

Dissertation Abstract

Report no.	(Course-based) No.1235	Name	Jyorthana Rajappa Muralidhar
Dissertation title	Design and synthesis of Functional perovskite or Polymeric Materials Induced by Chemo- or Photo-stimulation (化学物質あるいは光によって誘起される, 機能性ペロブスカイト材料, 高分子材料の設計と合成)		
Abstract			
<p>The purpose of the Ph.D. thesis is to develop functional materials showing chemo- or photo-stimulation. Stimuli-responsive materials have attracted attention for applications in gas adsorption and desorption, actuators, sensors, and drug delivery carriers etc. Their responses result in dynamic changes such as energy accumulation and dissipation, mass transfer, and formation and breaking of chemical bonding. However, a dynamic change leads to structural instability from high mechanical strain. Therefore, structural integrity remains as a key challenge in the dynamic process. In this thesis, I investigated stimuli-responsive materials showing photo- or chemo-response by designing the structure and function.</p> <p>Chapter 2 described photo-induced patterning of polythiophene films using photo-cleavable behavior. The polymer included a coumarin unit as a photo-cleavage group in a side chain. The number-average molecular weight and polydispersity were 17,000 and 1.4. Exposure to light at 313 nm showed photo-cleavage of the coumarin unit affording formation of carboxylic acid. Thus, the surface morphology for the polymer film became hydrophilic after photo-irradiation. Photoirradiation through a photomask gave the polythiophene patterns. The hydrophilic polymer remained in the patterned film and the unreacted polymer was removed by washing with organic solvents.</p> <p>In chapter 3, polythiophene dispersant PC₅₆T₄₄ featuring photocleavable solubilizing unit was developed. PC₅₆T₄₄ contained a photolabile coumarin and an octyloxy chain as a solubilizing unit. Exposure to light at 313 nm leads to photo-cleavage of the coumarin group including the solubilizing unit. Upon photocleavage, the surface morphology of the composite film changes from hydrophobic to hydrophilic due to the formation of hydrophilic carboxyl (COOH) groups in the polymer attached to the surface of the SWCNTs. The electrical conductivity for the photocleaved PC₅₆T₄₄/SWCNT composite film increased 38-times than that of the pristine film. This increase in electrical conductivity is due to photocleavage of the insulating solubilizing unit.</p> <p>Chapter 4 represented dynamic and reversible structural transformation of the vapochromic perovskite crystal in response to ammonia. The one-dimensional (1D) structure of ethylammonium lead iodide (CH₃CH₂NH₃PbI₃) formed two-dimensional (2D) structure of Pb(OH)I after exposure to aqueous ammonia (NH₃aq.) vapor. Single-crystal X-ray diffraction analysis revealed that the CH₃CH₂NH₃PbI₃ crystal showed a molecular packing of CH₃CH₂NH₃⁺ cations between the 1D columnar structures of [PbI₆]⁴⁻ octahedra. In contrast, the Pb(OH)I crystal including OH⁻ anions led to 2D layered structures stabilized by [OHPb₃] tetrahedra. This dynamic structural transformation through the cationic/anionic exchange reaction was reversible. The reversibility originated from the insertion and extraction of NH₃ in the crystal.</p> <p>In conclusion, I synthesized chemo- or photo-responsive functional materials. The polythiophene film made photo-induced patterning by photo-cleavage of the coumarin unit. The photocleavable polymer PC₅₆T₄₄ acted as a dispersant for solution-processed SWCNT film. The vapochromic perovskite crystal showed reversible structural transformation by insertion and extraction of NH₃. These stimuli-responsive materials are expected to be applied to chemical sensors and organic electronics in the future.</p>			