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Direct Fabrication of Patterned Functional Ceramic Films by Soft Solution Processing without Post-Firing

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ABSTRACT

We are proposing an innovative concept and technology, Soft Solution Processing (SSP) for ceramics, which aims to achieve direct fabrication of shaped, sized, located, oriented ceramic materials from solutions without firing and/or sintering. We have successfully fabricated thin and thick films of BaTiO_3 , SrTiO_3 , BaWO_4 , SrMoO_4 , LiCoO_2 , and LiNiO_2 by SSP in aqueous solutions from room temperature to 200 °C. In these experiments, interfacial reactions between a solid reactant (substrate) and component(s) in a solution have been designed and realized. By locally activating the reaction and moving the reaction point dynamically in these reactions, we can produce patterned ceramics directly in solution without masking, etching, pattern forming, or any post-heating such as firing or sintering. In this paper we present recent results for patterned ceramic films of PbS , CdS , and LiCoO_2 . The processes used to produce these films are entirely new, and represent the first examples of successful direct patterning of ceramics from solutions. In previous reports, heating processes have been essential for synthesis and/or sintering of powders and precursors to obtain patterns in ceramic materials. Such processes inevitably cost environmentally and economically. In contrast, our method, where no firing is needed, provides an environmentally and economically less expensive alternative.

INTRODUCTION

The present human society is supported by the tremendous consumption of resources, energy and advanced materials. Thin and thick films of functional materials, including ceramics, have traditionally been fabricated by processes requiring huge amounts of energy and resources, some of which are wasted to the environment [1-3]. Such processes have caused the exhaustion of resources and environmental contamination. Recycling of waste materials is possible when we put more energy into the recycling process than into the production/fabrication processes, but this brings about further thermal contamination. In order to address this problem, we must aim to minimize the total energy consumption during the whole life cycle of products, from mining and up-grading of raw materials, through production/fabrication, transportation, usage, and disposal to recycling. Only then will processes become more environmentally friendly [1-3].

In this regard, we are proposing Soft Solution Processing (SSP) for production of advanced materials such as ceramics, semiconductors, composites etc (figure 1) [4]. SSP aims, based upon thermodynamic considerations, to fabricate shaped, sized and controlled advanced materials from aqueous solutions without excess heat and energy consumption and without using expensive equipment and precursors, preferably in a single step [1-3].

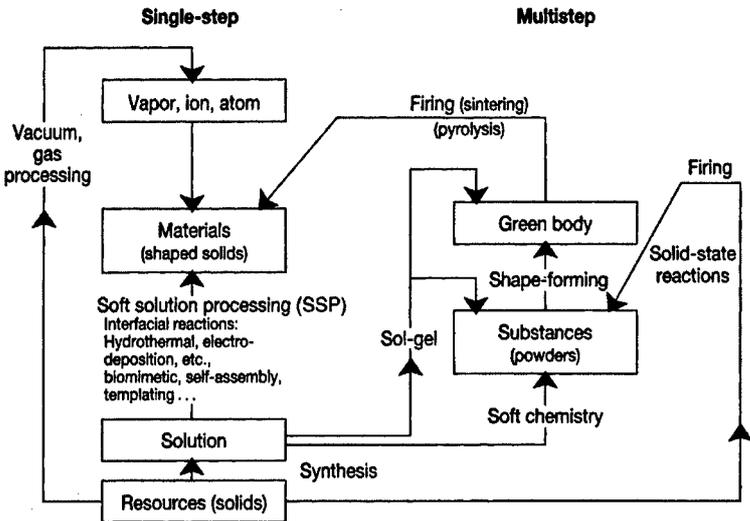


Figure 1. Schematic diagram of advanced materials processes showing the flow of single-step and multi-step processes. Soft Solution Process (SSP) aims to fabricate shaped materials, preferably in a single step, using solutions.

