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Soft solution processing: concept and realization of direct fabrication of shaped ceramics (nano-crystals, whiskers, films, and/or patterns) in solutions without post-firing

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Based upon thermodynamic consideration for materials cycling and processing on the earth, where environmental and energetical problems have been seriously considered, we can conclude that solution processing using aqueous solutions should be the most important processing for advanced materials. According to the concept, we are proposing Soft Solution Processing (SSP) where advanced ceramics also must be preferably fabricated in solution(s) directly into desired composition, structure, shape, size, location, orientation, etc., in a closed system. This is contrasting to conventional processings where advanced ceramics have been fabricated from solids, liquids, and/or gases including atoms and/or ions in vacuum by sophisticated processes using high temperatures, high pressures, expensive precursors, and equipments. In most those processes, exhausted materials and heats have never cycled but just discarded into the environment. We have succeeded to prepare nanocrystals of ZrO_2, HfO_2, HAp, $BaTiO_3$, CeO_2/ZrO_2, $LiCoO_2$, CdS, etc., whiskers of HAp, and films of $BaTiO_3$, $SrTiO_3$, $CaWO_4$, $BaMoO_4$, YVO_4, $LiCoO_2$, $LiNiO_2$, $ZnFe_2O_4$, etc., in solutions at low temperatures of RT-150°C. Recently, the fabrication of patterned films for $LiCoO_2$, PbS, CdS, $BaTiO_3$, $SrTiO_3$, etc., have also been succeeded in/from solutions at the low temperatures. Those "Direct Patterning of Ceramics" should be soft in comparison with conventional ceramic patterning where multi-steps like firing, sintering, masking, etching, etc., are required even after synthesizing ceramic powders.

1. Introduction: Why soft process is important? [1–3]

Modern human society has been developed by huge amounts of production, use and waste of advanced artificial materials, which are supported by huge consumption of energies and resources. The flow of those materials and energies seems to be already saturated or even over saturated on the earth. World annual consumption of energy has already reached to critical sizes: 10% of total photosynthesis energy and 0.1 – 0.5% of total atmospheric (wind, wave, tide, etc.) energy which is controlling global climates on the earth. Therefore, we must eliminate or sustain rather than increase those materials and energies flows. Recycling of materials (wastes) is possible when we put more energies to the recycling process than the production/fabrication process, but it brings about more thermal contamination. In order to prevent such thermal contamination, we must consider total processing for useful materials from mining and up-grading of raw materials, then production/fabrication, transportation, usage, waste and until cycling/recycling of products by environmentally friendly ways.

2. Thermodynamic principles of advanced materials processing [1–3]

Processing of advanced materials generally consists of two steps: (I) the synthesis of substances (ceramic, metallic, organic) that can be characterized by (1) a particular chemical composition, (2) a physical state including crystal structure, and (3) specific properties; and

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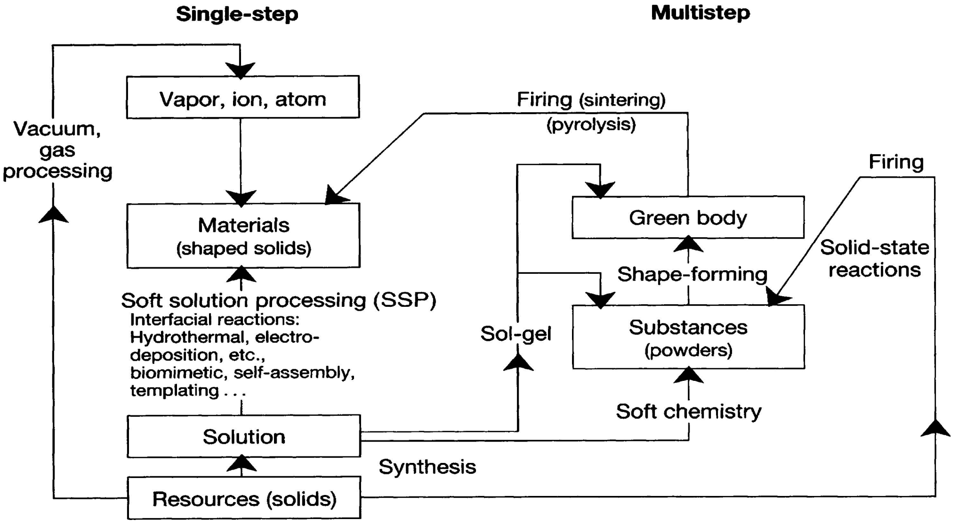

