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論 文 内 容 要 旨

Introduction

Nanoscale materials have increasingly attracted the academic and industrial interests; their nanosize effect (quantum effect) and high surface to volume ratio sparked their wide range of applications, including optics, semiconductors, catalysis, drug delivery, and bio–imaging. In all above mentioned applications three important aspects should be considered: 1) Particles size, 2) particles morphology and 3) particles dispersibility in the media, in which they are going to be used. Modifying the nanoparticles (NPs) surface with organic functionalizing compounds is a suitable way to achieve these criterions. Despite the numerous studies on the synthesis of NPs, a generalized method for the synthesis of shape and size controlled NPs has not been developed yet.

The aim of this research was to synthesize YAG one dimensional (1D) nanostructures, hafnium oxide (HfO_2) and europium doped HfO_2 (Eu:HfO_2) water dispersible NPs, and HfO_2 water dispersible nanoclusters . Due to their high aspect ratio, YAG 1D nanostructures have potential to fabricate the high performance nano–lasers. HfO_2 is a high refractive index optically transparent material; its NPs are expected to be a good candidate for the fabrication of high refractive index transparent nanocomposites. Rare earth doped HfO_2 NPs, are important scintillation materials that can emit luminescence under the irradiation of high energy beams such as X–rays or γ–rays; this property can be employed for the production of active radicals in biological tissues and cause the cell death. Such kind of materials can be conjugated with photodynamic therapy agents and be used in the area of the simultaneous radiation and photodynamic cancer therapy to kill the cancerous cells. Because of their nontoxic character, hafnium oxide nanoclusters can be conjugated with drug molecules and handled as drug carriers in drug delivery systems. So far, fabrication of these nano materials has been considered difficult by the conventional synthesis methods. Herein, we propose to use the supercritical hydrothermal reaction to solve the problems.

Synthesis of Metal Oxide NPs in Supercritical Water

Supercritical water is a state of water above its critical temperature and critical pressure (T_c=374 °C, P_c=22.1 MPa). In the supercritical area there is only one state–of–the–fluid and it possesses both gas– and liquid–like properties. Most of the properties of water drastically change with temperature or pressure around critical point. The dielectric constant of water at room temperature is 78 and with raise in temperature at a constant pressure, this value decreases greatly and around critical point it is nearly equal to the dielectric constant of polar organic solvents (in the range of 2 to 20). Under such conditions, because of lower solubility of metal oxides (*i.e.* high degrees of supersaturations), the nucleation takes place very fast and thus small size NPs could be synthesized. The low value of dielectric constant provides the miscibility of organic reagents in the supercritical water and consequently, a suitable environment will be achieved for the effective interaction of the organic ligand molecules with the surface of the NPs which is required for the synthesis of the organic–inorganic hybrid NPs. Addition of organic surface modifiers into the supercritical hydrothermal reaction mixture can stabilize the NPs against aggregation. The characteristics of the NPs can be easily tuned due to the facile adjustment of reaction conditions in supercritical water. By incorporating the organic molecules with selective affinity to the different crystallographic facets into the supercritical water the growth of nanocrystals can be controlled in favor of the formation of anisotropic nanostructures such as 1D structures. Using organic surface modifiers that have double–functional group, one can fabricate the self–assembled nanoclusters.

Synthesis of Yttrium Aluminum Garnet NPs

Yttrium aluminum garnet (YAG) with the chemical formula $Y_3Al_5O_{12}$ is one of the most applicable transparent materials. 1D nanostructures, including nanowires, nanotubes and quantum wires, are preferable building blocks for nanoscale optoelectronic devices. Despite the numerous studies on the importance of the synthesis of 1D nanostructures, there is still no report on the synthesis of 1D YAG nanostructures. In this study, we controlled the growth of YAG nanocrystals under supercritical hydrothermal conditions at the reaction temperature and pressure of T=420°C and P=47 MPa, and in the presence of organic surface modifiers to synthesize YAG with 1D morphology. For the purpose of organic surface modification, alkyl amines were added to the reaction mixture. In this experiment, supercritical water provided a very suitable atmosphere to control the selective attachment of the organic surface modifiers and adjust the morphology of YAG structures. Using alkyl amines such as *n*–decylamine, *n*–dodecylamine, 1–hexadecylamine, and oleylamine, high aspect ratio YAG nanostructures with chain–like morphologies were obtained. Figure 1 shows the characteristics of the obtained 1D YAG nanostructures. The electron

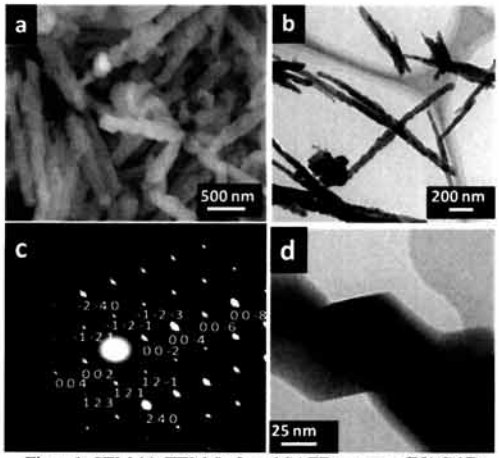

Figure1. SEM (a), TEM (b,d) and SAED pattern of YAG 1D nanostructures synthesized in the presence of alkyl amines.