There has been considerable interest in processes where interfacial reactions, mostly at liquid/solid interfaces, are performed by self-assembling, templating, and/or self-organizing of species. Such processes are sometimes referred to as “Bio-mimetic”. However, mimetic products cannot exceed the original products on which they are based; moreover bio-products are severely limited in terms of species, substances, and materials. For example, practically no metallic materials have been produced biologically, and biomineral species are limited in number to less than one hundred [2]. Although a huge range of organic substances can be synthesized, most common polymers and plastics, like polyethylene, polypropylene, vinyl, PET etc, have never been produced in bio systems. We, therefore, must learn about bio-processes, but not be limited by bio-products and/or bio-materials for the fabrication/production of advanced materials. Therefore, SSP, which should exceed the limitation of bio-processing and bio-products, might be bio-inspired but not be bio-mimetic. Figure 2 shows that Soft Processing (Soft Solution Processing) is the third area of production for advanced materials between bio-processing and industrial (so-called high technological or artificial) processing which is mostly used for semiconductors and inorganic materials, particularly for products with micro- and/or nano-sized features. In those industrial processing techniques, dry processes, such as CVD and PVD, using gas or vacuum systems, have been employed where highly energetic species like molecules, atoms, and/or ions are utilized for the production/fabrication of films. These dry processes consume huge amounts of energy compared to multi-step processes based upon solid state

reactions and wet process where solution precursors have been used as shown in figure 1. Without using such highly energetic species as dry process, or such high temperature heating as multi-step processes, SSP aims to fabricate directly shaped materials [1-3].

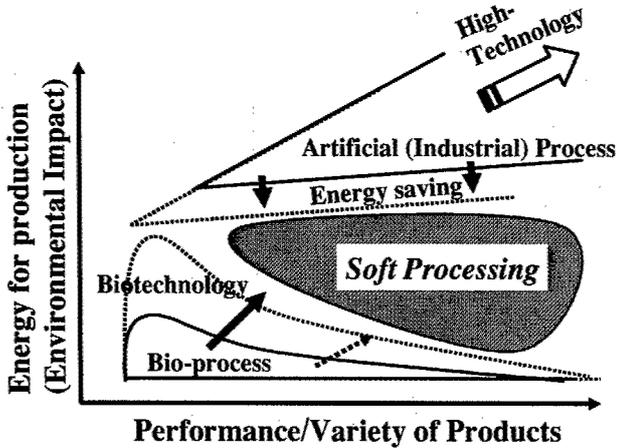


Figure 2. Energy vs. performance/variety in bio-processes and artificial processes. Soft Processing targets the production of high performance materials by environmentally benign methods.

We have reported the successful fabrication of various thin/thick crystalline films of double oxides such as BaTiO_3 , SrTiO_3 , AMO_4 ($A=\text{Ba, Sr, Ca, M}=\text{W, Mo}$), LiMO_2 ($M=\text{Co, Ni}$), YVO_4 , etc., by SSP in aqueous solutions at 150°C or lower temperatures without any post-firing [1-7]. In these experiments, interfacial reactions between a solid reactant (substrate) and component(s) in a solution have been utilized as illustrated in figure 3, where ABO_x crystals are formed on the substrate **A** by the reaction with the species **B** and **O** from H_2O in the solution. These interfacial reactions must be activated, either chemically, thermally, electrochemically, photochemically, sonochemically, mechanochemically, or by some other mechanism.

When we have activated/stimulated those reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any post heating, masking or etching [6, 7]. Those direct patterning methods differ from previous patterning methods which consist of multi-step processes, for example: (1) synthesis of particles of compounds or precursors, (2) dispersion of the particles into a liquid ("ink"), (3) patterning of the particles on a substrate by printing of the "ink", (4) consolidation and/or fixing of the particles' pattern by heating. For example, some results for zirconia ceramics and PZT films fabricated by ink-jet printing have already been reported [8, 9]. However, in almost all the reports, jet printing has been used only as a method to give a pattern of solid particles on the substrate. The substrate with the pattern of solid particles must be fired at a high temperature to fix, sinter or solidify them. Otherwise, the substrate using a special binder to fix the solid

particles must be fired to remove that binder. In any case, these techniques are not fabricating a patterned film by reaction, but fabricating a pattern of particle that requires post-firing (figure 4).

