Solvothermal/Hydrothermal Synthesis of Metal Oxides and Metal Powders with and without Microwaves

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Anatase and Ca, Sr and $Ca_{0.5}Sr_{0.5}$ hydroxyapatites were synthesized by conventional-hydrothermal (C-H) as well as microwave-hydrothermal (M-H) methods. Microwave-assisted reactions led to accelerated syntheses of anatase but no such acceleration of reactions could be detected with the syntheses of hydroxyapatites because the crystallization of the latter materials occurred at very low temperature. Cu and Au metal powders were produced by using glucose, fructose or sucrose as reducing agents under C-H conditions at 160 °C, where fructose and sucrose were found to be stronger reducing agents than glucose. The crystallinity of all the powders was characterized by powder X-ray diffraction, and morphology and particle sizes were determined by scanning or transmission electron microscopy.

Key words: Nanoparticles, Anatase, Apatites, Copper, Gold, Microwave-Hydrothermal Technique

Introduction

The solvothermal process including the hydrothermal process is one of the oldest "Green Chemistry" approaches, if not the oldest for materials synthesis. The hydrothermal/solvothermal process is a green process because of the closed system conditions used in hydrothermal reactors, and it has been extensively used for growing single crystals, for example, quartz [1] and many kinds of metal oxide [2 – 5], metal [6, 7] and semiconductor [8, 9] powders. The hydrothermal/solvothermal process has many advantages in addition to being a green process: (i) it is energy efficient because of low temperature synthesis, (ii) it is an environmentally friendly process because of closed system conditions, (iii) unused components can be recycled, (iv) precipitants are not always needed, (v) high-purity products can be synthesized, (vi) metastable and new phases can be accessed, (vii) hydroxylated and hydrated materials such as clays and zeolites can only be made by this process, and (viii) crystal size, morphology, composition, and polymorphism of the synthesized phases are easily controlled. Experimental parameters such as temperature and/or pressure, pH, Eh (oxidation-reduction potential), concentration of chemical species, and the use of inorganic additives for homogeneous and heterogeneous nucleation can also be carefully controlled. Although the conventional hydrothermal/solvothermal process has been in use for a long time, the hydrothermal/solvothermal process in combination with electric, microwave and ultrasonic fields is rather recent [10 – 18]. Starting about 1985, we developed the microwave-hydrothermal/solvothermal process [12] and employed it successfully for the synthesis of phases in the wide arena of materials families of interest including metal powders [12 – 17]. There are several obvious reasons to further develop, understand, and exploit the impact of this technique in the synthesis of materials which are technologically important. Some significant advantages are: (i) it can increase the reaction rate by one to two orders of magnitude, (ii) it can lead to novel phases, (iii) it can eliminate metastable phases, and (iv) it can lead to a rapid heating. Rapid heating along with rapid kinetics can lead to energy savings. The objectives of the present study are to show that the microwave-hydrothermal/solvothermal process is advantageous over the conventional hydrothermal process in synthesizing some metal oxide phases and to synthesize metal phases by the conventional hydrothermal process using biomolecules.

Experimental Section

TiO_2 syntheses

For the preparation of TiO_2, a 0.5 M Ti solution was prepared from a titanium oxysulfate sulfuric acid complex (Alfa

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Run no.	Metal compound	Carbohydrate	NaOH treatment	pH before NaOH	pH after NaOH
SK12	$CuSO_4 \cdot 5H_2O$	D-(+)-Glucose	n	4.3	–
SK13	$CuSO_4 \cdot 5H_2O$	D-(+)-Glucose	y	4.3	9.9
SK18	$CuSO_4 \cdot 5H_2O$	D-(–)-Fructose	n	4.3	–
SK20	$CuSO_4 \cdot 5H_2O$	D-(+)-Sucrose	n	4.7	–
SK30	$HAuCl_4 \cdot xH_2O$	D-(+)-Glucose	n	1.7	–
SK31	$HAuCl_4 \cdot xH_2O$	D-(+)-Glucose	y	1.7	10.8

Table 1. Synthesis conditions for metals with different metal compounds and biomolecules as reducing agents.