diffraction pattern of the products reveals that the obtained nanostructures have single crystalline nature and preferentially grown along [001] direction. These organic surface modified YAG structures showed hydrophobic surface characters and were dispersible in organic solvents. A systematic study has been conducted to elucidate the formation mechanism of the obtained nano-chains. For this purpose, the effect of reaction parameters such as presence of organic capping agents, reaction pH, and reaction temperature were investigated. We found that the reaction temperature above the critical point of water was the best condition for the crystallization of Y and Al combined oxide (YAG). The reaction pH between the isoelectric point of YAG and the dissociation constant of the alkyl amines was suitable condition for the formation of high aspect ratio YAG nanostructures. Under such pH conditions, amine groups protonated to NH_3^+. Depending on their degree of the acidity under supercritical hydrothermal conditions, some crystallographic planes became negatively charged. This caused the electrostatic attraction of NH_3^+ ions to those negatively charged facets. Therefore the growth of those facets was stopped, and the growth process was continued along other crystal facets and finally 1D YAG nanostructures formed.

Synthesis of Hafnium Oxide NPs

Hafnium oxide is an important ceramic material due to its large dielectric constant (~30), high melting point (2758 °C), excellent physical and chemical stability, and high refractive index (2.9). Incorporation of inorganic NPs into the polymeric matrices is a promising way to improve the poor refractive index of the polymers. Compared to the previously reported NPs such as TiO_2, ZrO_2, Nb_2O_5, ZnS, and PbS, besides its high refractive index, hafnia has higher physial and chemical stability for such kind of applications. However, optical transparency dictates the use of extremely small particles (<5 nm) in order to avoid excessive light scattering. Furthermore, uniform dispersion of NPs in the matrix is the key factor for the successful fabrication of a transparent, uniform organic-inorganic nanocomposite. To the best of our knowledge, still there is no generalized method for the direct synthesis of hafnium oxide NPs with above mentioned criterion. In this research, near- to supercritical water was employed to control the shape, size and surface properties of hafnium oxide NPs. A bi-functional organic surface modifier (3,4 dihydroxyhydrocinnamic acid, DHCA) was incorporated into the reaction mixture to synthesize NPs with hydrophilic surface characters. The

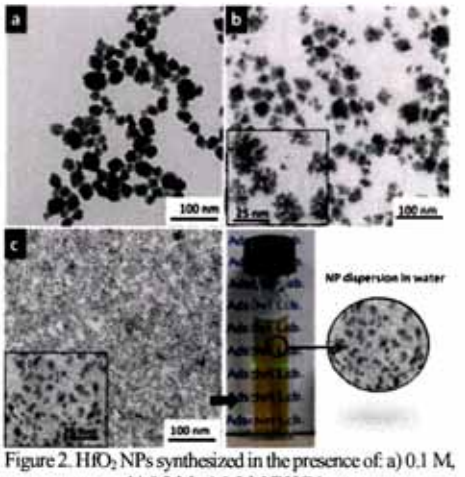

Figure 2. HfO_2 NPs synthesized in the presence of: a) 0.1 M, b) 0.2 M, c) 0.3 M DHCA.

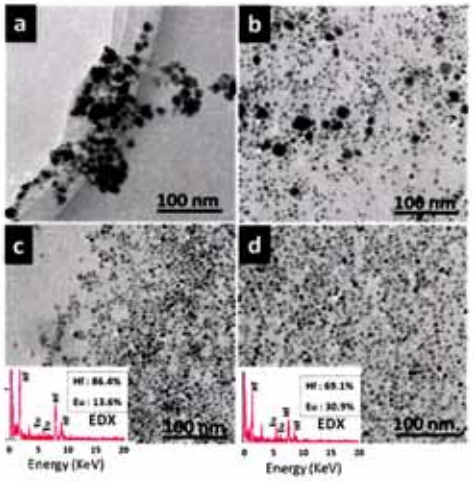

Figure 3. Eu:HfO_2 NPs with Eu content of: a) 5 mol%, b)10 mol%, c)15 mol%, d) 30 mol%.

synthesis process was performed under the near– to supercritical hydrothermal conditions of T=350 to 400 °C and P=16.5 to 37 MPa. Hafnium oxide NPs with various morphologies, such as terapezohedron, oval, nano–flowers, and nanoclusters with diameters from 4 nm to 27 nm were synthesized. Figure 2 shows the TEM images of the synthesized HfO_2 nanoclusters and NPs by addition of different amounts of DHCA into the reaction mixture. Hafnium oxide nanoclusters of 25 nm diameter and NPs of 4 nm diameter were successfully synthesized under the nearcritical hydrothermal conditions. These products had high affinity with water and their suspensions in water were transparent and stable for months.

