as nature of the combustion reaction. Mixed fuel experiments showed that lower crystallite size was formed in case of higher urea containing batches. Table 3 also shows the specific surface area (SSA) and particle size (d_{BET}) of the as-formed powder of various experimental batches. The HA powder obtained from the glucose containing precursor has the highest surface area, and the values increase with the increase of glucose addition. The glucose used in the combustion reaction results in the reduction of the flame temperature as well as the system temperature, which may prevent particle sintering and subsequent grain growth. Gas evolution due to glucose burning, results in highly porous structure of the product. A very small change of the surface area values were observed in case of mixed fuel batches. The equivalent particle diameter from S_{BET} was calculated and lowest value was obtained in case of glucose containing batch. The calculated d_{BET} values are comparable to those estimated using X-ray line broadening method.

3.2b *XRD of powders obtained by fuel excess ($\mu = 3{\cdot}75$) combustions*: Unlike stoichiometric fuel oxidizer ratio, fuel excess ($\mu = 3{\cdot}75$) system yields different products, sometimes pure HA and sometimes a mixture of HA and calcium pyrophosphate powders. Figure 4 (a, b, c, d) shows the X-ray diffraction patterns of as-formed powders obtained from different experimental conditions. However, all the reactions were smouldering in nature (because of excess fuel) and resulted in less flames except for glucose addition cases where flameless smouldering combustion results. Urea rich fuel mixtures produce pure HA, but pure glycine and glycine rich fuels yielded $Ca_2P_2O_7$ (calcium pyrophosphate) as minor phases along with HA. This change in yield may be due to prolonged combustion nature of the system (in case of glycine) which may change the initially formed HA to calcium pyrophosphate at higher duration of the combustion reaction. In glucose added cases, where system temperature and reaction duration are lower the resultant powders are HA in most cases.

Table 3. Specific surface area (SSA), particle diameter and crystallite size of various experimental batches are shown.

Fuel composition/glucose addition	SSA (m^2/g)	Particle diameter (nm)	Crystallite size from XRD (nm)
U	10·60	178	40
G	8·74	217	44
0·6U + 0·4G	9·22	205	34
0·4U + 0·6G	9·08	209	39
U + 0·5 g glucose	19·89	107	33
U + 0·8 g glucose	17·67	95	28
U + 1·0 g glucose (heat treated sample)	26·54	71	23

#U: Stoichiometric urea ($\mu = 1$); G: stoichiometric glycine ($\mu = 1$).