Aesar). 20 mL of this solution was treated in Parr reactors at different temperatures for different durations under conventional hydrothermal conditions. For comparison, microwave-hydrothermal reactions were carried out in Teflon vessels using a microwave-accelerated reaction system, MARS-5 (CEM Corp.). The microwave system operates at a frequency of 2.45 GHz with a maximum power of 1200 W. The experiments were carried out in double-walled digestion vessels having an inner non-reactive Teflon PFA liner and an outer Ultem polyetherimide shell of high mechanical strength. Temperature was controlled in a single reference vessel with a microwave-transparent fiber optic temperature probe (RTP-300 Plus, CEM Corp.). Accurate pressure feedback can also be achieved with the ESP-1500 Plus (CEM Corp.) for a single reference vessel. Temperature and pressure probes allowed the reaction to be controlled by precisely monitoring the temperature and pressure within a control vessel. The reported temperatures are measured temperatures in this microwave unit. The maximum operating temperature and pressure for the system are 240 °C and 350 psi, respectively. After the hydrothermal reactions, the solid and solution phases were separated by centrifugation and the precipitates washed several times with deionized water and dried at 60 °C.

Hydroxyapatite syntheses

For the synthesis of Ca, Sr, and $Ca_{0.5}Sr_{0.5}$ hydroxyapatites, $Sr(NO_3)_2$, $(NH_4)_2HPO_4$, and $Ca(NO_3)_2$ containing 15.7 % H_2O (Alfa Aesar) were used as precursors. The molar ratios of Ca or Sr : P for Ca- and Sr-hydroxyapatite syntheses was 5 : 3, and that of Ca : Sr : P for $Ca_{0.5}Sr_{0.5}$ hydroxyapatite synthesis 2.5 : 2.5 : 3. In a typical synthesis under the conventional hydrothermal conditions, appropriate amounts of $Ca(NO_3)_2$ and/or $Sr(NO_3)_2$, were dissolved in 20 mL of deionized water, and then 40 mL of a 0.375 M $(NH_4)_2HPO_4$ solution was added. After mixing, the pH was adjusted to 10 using NH_4OH. The mixture was treated hydrothermally in autoclaves at 50 – 160 °C for 2.5 – 4.5 h or 24 h. The resulting precipitates were washed several times with deionized water and dried at 60 °C. For room-temperature syntheses, some of the batches were stirred for 0.5 h after pH adjustment to 10 and subsequently washed with deionized water and dried at 60 °C.

For the synthesis of Ca, Sr, and CaSr hydroxyapatites under microwave-hydrothermal conditions, 10 mL of deionized water and suitable amounts of $Ca(NO_3)_2$ and/or $Sr(NO_3)_2$, were put into Teflon vessels followed by the addition of 20 mL of a 0.375 M $(NH_4)_2HPO_4$ solution. Then, the pH was adjusted to 10 using NH_4OH, and the reactants were heated in the microwave digestion system at precisely controlled temperatures in the range of 80 – 160 °C for 1 h. The resulting precipitates were washed several times using deionized water and dried at 60 °C in an oven prior to characterization.

Cu and Au metal particle synthesis using biomolecules

Copper(II) sulfate pentahydrate (¿ 98 %, Alfa Aesar) and tetrachloroauric acid hydrate (Au content = 49 %, Johnson Matthey Inc.) were used as metal source and D-(+)-glucose (99.5 %, Sigma), D-(–)-fructose (98 %, Sigma), and D-(+)-sucrose (> 99.5 % Fluka) were used as reducing agents. In a typical procedure, 0.64 mmol of the copper or the gold compound and 0.10 g of the biomolecules were fully dissolved in 10 g of distilled water with stirring at r. t. Aqueous NaOH solution (1.0 M, Alfa Aesar) was added to the above solutions to reach pH $\sim$ 10, or until no further change of color was observed. The detailed conditions for each sample are described in Table 1. Thereafter, each of the solutions was transferred to a Teflon-lined stainless steel autoclave, and heated at 160 °C under static conditions for 8 h. The products were washed with ethanol and separated by centrifugation. Finally, the samples were dried at 60 °C for 24 h.

Characterization

The synthesized solid phases were characterized by X-ray diffraction (XRD) using a Scintag X-ray diffraction unit with CuK_α radiation in the 2θ range of 5 – 40° at a scanning speed of 5 $^\circ$ min^{-1}. The morphology and particle size were determined by a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with a very thin carbon film or *via* transmission electron microscopy (TEM; Model 2010, JEOL, Tokyo, Japan).