Figure 1 Schematic diagram of the advanced materials processings and their energy consumptions. The right passes which have been widely used, consist of two steps: synthesis of powders of substances (having a particular chemical composition, a particular physical state including structure, and particular properties based upon composition and structure) and subsequent fabrication of the materials (via shape forming and shape fixing b firing/sintering, pyrolysis, melting, or casting). These passes are environmentally stressing, energy consuming, and expensive. An alternative processing using gas and/or vacuum can produce shaped materials by a single step but it require more energies than conventional multi-step one. Soft Solution Processing (SSP) aims to fabricate shaped materials preferably in a single step using solutions.

(II) materials fabrication (i.e., shape-forming and shape-fixing by firing/sintering, pyrolysis, melting, or casting) as shown schematically in Fig. 1 (right side). In this regard, it is very difficult to give desired shape, form, and size to inorganic ceramic materials, owing to their brittleness. Organic materials, such as polymers and plastics, or metallic materials can be generally deformed when local stresses are applied over their yield stresses, but ceramics are susceptible to brittle fracture rather than plastic deformation. Melt/Cast Processes have hardly been applied to ceramic materials except for glasses. Thus most of ceramics have been fabricated via the two-step processes. The "classical" two-step processing method usually requires high temperatures and consumes a lot of energy, particularly in the case of ceramics. More recent processing routes using a gaseous phase (e.g., chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), etc. and physical vapor deposition (PVD) methods in a vacuum system [e.g., sputtering, molecular-beam epitaxy (MBE), etc.] can produce shaped material in a single step, but require even higher energy than standard high-temperature processes. Generally speaking, all of these techniques have resulted in environmental problems because their consumed energy results in exhaust gas(es) or exhaust heat (entropy). Vacuum systems especially seem to put more stresses on the environment because they require continuous pumping to maintain a vacuum, and their exhaust gas(es) cannot be recycled due to their diluted large volumes.

However, one can fabricate specifically shaped, sized, reacted, and/or oriented materials, *in situ*, by Soft Solution Processing (SSP), in only one step (see left side of Fig. 1). SSP can be defined as environmentally friendly processing using solutions, preferably aqueous solutions. It may provide similar results to every other processes using fluids (such as vapor, gas, and plasma) or beam/vacuum processing, while it is consuming less total energy than other processing routes. More energy is needed to create melts, vapor, gas, or plasma than to form aqueous solutions at the same temperature. This can be demonstrated using the example of $BaTiO_3$ (Fig. 2), which is one of the most important materials for the electronics industry. The driving force (ΔG) for the representative syntheses: Reactions (1) – (5) of $BaTiO_3$ are 38 kcal/mol, 727 kcal/mol, 3685 kcal/mol, 17 kcal/mol, and –14 kcal/mol, respectively, at a room temperature of 298K:

$$BaO_{(crystal)} + TiO_{2(crystal)} = BaTiO_{3(crystal)} \tag{1}$$

$$Ba_{(vapor)} + Ti_{(vapor)} + 3/2O_{2(gas)} = BaTiO_{3(crystal)} \tag{2}$$

$$Ba^{2+}_{(gas)} + Ti^{4+}_{(gas)} + 3O^{2-}{}_{(gas)} = BaTiO_{3(crystal)} \tag{3}$$

$$TiO_{2(crystal)} + Ba^{2+}_{(aq)} + 2OH^{-}{}_{(aq)} - H_2O_{(aq)} = BaTiO_{3(crystal)} \tag{4}$$

$$Ba^{2+}_{(aq)} + Ti(OH)_{4(aq)} - H_2O_{(aq)} - 2H^{+}_{(aq)} = BaTiO3_{(crystal)} \tag{5}$$

Any processing technique involving the gas/vapor phase requires a huge amount of energy (727-3685 kcal/mol) to make these gas/vapor precursors from solid raw materials, which are oxide or carbonate ores, and this energy

