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One-step patterning of nano-structured ceramics from solution: Differences from conventional printing and/or lithographic methods

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Since 1989, when we found a method to fabricate $BaTiO_3$ film on Ti substrate in a $Ba(OH)_2$ solution at low temperatures of 60-200$^{\circ C}$, the method (hydrothermal-electrochemical method) have been applied for the fabrication of $SrTiO_3$, $CaMoO_4$, $BaWO_4$, YVO_4, $LiCoO_2$ and $LiNiO_2$, etc. Later the films of their solid solutions and/or graded compositions have also been fabricated. A flow cell system for continuous and/or fast production of films has been developed. A dual anode system, furthermore, could realize the formation of $LiCoO_2$ films on other conducting substrates as Pt, Ni, and graphite. Based on those direct fabrication of ceramics films by interfacial reactions between a substrate and a solution at low temperature, we have proposed an innovative concept and technology, soft processing or soft solution processing which aims low energetic (environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing. 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. Those direct patterning methods differ from previous patterning methods like direct printing which consist of multi-step processes: Synthesis of particles of compounds or precursors; dispersion of the particles into a liquid ("ink"); patterning of the particles on a substrate by printing of the "ink" and; consolidation and/or fixing of the particles pattern by heating. They use firing/sintering of powders or particles, thus are difficult to avoid the deformation of powders' layers, i.e. cracking, peeling, delaminating, etc. caused by 3D shrinkage during sintering. 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 powders. We have developed the direct patterning of CdS and PbS on papers by ink-jet reaction method and $LiCoO_2$ by electrochemically activated interfacial reactions. Furthermore, we have succeeded to fabricate $BaTiO_3$ patterns by a laser beam and carbon patterns by a needle electrode directly in solutions. Recent success in TiO_2 and CeO_2 patterns by Ink-jet deposition will be presented.

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