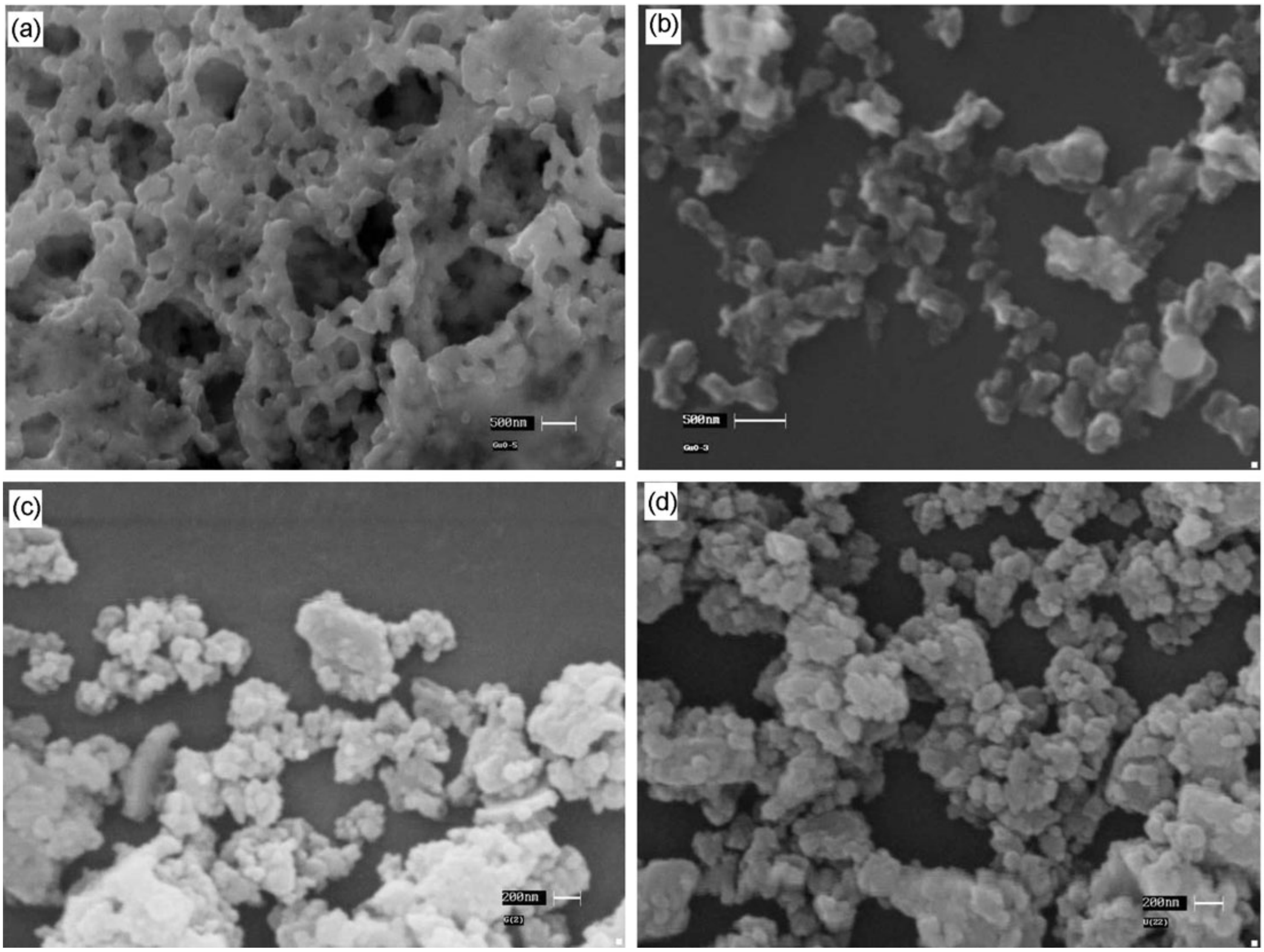

Figure 5. SEM micrographs of as-synthesized HA powders obtained from various experimental conditions: (**a**) 0·6U + 0·4G stoichiometric batch, (**b**) 0·8U + 0·2G stoichiometric batch, (**c**) addition of 0·5 g glucose with stoichiometric urea and (**d**) addition of 1·0 g glucose with stoichiometric urea.

3.2c *SEM and FESEM studies*: Powder morphology of as-synthesized powders was characterized by SEM and FESEM techniques. It exhibited foamy agglomerated particles with homogeneous distribution and presence of random distribution of voids in their structure. This highly porous, foam-like structure was formed due to the inherent nature of the chemical reaction associated with the evolution of large volume of gases, and short reaction period followed by fast quenching which prevented further agglomeration/sintering of particles. Figure 5 (a, b, c, d) showed the SEM micrographs of as-formed foamy structured powder. All photographs showed clearly dis-