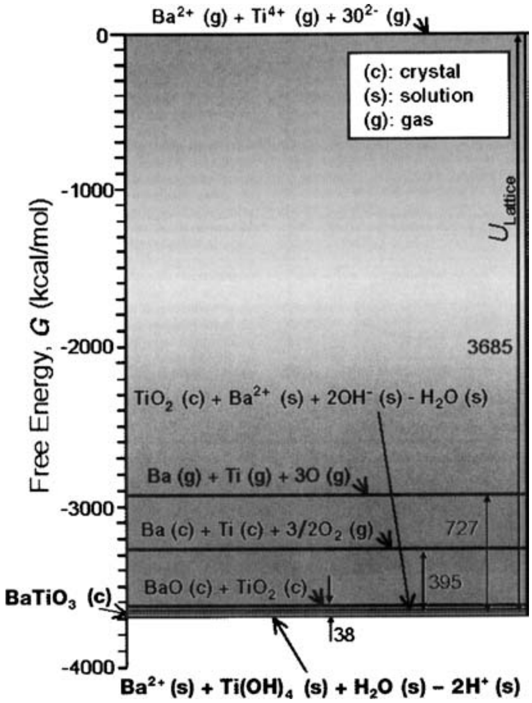

Figure 2 Energy diagram for the formation of $BaTiO_3$ at 25°C. Huge excess of energy is necessary to create, vapor, gas or ion (plasma) from the solid as compared to creation of aqueous solution at the same temperature. This gives the thermodynamic explanation why processing of the advanced materials using aqueous solution consumes low energy in contrast to vapor/plasma processing.

must then be released into the environment when solid $BaTiO_3$ is formed from these precursors. On the other hand, since the lattice energy of BaO and TiO_2 can be compensated by the hydration (solvation) energies of Ba^{2+} and Ti^{4+} ions, solution processing consumes very little energy, if activation energy (ΔG^*) for the synthesis can be overcome. Generally speaking, ΔG^* is inversely proportional to (ΔG^{-n}), where $n=2$ for the homogeneous nucleation process. The gaseous species are always in high-energy states, thus there is sufficient energy (ΔG, ΔG^*) for the reaction to yield crystalline compounds with a desired shape/size by means of several steps such as diffusion, adsorption, reaction, nucleation, and growth. On the other hand, species in aqueous solutions are hydrated (or chelated by some complexing agents), thus they are stabilized by the hydration (or chelation) energies and have only a small ΔG for the reaction. In those cases, relatively high activation energies are necessary for the reaction to occur by defeating those hydration (chelation) energies of ions. Electro- or electroless-plating for metals is achieved by reducing metal ion(s) electrochemically or chemically. However, in the case of ceramics, anions must be oxidized at the same time when cations are reduced. Therefore, some particular activation processes, such as electro-, photo-, sono-, complexo-, organo- or mechano-activation are required to accelerate the kinetics for synthesizing crystallized single- or multi-component ceramic materials from the solution.

3. Composition and shape controlled particles by solution processing [4–20]

Recently, nano-particles have been studied in various methods. Particularly, solution processings have been employed to fabricate those of double (multiple) component oxides because multiple components would be dissolved as solutes homogeneously in a solution. This is the main reason why such solution processings have been regarded as advanced processings for oxide powders. As seen in Table I, which has been revised from previous one [17, 18], traditional solid state syntheses would give products with poor quality [4, 6, 7]. Chemical processings like precipitation, coprecipitation, hydrolysis, pyloysis and/or physical processings like evaporation, burning and spraying, might give larger supersaturation to bring about formation of a huge numbers of nuclei. Therefore precipitation of nanoparticles from solutions have been rather common and easy task. However, there exist difficulties in controlling of the composition, shape and the crystallizing of particles in those methods. Because homogeneously reacted and crystallized particles require simultaneous supersaturations, precipitation and crystallization/reaction for different components, which are very difficult

TABLE I Comparison in advanced oxide powder processes, revised from previous Table [17, 18]. Solution (Chemical) processes give powders with higher purity, better reactivity, more homogeneous, and more controlled shape than solid state reaction. Among them, Polymerized Complex Method can give the most compositionally homogeneous one, and Hydrothermal Process can give morphology controlled one. The latter has also the merits of no requirement of calcinations and milling steps.

	Solid state reaction	Coprecipitation	Polymerized complex	Sol-gel	Hydrothermal
Cost	Low-moderate	Moderate	High	High	Moderate
State of development	Commercial	Commercial/ demonstration	R&D	R&D	Demonstration
Compositional control	Poor	Good	Excellent	Good-excellent	Good-excellent
Morphology control	Poor	Moderate	Moderate	Moderate	Good
Powder reactivity	Poor	Good	Good	Good	Good
Purity (%)	<99.5	>99.5	>99.9	>99.9	>99.5
Calcination step	Yes	Yes	Yes	Yes	No
Milling step	Yes	Yes	Yes	Yes	No

or almost impossible for multiple components of cations. Therefore these wet chemical methods, which have been called as Soft Chemistry (Chimie Douce) or Soft Chemical routes, need calcination after precipitation [3, 4]. The calcination might assure complete reaction and crystallization for multi-components particles but it would bring about sintering of particles (powders), thus milling(s) and/or grinding(s) after the calcination appear to be essential (see Table I) in most wet-chemical processings.