Results and Discussion

Syntheses of the anatase form of TiO_2 by C-H and M-H processes

The anatase form of TiO_2 was produced at all temperatures investigated by both the conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) processes using the titanium oxysulfate sulfuric acid

Table 2. Yields of TiO_2 (anatase) by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) processes.

Temperature (°C)	Heating time (h)	Anatase yield (%) C-H	M-H
120	2	[a]	91.7
120	4	26.3	[a]
120	8	73.8	[a]
140	0.5	[a]	12.6
140	1	[a]	87.8
140	2	14.4	90.8
140	4	87.5	[a]
160	0.5	[a]	90.3
160	1	16.3	88.2

[a] Syntheses not performed.

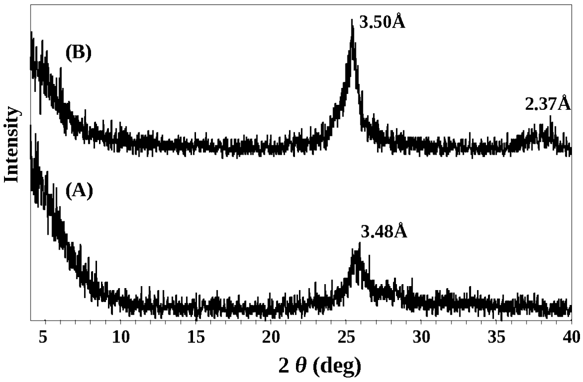

Fig. 1. Powder diffraction pattern (CuK_α radiation) of anatase prepared by a conventional-hydrothermal process at 120 °C/4 h (A) and by a microwave-hydrothermal process at 120 °C/2 h (B).

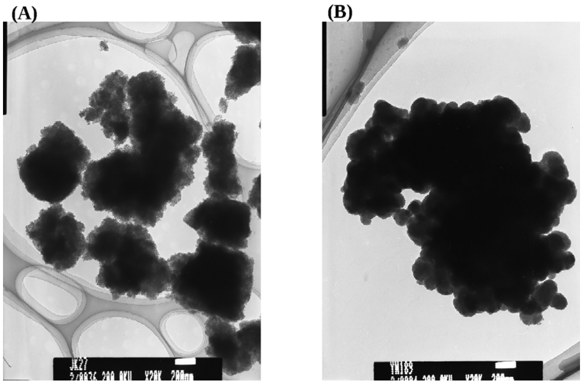

Fig. 2. Anatase prepared by a conventional-hydrothermal process at 120 °C/8 h (A) and by a microwave-hydrothermal process at 120 °C/2 h (B).

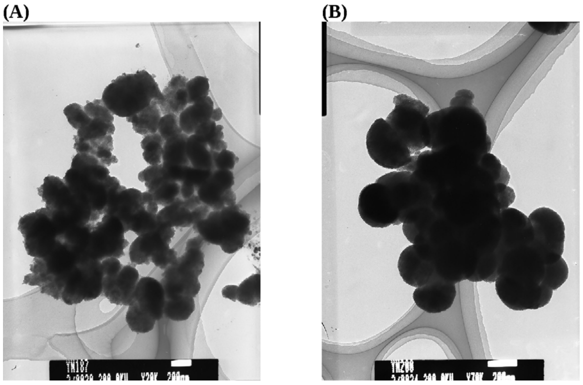

Fig. 3. Anatase prepared by a microwave-hydrothermal process at 140 °C/1 h without PVP (A) and with PVP (B).