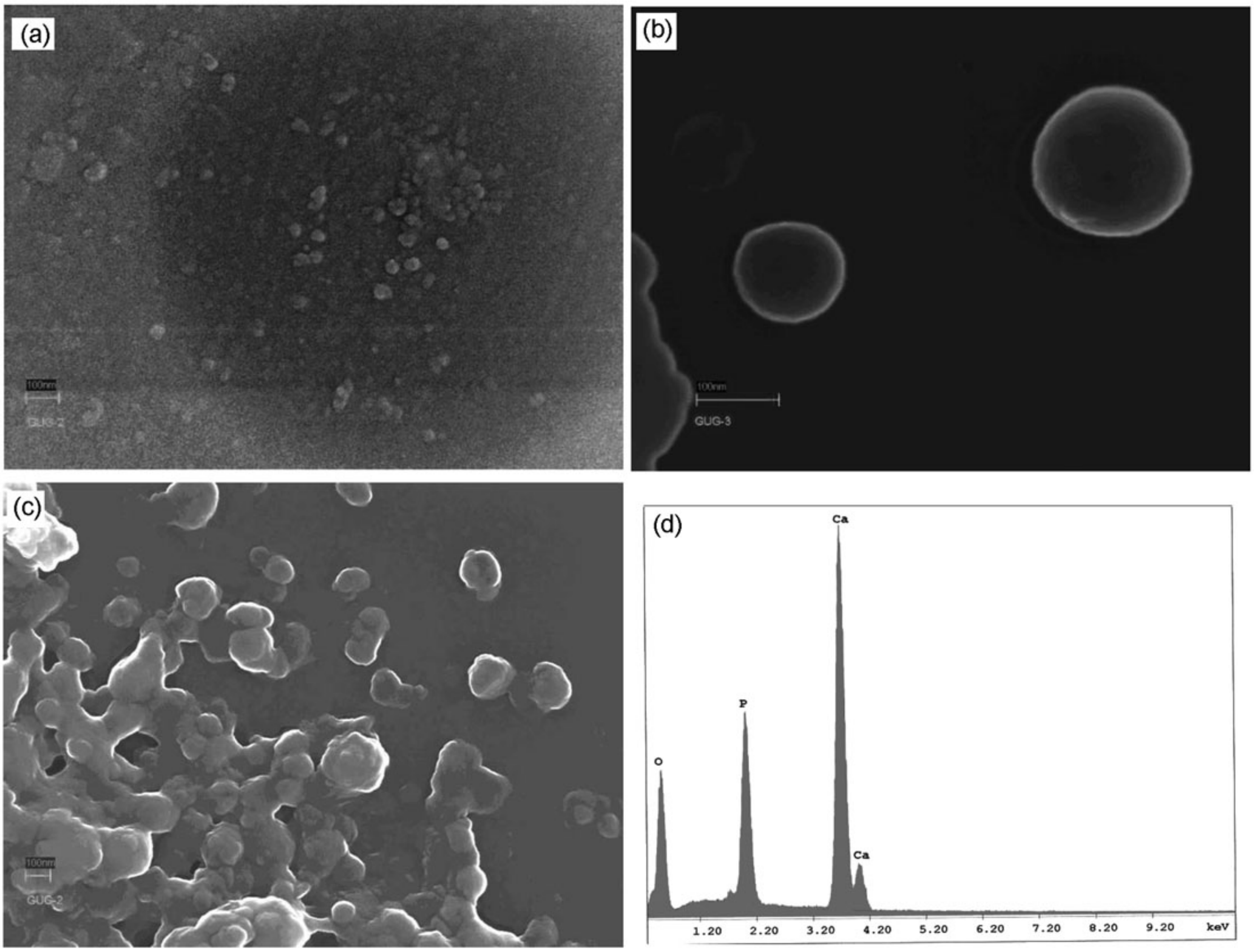

Figure 6. FESEM micrographs and EDXA of as-synthesized powders obtained from various experimental conditions: (**a**) addition of excess urea alone (F/O = 3·75), (**b**) addition of excess urea alone ($\mu = 3{\cdot}75$), (**c**) combination of glycine, urea and glucose (1·875U + 1·875G + 0·5 g glucose) and (**d**) combination of glycine, urea and glucose (1·875U + 1·875G + 0·5 g glucose).