To improve homogeneity of the composition, three dimensional net-work forming of components (gel forming) before calcinations seems to be important which prevent the separation/segregation of various components during pylorizing. In this regard, "Polymerized Complex Methods," which have been generalized from the Pechini method, have originally been proposed in our group in 1991/1992 [5, 6]. Various cations can form their complex by chelating agent like citric acid, and then those complex can be polymerized by polymerizing agents like ethylene glycol to polyester network (=polymer gel). The gel containing homogeneously distributed chelated cations can be pyrolized to amorphous solids then crystallized into homogeneous compounds and/or homogeneous solid solutions. These processes do not include any sol formation step, where compositional separation/segregation may often happen, nor include sol gel transformation. Therefore, we have given the name, "Polymerized (or Polymelizable) Complex Methods," as one of gel methods or polymer precursor routes but distinguished from sol-gel methods [5–7]. Now many of crystallized particles (powders) with homogeneous compositions could be fabricated for perovskites, photocatalysts, and superconductors [5–8]. As an example, the procedure and the result of $SrTiO_3$ by Polymerized Complex Method are shown in Figs. 3–4.

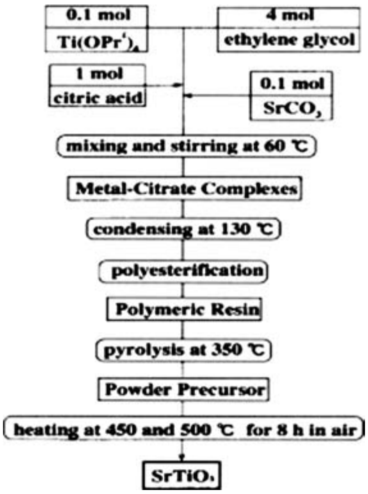

Figure 3 Flow chart for preparing $SrTiO_3$ by the Polymelized Complex Method. The molar ratio of $Ti(OPr^i)_4/SrCO_3$/CA/EG = 0.1/0.1/1/4 [6].

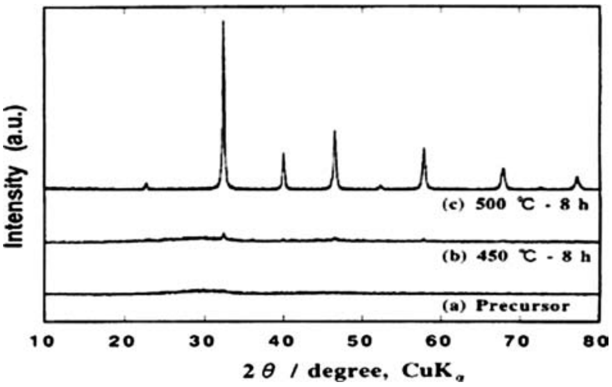

Figure 4 X-Ray diffraction patterns of the Polymerized Complex-derived Powder precursor for $SrTiO_3$ (a) and of samples heat-treated in static air at 450°C for 8 h (b) and 500°C for 8 h (c) [6].

Another direction has been investigated to improve crystallization and reaction of particles with multi-components without calcinations and/or firing. It is hydrothermal processing where those precipitates are activated to react and crystallize in crystalline particles through dissolution/precipitation and/or adsorption/desorption in a high temperature solution [17, 18]. Well crystallized shaped particles, from nano-meter size to centi-meter size, with desired morphologies; polyhedrons, needles, whiskers [17, 19], etc. Recently, numbers of people are interested in the hydrothermal processing of multi-components oxide particles due to their merits described above (Table I). We have published those works on ZrO_2 [9–11], CeO_2 [12], $LaCrO_3$ [13], HfO_2ss [14], CeO_2/ZrO_2ss [15], Hydroxyapatite [16–20], $BaTiO_3$ [21], $LiCoO_2$ [22], $LiFe_5O_8$ [23], $ZnFe_2O_4$ [24], NiS [25], CdS [26], ZnS [27], etc. Fig. 5 shows the nano-crystals of ZrO_2/CeO_2ss prepared hydrothermally [15]. Electrochemical reactions; anodic dissolution, anodic

