Development of Silver Nanoparticle and Fluorescent Carbon Dot Inks for Potential Application as Paper Device

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Development of Silver Nanoparticle and Fluorescent Carbon Dot Inks for Potential Application as Paper Device

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論文概要
[Abstract of Thesis]

論文題目[Thesis Title] *Development of Silver Nanoparticle and Fluorescent Carbon Dot Inks for Potential Application as Paper Device (紙デバイスに応用可能な銀ナノ粒子と蛍光カーボンドットインクの開発)

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論文概要 [Abstract of Thesis]

In Chapter Ⅰ, a well-dispersed self-assembled AgNPs ink was synthesized via AgNPs nanoemulsion prepared by blending an $AgNO_3$ aqueous solution and a liquid paraffin solution of both polyoxyethylene (20) sorbitan monooleate (Tween 80) and sorbitan monooleate (Span 80). The ink continued as a nanoemulsion at low temperatures, and its deposit became a continuous silver layer with high stability and conductivity after sintering at approximately 60 °C. The synthesized AgNPs had static particle diameters (d_S) of 8.6-13.4 nm measured by transmission electron microscopy (TEM), but the hydrodynamic diameter (d_H) measured by dynamic light scattering (DLS) showed almost twice as large as d_S, due to some functional groups stabilized on the surface, providing extra shells to the $AgNP_S$.

During the whole procedure, Tween 80 acted as a surfactant, reductant, and stabilizer. Tween 80 underwent an autoxidation process, where a free radical of an α-carbon of ether oxygen was formed by hydrogen abstraction, as confirmed by Fourier transform infrared (FTIR) spectroscopy. Besides, the mean diameter of the emulsified ink particles was reduced by decreasing water content and increasing the ratio of surfactant and concentration of $AgNO_3$ aqueous solution. DLS and ultraviolet-visible (UV-Vis) spectroscopy clarified that an increased concentration of $AgNO_3$ decreased the particle size. Consequently, the thermogravimetric analysis and X-ray diffraction (XRD) result clarified the high purity of the produced Ag^0 (96.6%).

In Chapter Ⅱ, a simple one-step synthesis approach for the preparation of fluorescent CDs with an average diameter smaller than 10 nm by the microwave-assisted method from 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) and different kinds of nanocelluloses (NCs) was reported. The raw nanocelluloses included 2,2,6,6-tetramethylpiperidine-1-oxyl radical oxidized cellulose nanofiber (TEMPO-CNF), cellulose nanocrystal (CNC) and aqueous counter collision cellulose nanofiber (ACC-CNF). Both of the FTIR and X-ray photoelectron (XPS) spectroscopy studies indicated the reaction mechanisms that the chemical reaction happened mainly on functional groups at the C_6 position. The reaction efficiency was related to functional group type, in order of decreasing efficiency, -COONa (TEMPO-CNF) > $-SO_3H$ (CNC) > -OH (ACC-CNF). Subsequently, the main focus was placed on

the synthesized TEMPO-CDs. The XRD spectra showed that the ratio between TTDDA and TEMPO-CNF dispersion influenced the product and TEMPO-CDs was fully converted into TEMPO-CDs at larger dose volumes of TTDDA, with only C element signals detected in the product structure. TEMPO-CDs appeared yellow and blue under day light and UV irradiation, respectively. The low thermal stability of TEMPO-CDs, proven by thermal analyses, was mainly attributed to the increase in amorphous content of C after the microwave treatment. The fluorescent quantum yield (QY) was measured in comparison to rhodamine B (RhB) in ethanol. The result showed that it was possible to improve QY of TEMPO-CDs by increasing the dose volume of TTDDA, microwave treatment time, and output power by approximately 24% at a maximum. TEMPO-CDs exhibited excitation-dependent emission, due to the quantized energy bands related to the energy states of C, N and O elements calculated via the Planck equation based on the HOMO-LUMO gap theory, showing the optimal excitation and emission wavelengths at 390 nm and 449 nm, respectively.

A TEMPO-CDs dispersion was applied as a water-based fluorescent ink for both hand-writing and printer application on filter paper, which was colorless under day light, but presented clear fluorescence under UV irradiation. Due to the same valence electrons of Fe^{3+} and Mn^{2+} ions ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$) with the five 3d-orbits half-filled, Fe^{3+} and Mn^{2+} ions are capable of adsorbing on surfaces of TEMPO-CDs and their coordinate bonds form complexes. The synthesized TEMPO-CDs could be effectively and selectively quenched by Fe^{3+} ions within seconds and by Mn^{2+} in 10 min. Based on this phenomenon, TEMPO-CDs are potential to be further applied to develop a fluorescent sensor for the detection of Fe^{3+} and Mn^{2+}.