crete spherical shaped nano-particles and their foam like agglomeration. Figure 5 (a, b) exhibited the SEM photographs of as-formed voluminous mass obtained from mixed fuel batches. The highly porous configuration was observed in case of first photograph (figure 5a). During the combustion reaction, the release of extensive gaseous by-products and the instantaneous reactions inhibit the particles sintering and create the pores in the structure of resultant powder. Figure 5 (c, d) also showed the SEM photographs of as-synthesized powder obtained from glucose containing batches. In both cases, very similar particles were observed and the size of individual particle was <50 nm. Figure 6(d) shows the qualitative EDX analysis which confirmed the presence of calcium phosphate phase in the micrographs at different regions. Figure 6 (a, b, c) shows the FESEM micrographs of as-formed powder. All micrographs clearly show that at first spherical nanoparticles formed under experimental condition undergoes extensive agglomeration. Some isolated spherical particles detected exhibit a size of <20 nm.

The median particle size distributions of the as-prepared powders by photon correlation spectroscopy have been found to decrease with increase in urea content. It was also found that glucose addition tremendously reduces the median particle size. The particle size distribution is multi-modal, and agglomerates are observed to be of different sizes. Particle agglomerates as large as 10·12 μm was observed in the distribution of only stoichiometric glycine containing batches. It has been observed that the degree of agglomeration increases with increase in glucose addition. Reduction of particle size causes the enhancement of surface activity that leads to larger agglomerated particles. Figure 7 (a, b, c, d) shows the particles size distribution of various combustion processed powders.

3.2d *FTIR study*: Figures 8 and 9 show the FTIR spectra of a few representative solution combustion processed powders obtained from different experimental conditions. Figure 8(a, b) represents the FTIR spectra of the samples

