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RAPID COMMUNICATION

Vegetable oil aided hydrothermal synthesis of cerium oxide nanocrystals

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Abstract−Hydrothermal synthesis of cerium oxide nanocrystals was performed with in-situ surface modification using soybean oil and palm oil as capping agents. The synthesized nanocrystals were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). TEM results showed single crystalline nature with stable dispersion. FT-IR spectra and TGA plots further confirmed the adsorption of fatty acid molecules onto cerium oxide surface. Our findings have the advantages of reduced materials costs compared to using single component surfactants and the production of valuable by-product glycerol.

Key words: Hydrothermal Synthesis, Supercritical Water, Surface Modification, Cerium Oxide, Vegetable Oil

INTRODUCTION

The recent trend of research in metal oxide nanocrystals is heavily focused on reducing size and modifying morphology due to the unique properties at nano-scale such as quantum size effect, change in optical properties and tuning of band-gap [1]. Cerium oxide (ceria, CeO_2) is a versatile material used in various applications such as catalysis, solid oxide fuel cells (SOFC), chemical mechanical polishing (CMP), ultraviolet light blocking, and insulators. Various synthetic methods have been exploited to obtain nanosized ceria crystals such as aqueous precipitation, sol-gel, mechanochemical, pyrolysis, thermal decomposition, sonochemical, and solvothermal [2]. Our method of choice was hydrothermal synthesis using supercritical water (SCW) with the aid of vegetable oils as surfactants to modify nanocrystal surfaces and prevent particle aggregation. SCW as a solvent is cheap, readily available, environmentally benign, easier to waste-treat than organic solvents and has proven continuous producibility which is already applied in the industry [3,4].

Traditionally in solution chemistry, surfactants such as oleic acid, decanoic acid, hexanoic acid and oleylamine have been employed to modify the size, morphology and surface characteristics of ceria nanocrystals. Various sizes and shapes such as spherical, cubic, octahedron, rod, wire and nanosheets with surface modification have been obtained [5-7]. These single component reagent grade surfactants are expensive due to various high temperature reactions and purification processes involved in obtaining high purity [8]. This research was aimed to study the surface modification of metal oxide nanocrystals using vegetable oils such as soybean oil or palm oil, which are cheap and readily available in mass quantities compared to the aforementioned single component surfactants. Vegetable oils or animal fats are mixtures of triglycerides where the fatty acids vary in their carbon chain length and in the number of double bonds [9]. As the oil and water mixture is heated, triglyceride molecules are hydrolyzed to yield three moles of fatty acids and one mole of glycerol where the free fatty acid molecules can act as surfactants that adsorb onto nanocrystal surfaces.

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EXPERIMENTAL

Cerium hydroxide ($Ce(OH)_4$) was purchased from Aldrich. Ottogi soybean oil was purchased from a local grocery store and palm oil was generously supplied by Dongnam Oil & Fats Co., Ltd., Korea. Fatty acid compositions of the oils used were provided by the oil suppliers and are as follows. Soybean oil : palmitic (16 : 0) 11%, stearic (18 : 0) 5%, oleic (18 : 1) 29%, linoleic (18 : 2) 50% and linolenic (18 : 3) 5%. Palm oil : myristic (14 : 0) 3%, palmitic (16 : 0) 41%, stearic (18 : 0) 5%, oleic (18 : 1) 42% and linoleic (18 : 2) 9%. Water was purified by Millipore, Milli-Q Advantage A10. All chemicals were used as received without further purification. 0.17 g of cerium hydroxide, 1.4 g of either soybean oil or palm oil and 6.6 ml of deionized water were placed in a SUS316 reactor of 23 ml inner volume. The hydrothermal reaction was carried out by using a thermostated salt bath at 400 °C and 300 bar. The reactor was constantly shaken for 10 minutes, which was followed by rapid quenching in a water bath at room temperature. The resulting powder was isolated by centrifugation and washed three times with ethanol and hexane to remove any remaining organic residues. The finally obtained products were dried in a vacuum oven at 80 °C for 24 hours. The obtained solid products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). XRD patterns were obtained with a Rigaku D/Max-3C diffractometer with Cu Kα radiation. TEM and HR-TEM images were taken from JEOL model JEM-3010. Sample solutions were dried on 300 mesh copper grids with carbon reinforcement prior to TEM analysis. FT-IR spectroscopy was conducted by Thermo Scientific model Nicolet 6700. TGA was analyzed by using TA Instruments model Q-5000 IR.