The proposed method was extended for the synthesis of water dispersible europium doped hafnium oxide NPs as an important X–ray luminescent material. We succeeded to substitute Eu ions into the hafnium oxide crystal structure up to 30 mol %. The synthesized Eu:HfO_2 NPs were also highly dispersible in water and their suspensions in water were transparent and stable for months. Figure 3 shows the TEM image of the Eu:HfO_2 NPs with different Eu concentrations.

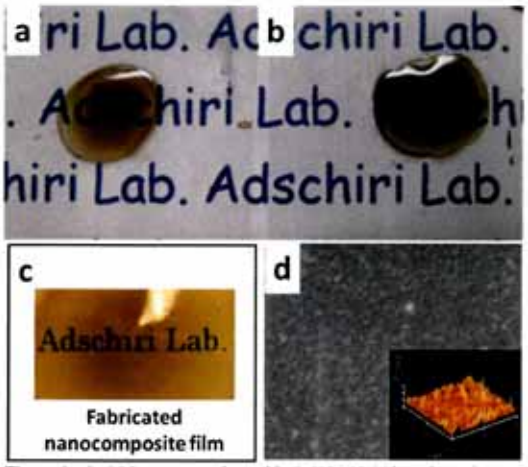

Figure 4. a,b,c) Nanocomposites with a) 60%, b) 80% volume loads of HfO_2 NPs, before and after fabrication of the films. d) SEM and AFM images of the fabricated nanocomposite films.

The synthesized water dispersible HfO_2 NPs showed great potential for the fabrication of high refractive index transparent polymeric films. For this purpose, polyvinyl alcohol was used as a water soluble polymeric matrix. Nanocomposite films with HfO_2 NP loads up to 80 vol% were fabricated in this research. Figure 4a–c shows the transparent nanocomposites with different volume loads of HfO_2 NPs, before and after fabrication of the films. The recorded AFM and SEM images from the fabricated films (figure 4d), showed that our NPs were uniformly dispersed in polymer matrix without any sharp aggregation.

Summary and Conclusions

Organic–inorganic hybrid YAG and HfO_2 nanostructures and NPs were successfully synthesized under supercritical hydrothermal conditions. By controlling the size, morphology and surface properties of NPs, YAG 1D nanostructures, HfO_2 and Eu: HfO_2 NPs with high affinity with water, and HfO_2 nanoclusters were obtained.

論文審査結果の要旨

本論文は、レーザ発光デバイスとしての応用が期待されるイットリウムアルミニウムガーネット（YAG），高屈折率材料やラジカル発生剤としての応用が期待される酸化ハフニウム（HfO_2）について、形態を制御したナノ材料の合成プロセスを対象として研究を行ったものである。合成方法としては、有機溶媒の使用を極力抑制し、超臨界水中で水熱合成を行う超臨界水熱合成法を用いている。また、ナノ粒子の表面に有機分子を複合化させることにより、ナノ粒子のハンドリングや分散媒との相互作用の最適化を実現した結果をまとめており、全体で6章より構成されている。

第1章では、本研究の背景について概要を述べ、さらに研究の目的を設定した。
第2章では、既往の研究についてまとめ、本研究の位置付けを明確にしている。既往の合成手法を概観するとともに、YAG については1次元構造を合成するプロセスが全く存在しないことを示し、HfO_2ナノ粒子については、超臨界水中で、しかも 5 nm 以下の粒子を合成することがこれまでに行われていなかったことを示し、本研究が極めて高い独自性を有することを明らかにした。
第3章では、超臨界水熱合成法を用いる YAG ナノ構造の合成に関して、実験結果をまとめるとともに考察を行った。実験手法、解析手法についてまとめたのち、反応温度、pH が生成物の形状、サイズにどのような影響を与えるか、明らかにした。さらに、有機分子修飾 YAG ナノ粒子の合成を行い、生成物のサイズや形状に加えて、有機分子の結合様式、存在量を評価した。ここで、合成条件によっては1次元ナノ構造が形成されるため、その形成機構を推察した。
第4章では、超臨界水熱合成法を用いて、HfO_2 ナノ構造の合成に関して、実験結果をまとめるとともに考察を行った。超臨界水、亜臨界水中で合成した粒子の形状・サイズから、合成メカニズムの議論をすると共に、有機分子修飾を試み、溶媒中に良分散するナノ粒子やナノ粒子どうしが結合して複合化した構造の形成に成功した。
第5章では、まとめと考察を行っている。

このように本論文は、今後さまざまな応用分野での利用がきたいされる YAG, HfO_2 ナノ粒子を対象として、これまでにまったく報告されたことのない 1D ロッド構造やナノ集積体の合成を行い、合成メカニズムの解明を行った。これらの成果は極めて独自性が高く、全く新しい研究分野の開拓につながる成果であると判断できる。

よって、本論文は博士(工学)の学位論文として合格と認める。