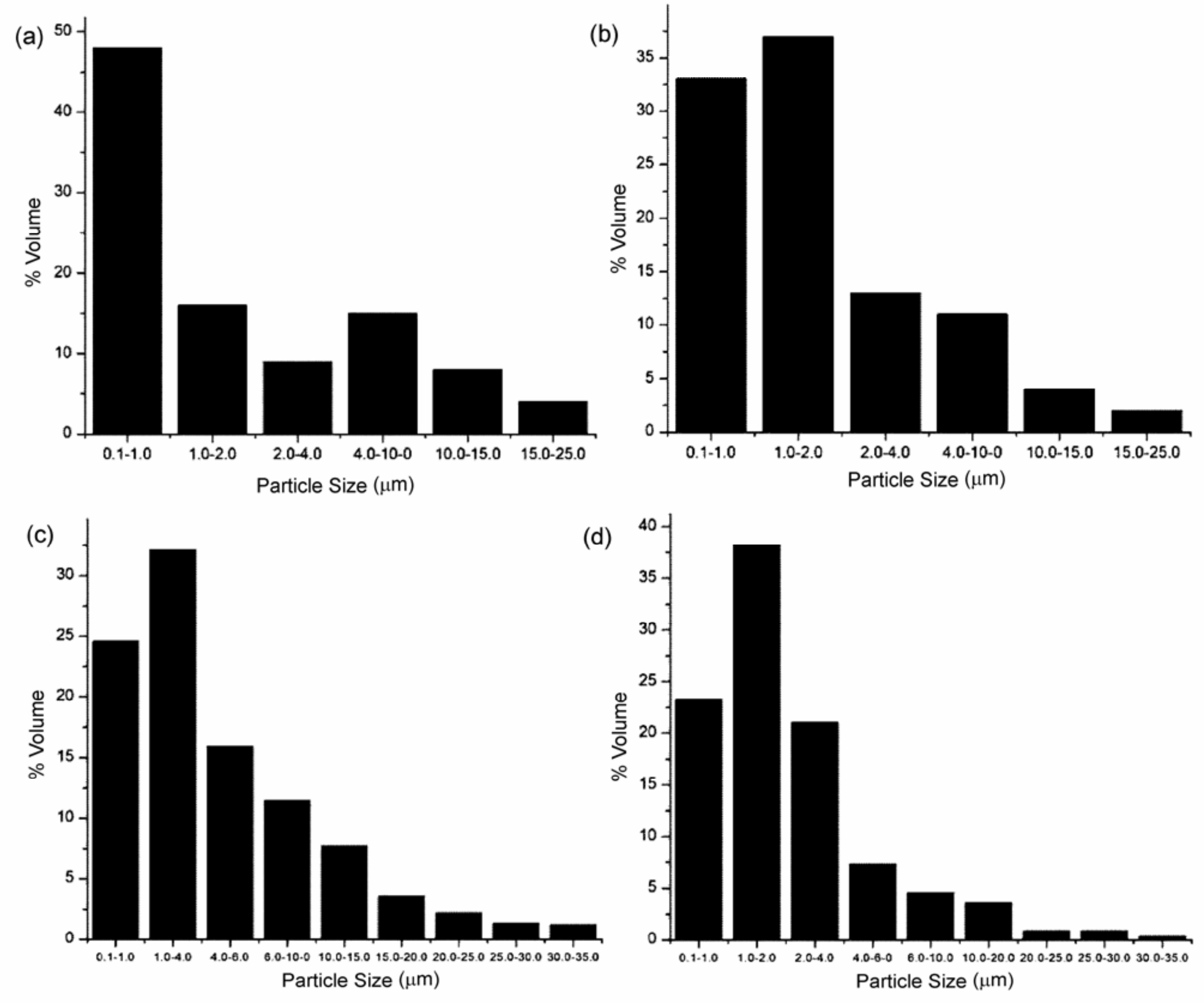

Figure 7. Particle size distribution of as-synthesized powders obtained from various experimental conditions: (**a**) U + 1·0 g glucose addition, (**b**) U + 0·5 g glucose addition, (**c**) 0·4 U + 0·6G and (**d**) 0·6U + 0·4G.

obtained from the batches containing combination of urea and glycine in stoichiometric F/O ratio (F/O = 1), whereas figure 8(c) shows the FTIR spectra of sample obtained from mixture of stoichiometric urea and 0·5 g of glucose. The characteristic features of the as-synthesized powder spectra, viz. the PO_4^{3-} bands at 1046, 1023, 963, 492, 472 and 435 cm^{-1} and OH^- stretching mode at 3571·92 cm^{-1} and bending vibration at 634 cm^{-1}, are typical for the HA phases. The presence of CO_3^{2-} peaks in all the samples at 877 cm^{-1} and a broad band at 1652–1530 cm^{-1} indicate that the carbonate ion substitution has occurred at the phosphate site of HA. On the basis of FTIR results it can be further inferred that the powders are essentially free of the nitrate-group (2213–2034 cm^{-1}) that is very much important for biomedical applications. Figure 9 (a, b, c, d) shows the FTIR spectra of as-formed powders obtained from different combinations of urea–glycine and urea–glycine–glucose batches where fuel to oxidizer ratio (F/O) is always maintained at 3·75. From the FTIR spectrum, it is clear that some characteristics features of calcium pyrophosphates along with HA appeared at the wave length around 1454, 1423, 1139, 1085, 1069, 1039, 1031, 939, 962, 562, 569, 431 and 492 cm^{-1}. These absorbance bands are possibly due to presence of various P–O bonds in the structure of calcium pyrophosphate ($Ca_2P_2O_7$). The O–P–O bending is recorded at 562 cm^{-1} and 569 cm^{-1}. The P–O symmetric stretching vibrations correspond to the absorptions occurring at 1454, 1423, 1139, 962, 939 cm^{-1}, whereas the asymmetric stretching vibrations give rise to absorptions at 1085, 1069, 1039 and 1031 cm^{-1}. The absorptions between 431 and 492 cm^{-1} are due to the presence of oxygen–calcium bonds.