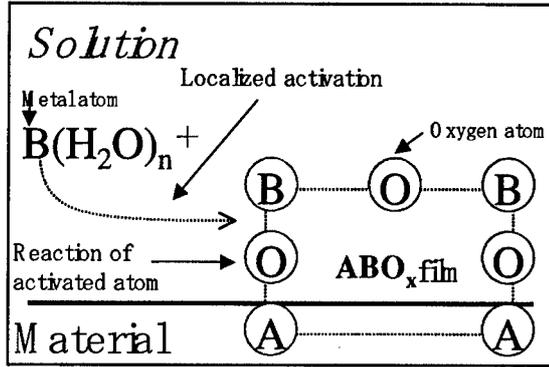
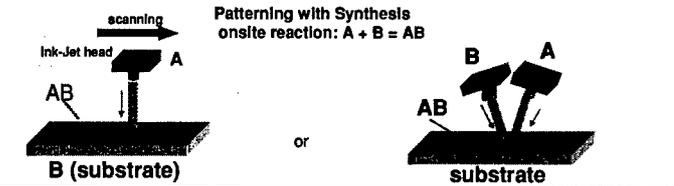


Figure 3. Concept of direct patterning by localized activation of interfacial reactions.

Direct Patterning method for ceramics (single-step without firing)



Normal mask-less patterning method for ceramics

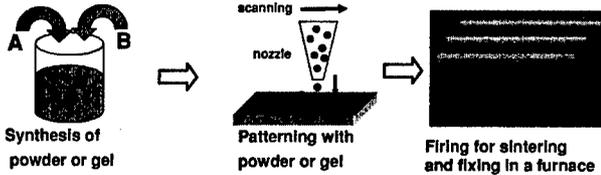


Figure 4. Comparison of “direct patterning” and “normal mask-less patterning” methods for ceramics.

The notable feature of direct patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction, $A+B = AB$, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of post-firing is mostly used for the consolidation of the particles. The present technique has many merits as follows: (1) it needs simple equipment that is easy to control, (2) the process

is therefore very safe and harmless, (3) it allows direct patterning without masking, etching or complicated surface treatments, (4) it needs fewer reactants and lower energy and cost and (5) it is easy to recover the reactants.

Therefore, our direct patterning methods should be economically and environmentally friendly, avoiding excess consumption of energy and resources, and minimizing emission of waste, for example excess heat and gaseous by-products like CO_2 and H_2O .

DIRECT PATTERNING OF CdS AND PbS ON PAPER BY INK-JET REACTIONS [10]

Ink jet printing has been widely used for color printing on paper, where color particles are printed in a pattern. Ceramic particles can be similarly printed as a pattern on a substrate. However, they must be fired to fix and/or to consolidate the pattern on the substrate as mentioned above. We have recently developed a new method to fabricate ceramic patterns directly from solutions by the interfacial in situ reactions between two liquids, using an ink jet printer.

In the example of PbS, an aqueous solution of $\text{Pb}(\text{NO}_3)_2$ was soaked on a paper, then a solution of Na_2S was ink-jetted as a pattern at room temperature. A pattern of PbS was formed on the paper, which consisted of crystalline PbS particles as revealed in figure 5. These particles were less than 100 nm in size, but well crystallized and well embedded in the fibers of the paper (figure 6). Similarly, CdS was formed on paper from CdCl_2 and Na_2S solution. This material consisted of ≈ 30 nm size crystals with a band gap of 2.45 eV. Other ceramic patterns can be fabricated by similar methods.

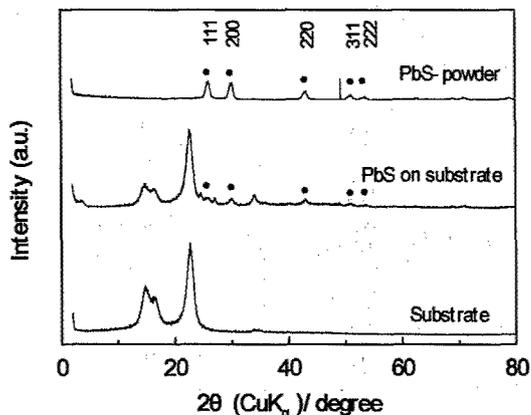


Figure 5. XRD patterns of PbS samples on paper prepared by ink jet reactions at room temperature. (a) Substrate, (b) PbS pattern on paper, (c) PbS powder synthesized in solution by ink jet reactions.

