氏名	Radovan Kukobat
学位の種類	博士（工学）
学位記番号	甲　第673号
学位授与の日付	平成29年3月20日
学位授与の要件	信州大学学位規程第５条第１項該当
学位論文題目	Design of sol-gel chemistry-derived dispersants for SWCNT and its application （ゾルゲル化学を用いたSWCNT分散剤のデザインとその応用性）
論文審査委員	主査　教授　林　卓哉 教授　橋本　佳男 教授　新井　進 准教授　竹内健司 教授　酒井秀樹（東京理科大学）

論　文　内　容　の　要　旨

The first chapter is general introduction, showing an overview of sol-gel chemistry in the materials processing and materials for the transparent and conductive films (TCFs) fabrication. A great deal of attention was paid on Single Wall Carbon Nanotubes (SWCNTs) which were used for the TCFs fabrication from SWCNT inks. The SWCNTs normally appear in the bundles of several hundreds of nanotubes bound by van der Waals interactions. This attractive energy is strong, so that the nanotubes re-aggregate after ultra-sonication treatment. In order to exhibit excellent properties of nanotubes, preparation of highly stable dispersion of SWCNTs, consisted of isolated bundles or tiny bundles is strongly encouraged. Thus, this thesis deals with the preparation of stable dispersions of SWCNTs for the TCFs which should have wide application in transparent electronics.

The second chapter deals with the synthesis of the dispersants for SWCNTs in aqueous media. It shows a route for the synthesis of Zn/Al complex dispersant by sol-gel method from Zn-acetate and Al-nitrate. The SWCNTs are hydrophobic and aggregate upon dispersing by aid of ultra-sonication. In the presence of Zn/Al complex, nanotubes are coated by Zn/Al complex dispersant and hydrophilicity is induced. The Zn/Al complex consists of amorphous Al-acetate and Zn-nitrate which have hydrophilic and hydrophobic parts. Thus, hydrophobicity arises from Al-acetate, in particular from hydrophobic C-C chain which adsorbs onto the hydrophobic nanotubes. The Zn^{2+} and NO_3^- ions of Zn-nitrate are electrostatically attracted to SWCNTs, inducing positive charge and electrostatic stabilization. The magnitude of surface charge of +55 mV suggests the presence of strong electrostatic repulsive interactions. The SWCNT dispersion remains stable over period of one year and change of dispersibility is almost negligible. The dispersibility of Zn/Al complex is pH dependent, thus below 3.5 pH units dispersant is dissolved and nanotubes precipitate. The same effect is observed above 6.5 pH units, the Zn/Al complex transforms to Al-hydroxide and Zn-hydroxide which cannot induce stability to nanotubes, leading to the precipitation.

The third chapter deals with the TCF fabrication from Zn/Al complex-SWCNT inks by bar coating method. The film homogeneity is governed by viscosity of SWCNT inks. As viscosity increases, the homogeneity of SWCNT film in terms of the sheet resistance and optical transmittance increases as well. The homogeneous film of SWCNTs can be obtained at the concentration of SWCNTs and Zn/Al complex of 0.05 wt.% and 1.00 wt. %, respectively. At this concentration viscosity of the ink is sufficient to allow the uniform coating on Polyethylene terephthalate (PET), giving Zn/Al complex-SWCNT based film. The Zn/Al complex is removed by washing with 1 M HNO_3 for 10 min and resistance decreases significantly. Removal of the Zn/Al complex is confirmed by X-ray photoelectron spectroscopy (XPS). The XPS spectra show that atomic percentages of Zn and Al atoms become 0.00 % after HNO_3 treatment for 10 min. Removal of Zn/Al complex is observed by Atomic Force Microscopy (AFM). Before HNO_3 treatment SWCNTs cannot be observed due to the complete coverage by Zn/Al complex dispersant. After treatment SWCNTs are observed and average bundle size distribution is estimated to be nearly 40 nm. The SWCNT film has sheet resistance of 150 ohm/sq at transmittance of 90 % at 550 nm.

The fourth chapter shows an importance of the interfacial properties of SWCNT ink and PET substrate interactions for the homogeneous film formation by bar coating method. The surface tension, contact angle, and viscosity play a key role in the homogeneous film formation. These parameters are examined for Sodium Dodecyl Sulfonate (SDS), Sodium Dodecyl Benzene Sulfonate (SDBS), Zn/Al complex, and Silica based SWCNT inks. The SDS and SDBS based inks give inhomogeneous films and Zn/Al complex and Silica gives homogeneous films in terms of sheet resistance and optical transmittance. The film formation occurs in two stages: spreading and drying of the ink on substrate. The contact angle and surface tension should be low enough to allow spreading and drying of SWCNT ink on substrate. Consequently drying process takes place and film can turn to be homogeneous or inhomogeneous, depending on viscosity. The SDS and SDBS based films become inhomogeneous after bar coating which means that viscosity is not high enough to suppress local flow of the ink. On the other hand, the initial homogeneity of Zn/Al complex and Silica based films is preserved; viscosity is high enough to stop the flow of SWCNTs and films are homogeneous.

The fifth chapter is general conclusion which briefly summarizes the entire thesis.