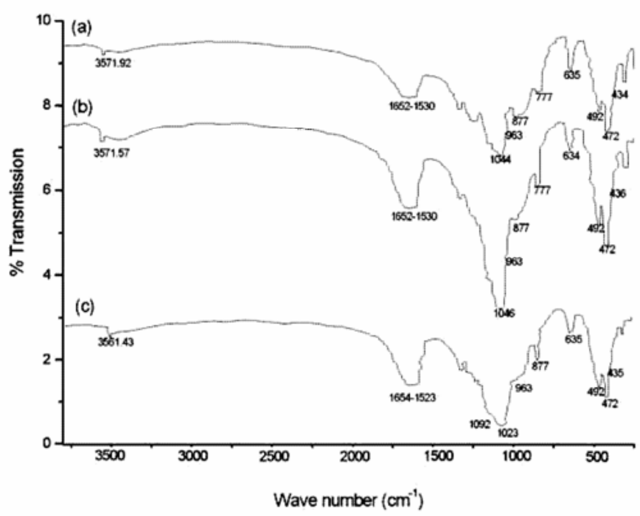

Figure 8. FTIR spectra of combustion processed powders obtained from different experimental conditions: (a) 0·6U + 0·4G stoichiometric mixture, (b) 0·4U + 0·6G stoichiometric mixture and (c) U + 0·5 g glucose addition.

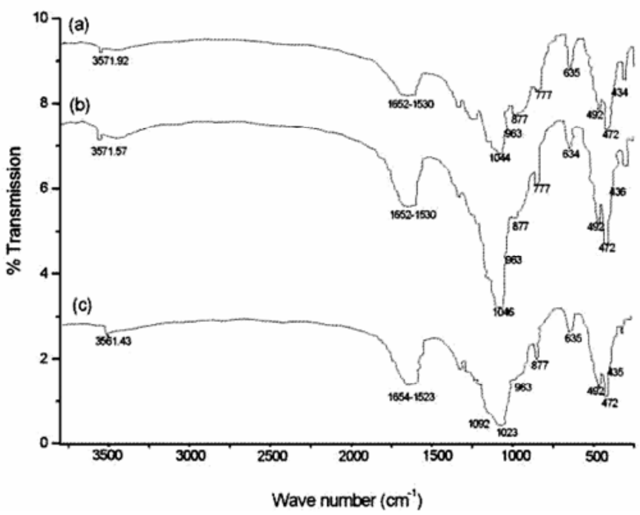

Figure 9. FTIR spectra of combustion processed powders obtained from different experimental conditions wherein fuel to oxidizer ratio (μ) is always maintained at 3·75: (a) 2·4375U + 1·3125G, (b) 3·75U alone, (**c**) 1·875U + 1·875G + 0·5 g glucose addition and (d) 3·75G alone.

4. Conclusions

The present work showed that the mode of combustion reaction could be controlled by tailoring the fuel composition. A very small quantity of glucose addition to stoichiometric and fuel excess urea or glycine or combination of them significantly reduced the combustion flame temperature (T_f). The investigation also showed that with increase in the percentage of glucose addition in the precursor batch, the vigorous mode of self-propagating combustion reaction became smouldering in nature. The specific surface areas (SSA) of as-synthesized powders obtained from glucose–stoichiometric urea/glycine batches were found to be higher than that obtained from pure urea–glycine mixed fuel batches. SEM, FESEM, XRD and surface area measurement data confirmed the formation of nanocrystalline HA powder (pure as well as mixed with calcium pyrophosphate) by this newly adapted solution combustion technique. It is observed that nano-sized (≤50 nm) HA powder could be prepared conveniently and economically by this technique. The experimental work also suggested that by addition of appropriate quantity of glucose with precursor batch, the solution combustion synthesis technique could be tailored to yield a variety of calcium phosphates or their mixtures with a control over the resultant particle size.

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