学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Fabrication and Characterization of New Nanocomposite Materials Based on Transition Metal Cluster
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Nowadays, the functional material-coated glasses with specific characteristics including self-cleaning, UV-NIR light blocking or electrochromic property have widely been studied in smart window applications. Most studies have reported the optimization and possibility of the fabrication processes in order to enhance the intrinsic properties and reduce the production cost. The octahedral metal clusters based on molybdenum and tantalum transitional metals exhibit interesting photochemical, oxidation-reduction and prominent optical properties that are potentially applicable in energy, photocatalyst or biotechnology fields. The application fields of the metal cluster would be extended by applying some coating techniques, preparing the nanocomposites based on the inorganic and organic support, or synthesizing the hybrid with directly polymerization. In this thesis, the main expectation is to immobilize the metal cluster on supporting material as glass, silica or polymer, however, the last materials have to retain the specific characteristics of metal cluster. For these purposes, the essential techniques to fabricate the metal cluster are colloidal solution chemistry, electrophoretic deposition (EPD) and vacuum impregnation process (VIP).
The electrophoretic deposition (EPD) process, a fairly rapid and low cost two-step process well-known for ceramic shaping, conductive surface coating and easily scalable to industrial level thin, have been applied to prepare an octahedral metal cluster homogeneous film on the ITO-coated glass. The impressive advantage of this technique is to bring out the pure octahedral metal cluster film without counter cation that changes a cluster framework, following the modification of the optical property. In addition, the EPD process are useful to consume a small cluster concentration on a large area of the glass that reduce producing cost. The optimizations of the suspension and EPD parameters were investigated to obtain the octahedral cluster thin films with the best quality. A lots of techniques were used to characterize the colloidal suspensions (zeta potential, conductivity and particle size), the homogeneity and surface morphology (color 3D laser microscopy, FE-SEM, STEM), chemical property or crystal pattern (X-Ray diffraction, Fourier Transfer Infrared, X-ray fluorescence, X-ray Photoelectron Spectroscopy) and optical property (UV-Vis-NIR spectroscopy, high performance fluorescence spectroscopy, micro photoluminescence (PL) system, PL quantum yield spectrometer, CL measurement).
Summary of Chapter 2: The cluster film based on face capped $Mo_6L^i{}_8L^a{}_6$ units with L^i = inner ligands and L^a = apical ligands ($L^i = L^a$ = Cl, Br, I) were fabricated by the EPD process. Photoluminescence properties characterized by multicomponent emission in the deep-red/ near infra-red (NIR) region with a continuous excitation window from UV to visible as well as photo catalytic activity of the molybdenum octahedral cluster is particular interest for the application in biotechnologies, lighting and displays. The stabilization of the cluster solutions during EPD is very important to obtain high quality film. Several kinds of liquid, distilled water, ethanol, 1-propanol, acetone, methyl-ethyl ketone (MEK) and acetyl acetone, were selected as dispersing media of the Mo_6 cluster compound. Homogeneous, transparent $Cs_2Mo_6Br^i{}_8Br^a{}_6$ cluster films with prominent luminescent property were obtained on conductive ITO glass by EPD when dissolving the $Cs_2Mo_6Br^i{}_8Br^a{}_6$ in MEK. The UV-Vis absorption spectra exhibited a high transparency in the visible light range (500 – 850 nm) accompanied by many peaks in the wavelength range from 400 nm to 2000 nm due to light interference. For

the first time, the mechanism of deposition process is proposed, based on results obtained by the combination of X-ray analysis, electron microscopy and optical characterization. The Mo_6 film exhibiting Br rich layer, quickly deposited on ITO glass at the first stage of EPD, followed by the formation of a multilayered structure composed of two types of clusters compounds $[Mo_6Br^i{}_8Br^a{}_4(H_2O)_2]$ and $[H_3O^+]_2[Mo_6Br^i{}_8Br^a{}_4(OH)_2]$. Thanks to a nanometric size and the synergy of specific optical properties of metal atom clusters and substrate, films with high transparency in the visible range and strong absorption in UV and IR range are obtainable.
Summary of Chapter 3: Due to the limitation of the stabilization of the octahedral cluster film in the air, organic supporting materials (polymer) were used to simultaneously fabricate or top coating on the Mo_6 cluster film. The results conclude that poly dimethyl siloxane as an excellent top coating and poly methyl methacrylate, cellulose acetate phthalate (CAP) or poly vinyl pyrrolidone (PVP) as a prominent dispersing medium significantly improved the stabilization of the octahedral cluster film.
Summary of Chapter 4: The potential of luminescent silica nanoparticle has been widely studied in the field of biological science as cancer diagnosis, optical imaging and biosensor. In order to promote the luminescent or UV absorption ability of the octahedral molybdenum clusters in the luminescent bioapplication, the $Cs_2Mo_6Cl_{14}$ and $Cs_2Mo_6I_8C_2F_5$, exhibiting excellent luminescent characteristic, were incorporated with hollow silica nanoparticles by a vacuum impregnation process. The prepared luminescent silica nanocomposite film has been prepared by EPD process on ITO glass or coated on sodium glass by dip coating with the support of the top coat solution.
Summary of Chapter 5: The octahedral $Ta_6Br_{14}{\cdot}8H_2O$ or $[Ta_6Br^i{}_{12}(H_2O)^a{}_6]Br_2$ cluster, which exhibits interesting oxido-reduction and optical properties in the solution, were investigated to fabricated the Ta6 cluster film by EPD process. The application of the $\{Ta_6Br^i{}_{12}\}^{2+}$ core species has been potentially studied in biotechnologies, optical devices, photovoltaic cells and UV blocking device. The interesting characteristic has been recognized that the green $\{Ta_6Br^i{}_{12}\}^{2+}$ core (adsorbing ultra-visible range) easily transfers to brown $\{Ta_6Br^i{}_{12}\}^{3+/4+}$ core (absorbing near-infrared range) when dissolved in different solvents. Due to the interesting characterization of the $\{Ta_6Br^i{}_{12}\}^{2+}$ core species (green), the selection of the dispersing medium and optimization of the concentration of the $Ta_6Br_{14}{\cdot}8H_2O$ cluster in a solvent are the main purpose of the study in order to obtain the green homogeneous Ta_6 film. In addition, the EPD parameters such as applied voltage and deposition time were investigated to fabricate the $\{Ta_6Br^i{}_{12}\}^{2+}$ green film that was confirmed through the FE-SEM image and optical characterization. By the EPD process, the green film based on the $\{Ta_6Br_{12}\}^{2+}$ core species was successfully fabricated, however, the stability of the oxidation state and transmittance of the Ta_6 octahedral cluster film were limited. For this reason, poly vinyl pyrrolidone (PVP) was used to improve the dispersion of the $\{Ta_6Br^i{}_{12}\}^{2+}$ green octahedral cluster in the EPD suspension for reducing the crystal size and preventing the interaction of the $\{Ta_6Br^i{}_{12}\}^{2+}$ green octahedral cluster in the deposition film with oxygen in air. As the result, thin and high transmitance Ta_6 cluster@PVP film with emerald-green color exhibiting the strong UV absorption under 400 nm was successfully fabricated.
Finally, the results of thesis effectively modify the knowledges relating to characteristics of the optical nanoarchitecture materials based on the octahedral metal atom clusters or the processability to extend the energy saving application for the building.