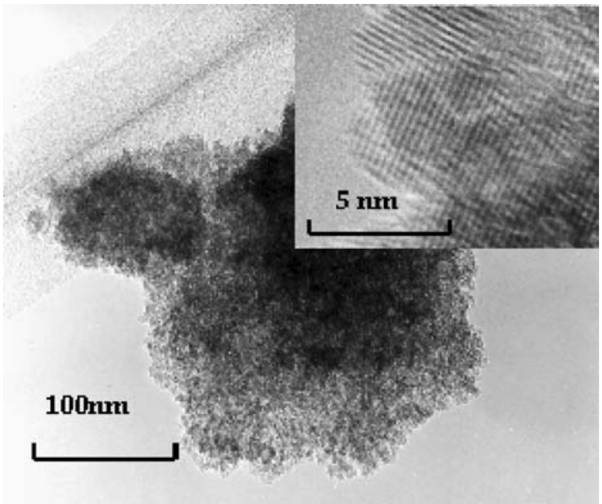

Figure 5 $Zr_{0.6}Ce_{0.4}O_2$ nano-crystals by Hydrothermal method with ball milling at 120°C for 6 h, 100 mn size powders consist of about 6 nm crystals [15].

oxidation, or even discharging, etc., might help to form those crystalline particles. We have, therefore, proposed Hydrothermal-Electrochemical Methods for the fabrication of multi-components oxides particles and/or films.

4. Films of double oxides by solution processing [27–43]

Fabrication of double oxide films from solutions is rather easy when the solutions and/or derived gels on a substrate can be fired (calcined, pyrolized, sintered) after dried and/or solvent removal, thus most of studies have used these procedures like dip, spin or spray coatings, sol-gel methods and/or electrophoretic depositions as seen in Fig. 1. Those processes have significantly been developed in recent works, but they still have similar problems for particles; inhomogeneous reactions and crystallization as described previously. In addition, other problems must be considered for films, that is; (1) adhesion of the film to the substrate and (2) cracking of the film on the substrate, both of which are caused from shrinkage of materials during crystallization upon firing. Thus thicker and denser film have more serious problems in those processings.

Moreover, we must consider (1) why "firing" is required to fabricate double oxide films?, (2) how much does it cost both economically and environmentally? One has burned fuels which have high chemical potentials to get a high temperature for "firing" ceramic or its precursor materials (and its substrate, too), and then wasted exhaust gases and heats into the environment. Those exhaust gases and heats must be counted as an environmental cost [1–3]. Use of gaseous precursors instead of solution precursors is much more costed as described in the Section 2.

If we can directly fabricate ceramic (i.e. double oxides) films in a solution without post-firing, we can avoid most of above mentioned problems. Of course it is difficult, more difficult than fabrication of ceramic particles because nucleation and growth rates of ceramic compounds must be matched with the precipitation rates of the multiple components. Particularly it is difficult that reactions must proceed among multiple components to form ceramic compounds without "firing." However, it is not impossible that crystalline double oxide films can be fabricated directly in a solution when a chemical driving force existed to form and to crystallize the double oxide [1–3]. For example, interfacial reactions between the substrate [**A**] and the solute [**B**] could be activated chemically and/or electrochemically to form the compound **ABO**$_x$ in film shapes. In 1989 [28], we succeeded at the first time to fabricate $BaTiO_3$ thin film on a Ti substrate in a $Ba(OH)_2$ solution at $\geq$ 100°C with electrochemical activation; anodic oxidation/dissolution by 1-10 mA/cm^2.

Since then similar techniques, called by Hydrothermal electrochemical Methods, have been applied to fabricate a lot of double oxides successfully at low temperatures of RT-200°C: $SrTiO_3$ [29, 30], (Sr, Ba)TiO_3 [31], $CaWO_4$ [32], (Ba, Sr, Ca)WO_4 [33, 34], $BaMoO_4$ [35], YVO_4 [36], $LiNiO_2$ [37], $LiCoO_2$ [38 – 40], $PbTiO_3$ [41], $LiNbO_3$, $BaFeO_3$, MFe_2O_4 (M=Zn, Mg) [42], etc., in our group. The mechanism of formation and nano-/micro-structure control have been investigated in detail for $SrTiO_3$ [30, 31], $BaTiO_3$ [31, 43], and $LiCoO_2$ [37 – 40]. Fig. 6 shows the nanostructure of $SrTiO_3$ film prepared by hydrothermal electrochemical method [30]. $BaTiO_3$ film can be formed by microwave heating of Ti substrate in $Ba(OH)_2$ solution upto 100°C as seen in Fig. (7) [44].

