別紙様式８

研 究 主 論 文 抄 録

論文題目　Physicochemical Properties of Metal Oxide Nanosheets and Their Layered Materials
（金属酸化物ナノシートおよびその層状物質の物理化学的性質）

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主論文要旨

Exfoliation is the process to delaminate the layered oxide and layered hydroxide materials to get two dimensional structures called nanosheets having approximate thickness of 1 nm and width of 1 μm. Because nanosheets have intriguing chemical properties used in electrochemical and photoluminescent applications, delamination of host layers into individual layers has been widely studied. In this study, several metal oxide and hydroxide nanosheets are synthesized and used as building blocks to architect hybrid films grown with layer-by-layer self assembly, and Langmuir Blodgett techniques. The electrochemical and photoluminescence of nanosheets and hybrid films were investigated.

In Chapter I, basic introduction about structures of layered metal oxides and layered metal hydroxides were given. The synthesis of nanosheets by exfoliation and multilayer film preparation techniques were demonstrated.

In Chapter II, photoluminescence properties of several layered materials prepared by using nanosheets were demonstrated. The layered materials were synthesized by performing electrostatic self assembly or layer-by-layer assembly methods. The titanate layered oxides intercalated with Tb^{3+} and hydrated Eu^{3+} ions prepared by electrostatic self assembly method with using Ti_4O_9 nanosheets. The Ti_4O_9 nanosheet was an excellent host for Tb^{3+} ions and this material could yield efficient green luminescence through energy transfer from the host to the Tb^{3+} ions. In the case of Eu^{3+} intercalation, the excitation spectra changed drastically at any given wavelength upon irradiation with UV light. A comparison of the excitation spectra before and after irradiation reveals that only the excitation peak at around the irradiation wavelength decreased upon irradiation, as in the case of spectral hole burning. In addition, the exfoliation of $Bi_2SrTa_2O_9$ (BST) to a single nanosheet was carried out. It should be noted that the BST-nanosheet itself

shows blue luminescence under excitation at 285 nm at room temperature. We prepared a film of a monolayer of the BST-nanosheet on a quartz substrate with the LBL method, and its luminescence property of the film was measured in various pH conditions. As a result, it was found that the blue emission was influenced by pH.

In Chapter III, electrochemical behaviors of layered oxides prepared by layer by layer self assembly method were introduced. Electrochemical reactions of layered double hydroxides (LDH) intercalated with potassium metal hexacyanoferrate and various layered oxides intercalated with Ag^+ ions were investigated. The films LDH with potassium metal hexacyanoferrate complexes showed that typical electrochemical response of metal hexacyanoferrate, which was believed to be formed in the interlayer as a result of the interaction of interlayer cyano complex with the host layer. Ag^+ intercalated layered oxide films showed very unique characteristics when compared to other similar Ag^+ exchanged zeolite and clay electrodes. The peaks are very sharp and clear, which shows that the redox reaction in the interlayer is fast. In addition, there is an energy gap between the onset potentials of redox reactions, which is different from the behavior of other electrodes. The formation of the energy gap was assigned to the energy barrier in the host layer.

In Chapter IV, syntheses of zinc oxide and zinc hydroxide nanosheets and the photoluminescence properties of their layered materials intercalated nickel phthalocyanine were introduced. ZnO nanosheet was prepared by delamination of layered ZnO film intercalated with dodecyl sulfate ion which was synthesized by cathodic electrodeposition process. In this case, the addition of La^{3+} ion into the electrolyte was very critical for the further delamination process. On the other hand, $Zn(OH)_2$ nanosheet was prepared by delamination of layered $Zn(OH)_2$ intercalated with DS^- ion that was prepared by soft solution process using hexamethylenetetramine . The thicknesses of the ZnO and $Zn(OH)_2$ nanosheets were about 0.7 and 1.0 nm, respectively. Moreover, addition of potassium (K^+) and lithium (Li^+) resulted crystal change of $Zn(OH)_2$ host layer to ZnO host layer having broad yellow emission. Also, the hybrid films of layered $Zn(OH)_2$ and nickel phthalocyanine (NiPC) were synthesized for the first time. Extremely small amount of NiPC in the interlayer domain resulted very intense blue emission.

In Chapter V, the results given in the previous chapters were summarized.