complex (Table 2). The presence of sulfate led to the formation of the anatase polymorph unlike when titanium chloride was used previously, which led to rutile [13]. These results are supported by previous findings under C-H [19] and M-H conditions [20]. The previous studies showed that Cl^- ions led to rutile while $SO_4{}^{2-}$ ions led to anatase, because chloride coordinates weakly to TiO species while the sulfate coordinates strongly. Thus the Ti oxysulfate salt is a good precursor for the pure anatase polymorph, which is useful in photocatalytic applications. Table 2 shows that the M-H process led to higher yields in a shorter time at all temperatures compared to the C-H process. For example at 120 °C, the M-H process led to 92 % yield in 2 h as compared to the C-H process which yielded only 26 % after 4 h of treatment. Powder X-ray diffraction analysis of anatase crystallized at 120 °C/4 h under C-H conditions showed broader and less intense peaks compared to that crystallized at 120 °C/2 h under M-H conditions (Fig. 1). Thus the M-H process led to increased crystallization compared to the C-H process supporting our previous results for other systems [21, 22]. The faster crystallization under M-H conditions, however, led to more agglomeration of the powders compared to those prepared by the C-H process (Fig. 2). The faster crystallization is attributed here to localized "super heating" [23] rather than any special microwave effect. We used polyvinylpyrrolidone (PVP) during M-H synthesis to see if we can prevent an aggregation of anatase. As can be seen from Fig. 3, the presence of PVP did not disperse anatase but led to well rounded anatase aggregates. Both samples, however, showed high surface areas. The surface areas of the two samples without and with PVP shown in Fig. 3 are 132 and 77 $m^2\,g^{-1}$, as determined by BET-N_2 analysis. This aggregation problem may be avoided by stirring during the M-H process as has been shown with $BaTiO_3$ [24].

Table 3. The formation of hydroxyapatites by conventional-hydrothermal and microwave-hydrothermal treatments.

Temperature (°C)	Time (h)	Ca apatite	CaSr apatite	Sr apatite
25[a]	–	Monetite formed	Monetite formed	Phase crystallized + impurties
Conventional-hydrothermal method:				
50	2.5, 4.5	Phase crystallized	Phase crystallized	Phase crystallized
80	2.5, 4.5	Phase crystallized	Phase crystallized	Phase crystallized
100	2.5, 4.5	Phase crystallized	Phase crystallized	Phase crystallized
160	2.5, 4.5	Phase crystallized	Phase crystallized	Phase crystallized
Microwave-hydrothermal method:				
80	1	Phase crystallized	Phase crystallized	Phase crystallized
100	1	Phase crystallized	Phase crystallized	Phase crystallized

[a] After adjustment to pH = 10, the mixtures were stirred at r. t. for 0.5 h.

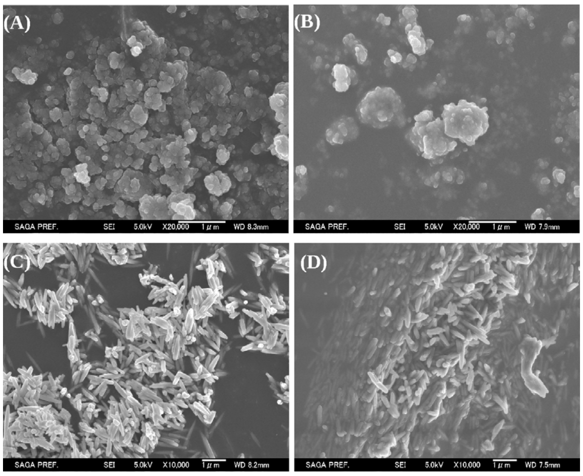

Fig. 4. $Ca_{0.5}Sr_{0.5}$ hydroxyapatites synthesized by C-H (A) and M-H (B) processes at 80 °C/2.5 h and Sr-hydroxyapatites synthesized by C-H (C) and M-H (D) processes at 80 °C/2.5 h.

Syntheses of apatites by C-H and M-H processes

Table 3 shows the results of Ca, Sr and $Ca_{0.5}Sr_{0.5}$ hydroxyapatite syntheses. As can be seen, apatites could be synthesized at very low temperatures. In fact, Sr apatite was synthesized even at r. t. but not Ca and $Ca_{0.5}Sr_{0.5}$ apatites. Because of the low temperatures involved, we could not see the effect of microwaves on reaction kinetics of the apatite syntheses. However, the M-H process led to somewhat more agglomerated powders than those obtained by the C-H process, as can be seen from Fig. 4.