RESULTS AND DISCUSSION

Initially, a clear two-phase layer is formed when the reactor is filled with water, cerium hydroxide powder and vegetable oil. As the temperature is increased, the heated water rapidly hydrolyzes triglyceride molecules to release fatty acids which are soluble in subcritical water, making the whole system homogeneous. Simultaneously, the released fatty acids chemically adsorb in a selective manner on the ceria nanocrystal surfaces to retard crystal growth, thus controlling the nanocrystal size and morphology [10]. A two-phase mixture exists when the reaction is complete: the upper layer containing nanocrystals dispersed in fatty acid phase and the lower layer containing glycerol dissolved in water. Glycerol is a commonly used raw material for pharmaceutical, medical and personal care applications. The lower water phase solution can be collected for glycerol separation and purification in a large scale process.

The XRD patterns of the synthesized ceria nanocrystals showed cubic fluorite structure (JCPDS Card No. 34-0394), shown in Fig. 1. The XRD patterns for soybean oil assisted nanocrystals showed that pure cerium oxide was formed (Fig. 1(b)). However, for the case of palm oil assisted nanocrystals (Fig. 1(c)), a small residual free fatty acid peak at 21.3° region was observed. It was found that after the hydrothermal synthesis, the removal of free fatty acid residues is more difficult for palm oils than that of soybean oils. This is attributed to the fact that palm oil has higher degree of alkyl chain saturation than soybean oil. Palm oil is semi-solid at room temperature, whereas soybean oil is liquid.

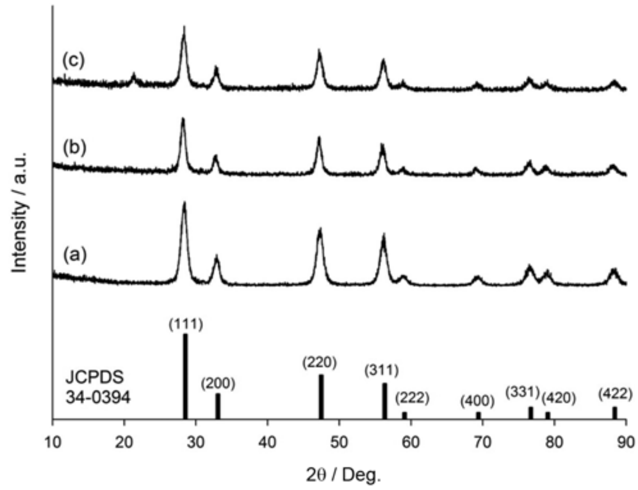

Fig. 1. XRD patterns of cerium oxide nanocrystals synthesized in supercritical water at 400 °C: (a) Without any surface modifiers, (b) with soybean oil and (c) with palm oil.

Fig. 2 is a collection of TEM and HR-TEM images of the synthesized nanocrystals. The unmodified ceria nanocrystals were aggregated with quasi-spherical shape (Fig. 2(a)). The average particle size calculated by Scherrer equation was 9.2 nm. Ceria nanocrystals surface-modified by soybean oil and palm oil were well-dispersed (Figs. 2(b) and 2(c), respectively), having a size distribution of 7-10 nm base length. The HR-TEM images of unmodified, soybean oil modified and palm oil modified nanocrystals showed parallel lattice pattern, demonstrating the high crystallinity and single-crystalline nature (Figs. 2(d), 2(e) and 2(f), respectively).