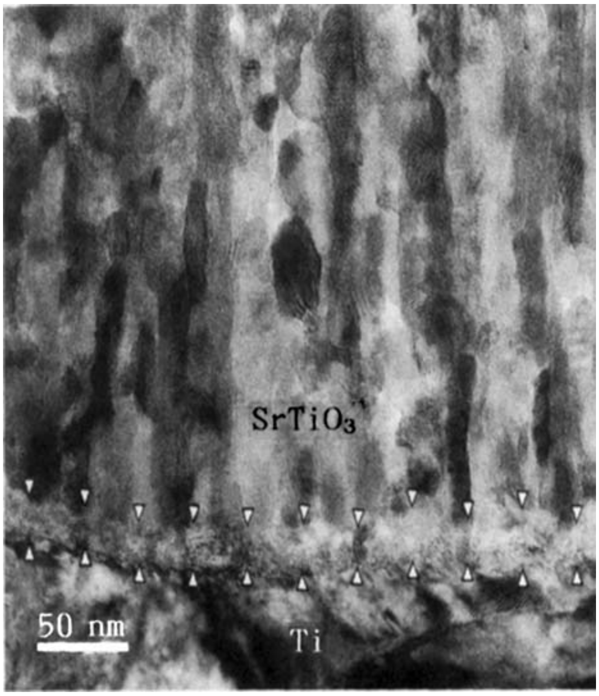

Figure 6 Magnified TEM Image of the $SrTiO_3$ film/Ti substrate interface of the $SrTiO_3$ film with potentiostatic electrolysis at + 8.0 V vs. Ag/AgCl in 0.5M $Sr(OH)_2$ Solution of pH 14.2 at 150°C. Arrows indicate boundaries of a polycrystalline layer of Ti oxides whose microstructure is different from the columnar one of the overlying, inner $SrTiO_3$ layer [30].

Recently flow-type cells have been developed (a) to control nano-/micro- structures: layered or graded, (b) to control compositions: doping, solid solution, (c) to minimize heating volume, and (d) to realize local activations by some beams like photo (laser)-radiation, electric current, and (e) to make a complete closed system which allows us to minimize the waste. [36,45,46] Fig. (8) is an example of flow-cell system and its result for $LiCoO_2$ crystalline films [40].

5. Direct patterning of ceramic films by solution processing [46–49]

As a second stage break through in solution processing, we have succeeded to fabricate patterned ceramic films directly in/from solution without any post-firing. It has been realized by local activation in interfacial reactions between solid (reactant/substrate) [**A**] and