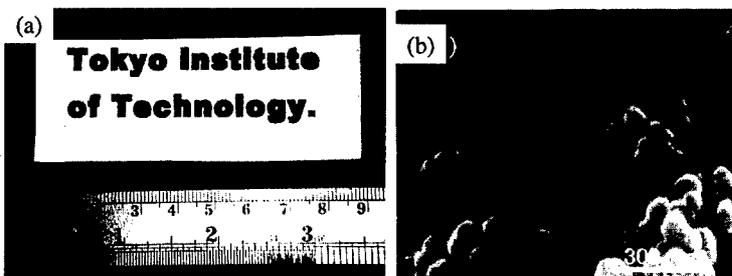


Figure 6. (a) Photograph of a PbS pattern on paper prepared by ink jet reactions at room temperature, (b) SEM photograph of the same sample.

DIRECT PATTERNING OF LiCoO_2 ON POROUS SUBSTRATES BY ELECTROCHEMICALLY ACTIVATED INTERFACIAL REACTIONS [11, 12]

Bio-minerals have been synthesized in aqueous solution by ion transfer reactions through a cell membrane. However, these biological processes can produce only a limited range of materials like amorphous silica, calcium carbonate, calcium phosphate, calcium sulfate and iron oxide, but not others like LiCoO_2 , BaTiO_3 [1-2]. We propose electrochemically activated interfacial reactions for film fabrication by "Artificial Biomineralization" [11], where the interfacial reactions between solutions separated by membranes are used with the assistance of electrochemical reactions to fabricate crystallized LiCoO_2 films directly on paper at low temperatures (figure 7).

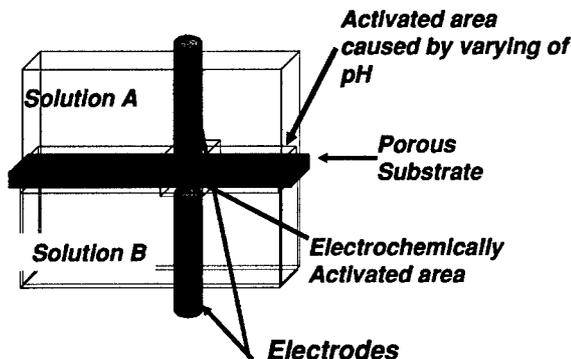


Figure 7. Schematic diagram of an electrochemically activated interfacial reaction method.

A LiCoO_2 film can be synthesized by the reaction between Li^+ and CoO_2^- ions in a solution. CoO_2^- ions can be produced by chemical or electrochemical oxidation of HCO_2^- or Co^{2+} ions. Therefore electrochemical dissolution of a Co anode or electrochemical oxidation of

HCoO_2^- ions near a carbon anode can give a CoO_2^- flux to a porous substrate like paper in the shape of the anode. This can give a LiCoO_2 crystalline film in the pattern of the anode on the paper (figure 8). Typically this consists of plate-like crystals a few μm in size. However the phases, shapes and sizes of the crystals produced by this method can be controlled by the flow of solution(s), electrical current, and/or geometry of electrodes and substrates.

Other direct patterning methods using laser activation or localized electrochemical activation have been under development in our group. These are demonstrating that the fabrication of patterned ceramics can be realized in solutions at low temperatures below 150°C , or even at room temperature, without any post-firing, masking and etching, which have been regarded as essential processing in conventional patterning of ceramics.

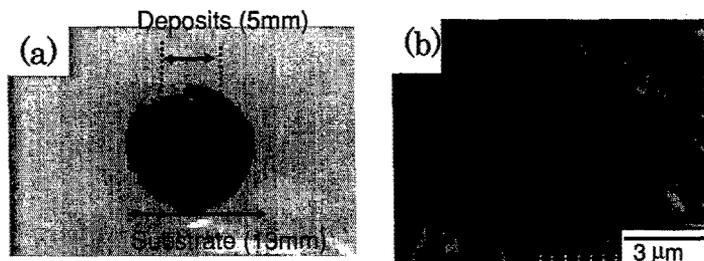


Figure 8. (a) Photograph of a patterned LiCoO_2 sample prepared electrochemically by interfacial reaction on paper at 120°C , (b) SEM photograph of the same sample.

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