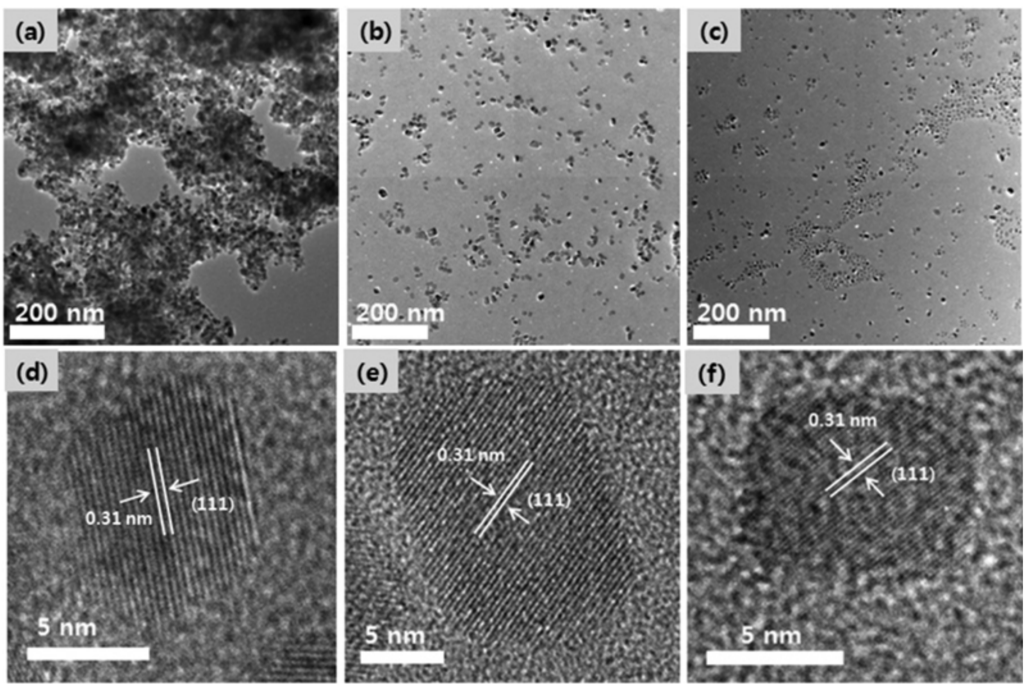

Fig. 2. TEM and HR-TEM images of cerium oxide nanocrystals synthesized in supercritical water at 400 °C: (a) and (d) without any surface modifiers, (b) and (e) with soybean oil (c) and (f) with palm oil.

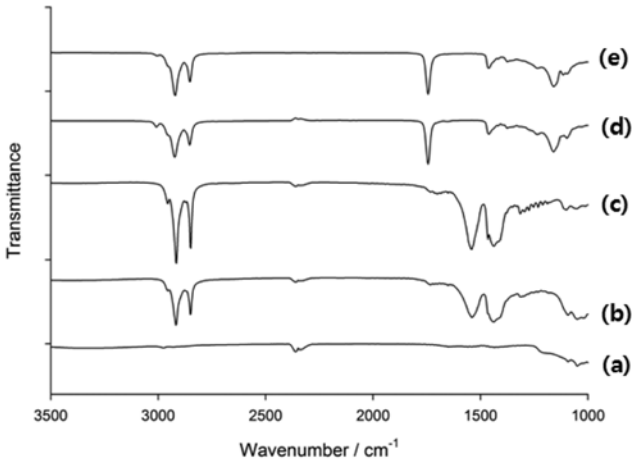

Fig. 3. FT-IR spectra: (a), (b), (c) are CeO_2 synthesized without any surface modifiers, with soybean oil and with palm oil, respectively, and (d) and (e) are soybean oil neat and palm oil neat, respectively.