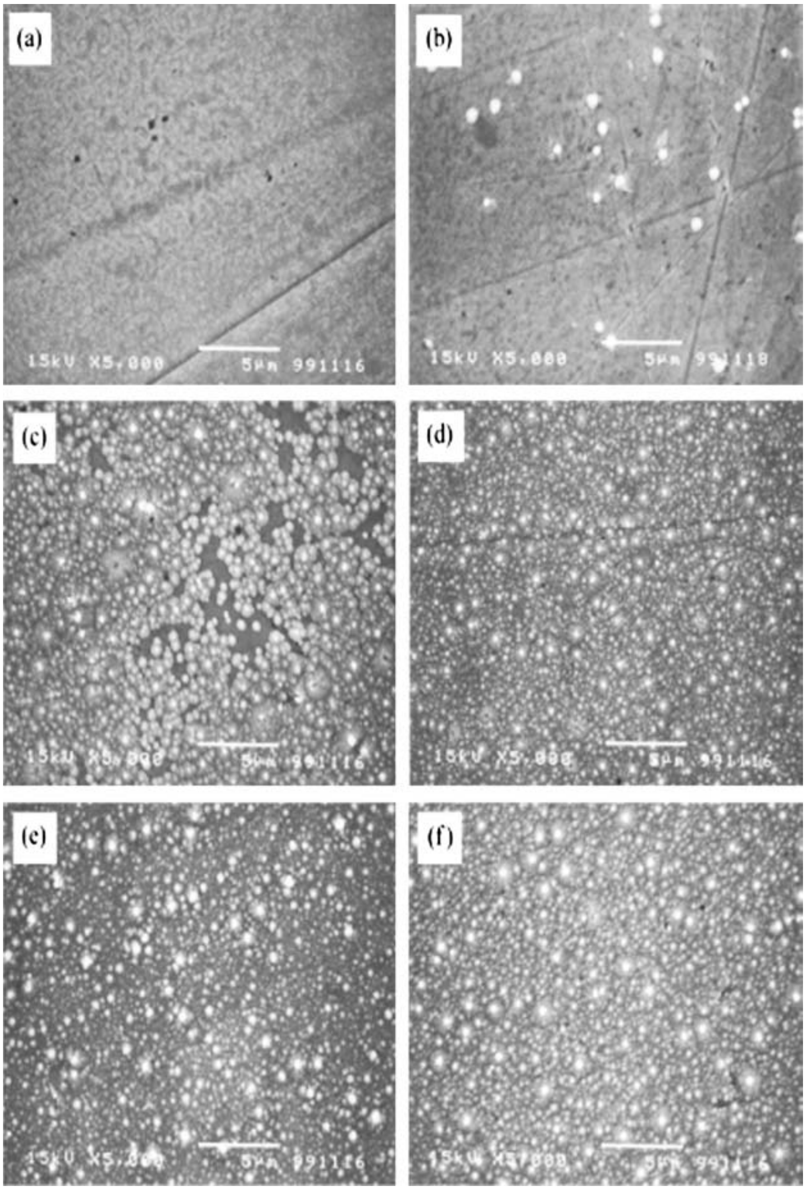

Figure 7 $BaTiO_3$ film formation on a Ti substrate by microwave-hydrothermal method in $Ba(OH)_2$ solution at 100°C, (a) Ti substrate, (b) 5 min, (c) 10 min, (d) 15 min, (e) 30 min, and (f) 60 min. [44].

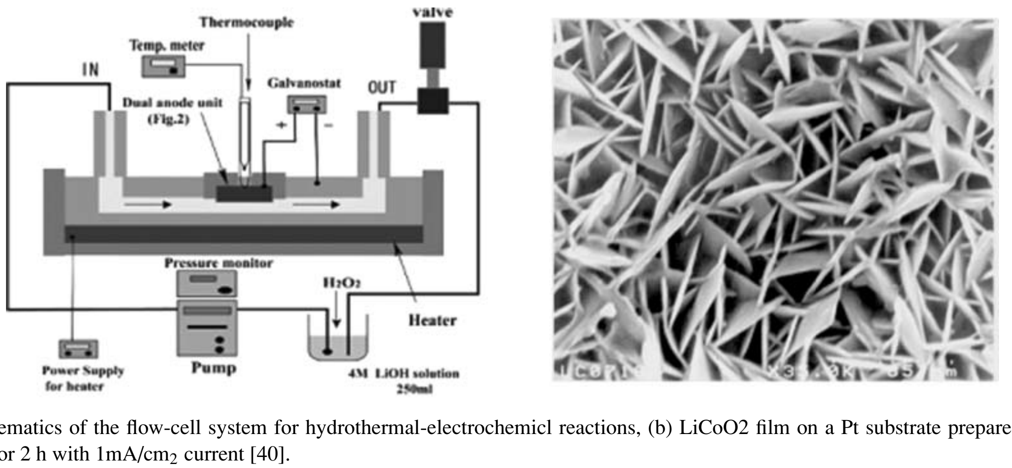

Figure 8 (a) Schematics of the flow-cell system for hydrothermal-electrochemicl reactions, (b) LiCoO2 film on a Pt substrate prepared in the flow-cell system at 150°C for 2 h with $1mA/cm_2$ current [40].

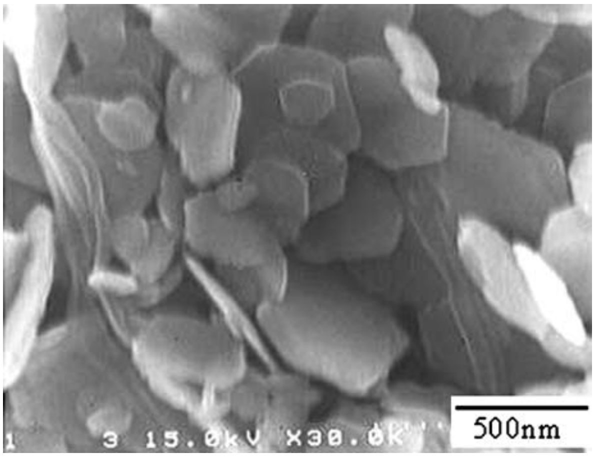

Figure 9 $LiCoO_2$ films composed of nano- powders fabricated on PTFE membrane by electrochemically activated interfacial reaction methods at 1mA/cm_2 in 0.1M $CoSO_4$ and 5M LiOH at 120°C for 30 min [46].