Syntheses of Cu and Au metal particles by C-H process

Powder X-ray diffraction showed that both Cu and Au crystallized under all the experimental conditions listed in Table 1. Simple sugars acted as reducing agents for both Cu and Au salts to form metal powders. Glucose has been used previously as a reducing agent at r. t. to prepare Au nanoparticles from $HAuCl_4$ under alkaline conditions using NaOH [25]. The objective here was to see what kind of morphologies could be obtained using biomolecules under higher temperature conditions. Figs. 5A and 5B show the morphologies of Cu particles using glucose with and without adjusting the pH. Nanoparticles of Cu were obtained at 160 °C under acidic pH (Fig. 5A), but large hexagonal plates and other structures were obtained under alkaline conditions (Fig. 5B). Fructose and sucrose led to very large

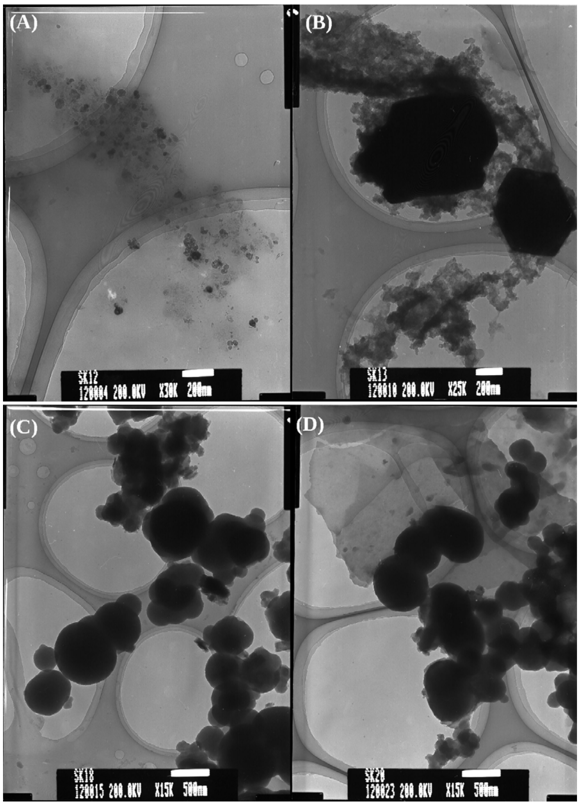

Fig. 5. Cu metal particles prepared by a conventional-hydrothermal process at 160 °C/8 h: (A) $CuSO_4$ plus glucose; (B) $CuSO_4$ plus glucose and adjusting the pH to about 10 using NaOH; (C) $CuSO_4$ plus fructose; (D) $CuSO_4$ plus sucrose.

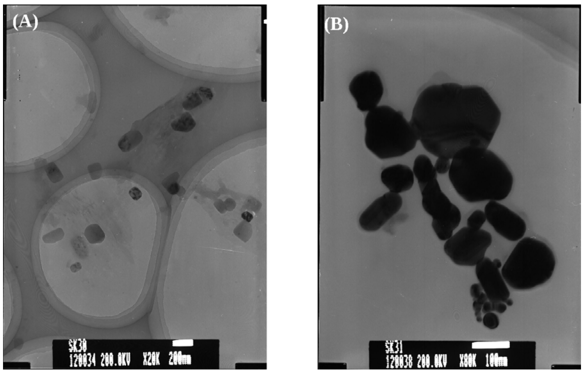

Fig. 6. Au metal particles prepared by a conventional-hydrothermal process at 160 °C/8 h: (A) $HAuCl_4 \cdot xH_2O$ plus glucose; (B) $HAuCl_4 \cdot xH_2O$ plus glucose and adjusting the pH to about 10 using NaOH.

Cu particles (Figs. 5C and 5D) under acidic conditions unlike glucose which led to nanoparticles. Thus, fructose and sucrose appear to be stronger reducing agents than glucose. Uniform particles of about 200 nm of gold were formed under acidic conditions (Fig. 6A), while non-uniform particles of different sizes were formed under alkaline conditions (Fig. 6B). Further studies are needed to control the size and shapes of both Cu and Au metal particles under hydrothermal conditions.

Conclusion

The presence of a microwave field during hydrothermal processes increases the kinetics of crystallization of anatase, TiO_2. An effect of microwaves on the crystallization of Ca, Sr, and $Ca_{0.5}Sr_{0.5}$ hydroxyapatites could not be detected because these phases crystallized easily at low temperatures. Biomolecules such as glucose, fructose and sucrose were shown to reduce Cu and Au salts to metal powders under conventional-hydrothermal conditions.

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