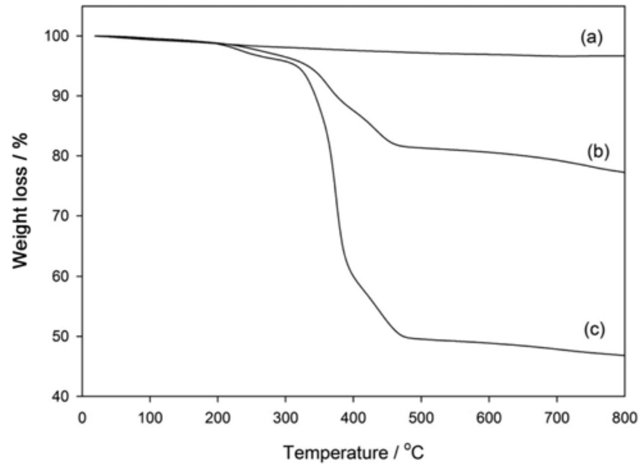

Fig. 4. TGA thermograms of cerium oxide nanocrystals synthesized in supercritical water at 400 °C: (a) Without any surface modifiers, (b) with soybean oil and (c) with palm oil.

FT-IR studies were conducted to characterize the surface-bound fatty acids of cerium oxide and the resulting spectra are shown in Fig. 3. There were no characteristic peaks found for the synthesis without any modifiers, shown in Fig. 3(a). When either soybean oil or palm oil was used to aid the synthesis (Fig. 3(b) and 3(c), respectively), following surface-bound fatty acid peaks were observed: -CH_3- asym str at 2,955 cm^{-1}, -CH_2- asym str at 2,915 cm^{-1}, -CH_2- sym str at 2,847 cm^{-1} and -COO str at 1,544 cm^{-1}. These peaks suggest that the carboxylate group of the fatty acid molecules was chemically bonded on the surfaces of synthesized nanocrystals [11]. Soybean oil and palm oil were also analyzed with infrared, and the resulting spectra are shown in Fig. 3(d) and 3(e), respectively. Both oils had a characteristic carbonyl peak at 1,745 cm^{-1} which were shown to disappear when the fatty acids chemically adsorbed onto CeO_2. It appears that the hydrothermal reaction that reaches conditions up to supercritical region allows rapid hydrolysis of the triglycerides and the chemical bond formation between the released fatty acids and the nanocrystal surfaces, resulting in nanocrystal surface stabilization. An increase in peak intensity when palm oil was used instead of soybean oil suggests the existence of residual fatty acids, which is consistent with XRD data shown above.

TGA was performed to quantitatively investigate the presence of organic modifiers on nanocrystal surfaces. Samples were heated to 800 °C at a rate of 10 °C/min under constant flow of nitrogen and the resulting thermograms are shown in Fig. 4. Unmodified nanocrystals had a weight reduction of 3.5% at 800 °C (Fig. 4(a)). This small decrease is thought to be due to the removal of hydroxyl groups at the surface. Nanocrystals synthesized with the aid of soybean oil and palm oil had lost 22% and 53% of its original weight at 800 °C, respectively. There are two possible reasons for the large weight decrease in palm oil assisted nanocrystals. One is due to the existence of residual fatty acids that were also shown in the XRD patterns, Fig. 1(c). Another explanation is the higher nanocrystal surface coverage of palm oil derived fatty acids. This is consistent with the fatty acid composition data where palm oil has higher degree of alkyl chain saturation, which provides less steric hindrance when chemically bonded onto nanocrystal surfaces. Our future work will focus on the complete removal of residual organic matter from hydrothermally synthesized oxide nanomaterials.

CONCLUSIONS

Well-dispersed cerium oxide nanocrystals were successfully synthesized and surface-modified by using cheap edible oils. Fatty acids from either soybean oil or palm oil were successfully bonded to ceria nanocrystal surfaces for stable surface modification and dispersion. Our novel method of synthesis was proven to be facile, highly economical and environmentally friendly. Soybean oil and palm oil are not the only suitable surface modifiers; all forms of triglycerides from vegetable oils to animal fats are possible candidates for such purpose.

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