solution [**B**] or two solutions [**A&B**] with a porous membrane. Patterns of $BaTiO_3$/Ti and $LiCoO_2$/Paper (Fig. 9 [46]) could be fabricated. Well crystallized hexagonal $LiCoO_2$ plates were packed on a PTFE membrane as the pattern of the electrode for electrochemically activation [46, 49]. Another method using ink-jet reaction could produce CdS and PbS pattern on various papers or cloths [47] as seen in Fig. 10. Those direct patterning technology for ceramics in/from solution(s) without post-firing should be developed in near future to eliminate the consumption and the waste of energies and materials in the production of ceramic materials where high temperature firing and/or high energetic processing have generally been used. Moreover low temperature fabrication of ceramics without firing may open doors for new materials like hybrids/composites/laminates of ceramics/organics, ceramics/bionics, in addition to ceramics/semiconductors and ceramics/metals that have already been well studied. Highly energetic industrial (artificial) production of advanced materials like ceramics is more effective but cost environmentally in comparison with biological (ecological) productions, where only solution processings can be allowed with templating and self-assembly of supra-molecules (see Fig. 1. It seems to be one of the major reasons why bio-minerals (bio-produced inorganic materials) have been limited almost in calcium carbonates, phosphates and sulfates, ion oxides (hydroxides), and silica [1–3]. We need more variety of materials than such biominerals, therefore we must learn from biological systems, but need not be limited by biomaterials or bio-processes. Therefore we have proposed Soft Solution Process (SSP) or Soft Processing (SP) instead of "Biomimetic" or "Biomimic" Processes. [Mimic (or mimetic) can not exceed the original, thus it seems that "Bio-inspired" may be preferable than "Biomimic" or "Biomimetic."]

6. Conclusion

Considering themodynamical factors in the materials and their processings, we have been proposed Soft Solution Processing (SSP) for advanced materials particularly ceramics, because ceramics have generally been fabricated by highly energy consuming processes like multi-step processes including powder synthesis, shape forming and shape fixing, or more energetic processes using gaseous molecules, atoms and/or ions under vacuum.

SSP has been developed from Soft Chemistry (Chimie Douce), which aims low energetic synthesis of inorganic substances using aqueous solutions as precursors or reaction media. SSP targets to fabricate directly shaped/sized/located and/or oriented materials rather than synthesis of substances in solutions with minimum steps because shape forming and shape fixing seem to consume more energies for ceramic materials rather than their syntheses.

We have developed (1) Polymelized (or Polymelizable) Complex Methods to prepare ceramic powders with homogeneous compositions, (2) Hydrothermal Methods to prepare well crystallized shaped ceramic particles. Furthermore, we have succeeded to prepare (3) various ceramic films and patterns on substrates directly in/from

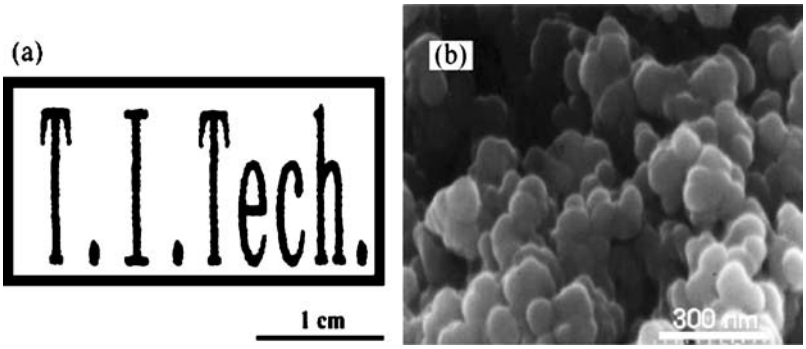

Figure 10 (a) Photograph of a PbS pattern on a paper prepared by the ink jet reaction from aqueous solutions at a room temperature, (b) SEM photograph of the same sample. The pattern consists of consolidated PbS crystals with 50-100 nm size [47].

solution(s) without post-firing as the developments of SSP. We believe the SSP, which have learned from nature but not limited in natural products like biominerals, should become more important for near future to establish "sustainable societies" if possible.

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