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Colloidal europium nanoparticles via a solvated metal atom dispersion approach and their surface enhanced Raman scattering studies

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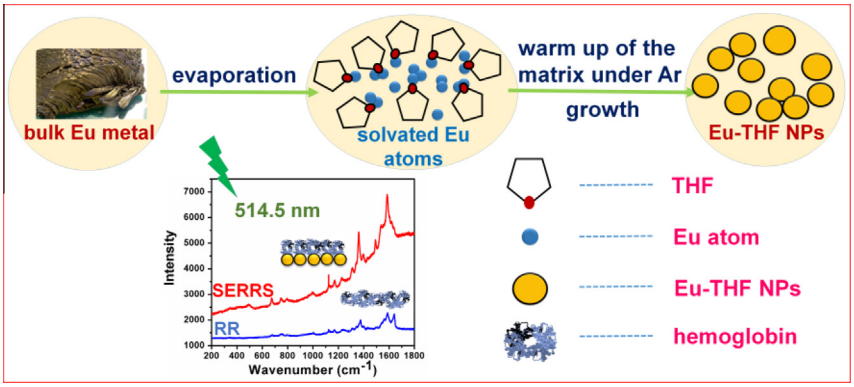
HIGHLIGHTS

- Synthesis of europium nanoparticles, the most reactive of lanthanide elements in the size regime of 4–5 nm.
- First experimental investigation of a rare-earth nanoparticles as SERS substrate.
- First time demonstrating the interaction of europium nanoparticles with biomolecules like Hb and Cyt-*c*.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemistry of lanthanide metals in their zerovalent state at the nanoscale remains unexplored due to the high chemical reactivity and difficulty in synthesizing nanoparticles by conventional reduction methods. In the present study, europium(0) nanoparticles, the most reactive of all the rare earth metals have been synthesized by solvated metal atom dispersion (SMAD) method using hexadecyl amine as the capping agent. The as-prepared europium nanoparticles show surface Plasmon resonance (SPR) band in the visible region of the electromagnetic spectrum. This lead to the investigation of its surface enhanced Raman scattering (SERS) using visible light excitation source. The SERS activity of europium nanoparticles has been followed using 4-aminothiophenol and biologically important molecules such as hemoglobin and Cyt-*c* as the analytes. This is the first example of lanthanide metal nanoparticles as SERS substrate which can possibly be extended to other rare-earth metals. Since hemoglobin absorbs in the visible region, the use of visible light excitation source leads to surface enhanced resonance Raman spectroscopy (SERRS). The interaction of biomolecules with Eu(0) has been followed using FT-IR and UV–visible spectroscopy techniques. The results indicate that there is no major irreversible change in the structure of biomolecules upon interaction with europium nanoparticles.

1. Introduction

Lanthanide metals and their compounds find uses in various fields like high performance magnets, magnetic refrigeration, catalysis, luminescent materials, chemical sensors, high-temperature super conductors, nuclear reactors and medicine

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due to their unique physical and chemical properties arising from the unpaired 4f electronic configuration [1–7]. Of the lanthanides, europium is of particular interest because of its optical properties. It has immense use as a phosphor activator and is widely used in europium-activated yttrium compounds to produce red color in television and computer displays [8]. $Eu_{1-x}Se$ nanoparticles are wide band gap semiconductors; they have improved magneto-optical properties over others [9]. The low cytotoxicity and biocompatibility of Europium-based nanomaterials (Eu_2O_3, $Eu(OH)_3$, etc.) have shown promise in biomedical applications [10–13]. In addition, it has been shown by theoretical calculations that Eu nanoparticles can act as a new candidate that exhibits SERS effect [14]. To date, there are no experimental reports of any of the f-block elements that show SERS effect; this is primarily due to their synthetic difficulties. Conventional reduction methods are incapable of producing europium nanoparticles due to their high reduction potential and their high reactivity at the nanoscale. Therefore, only very few attempts have been made towards the synthesis of europium(0) nanoparticles [15,16]. The attempts that have been made to synthesize these metal nanoparticles suffer from limitations associated with incomplete reduction, difficulties in removing side-products, poor size control, and low yield. In this regard, solvated metal atom dispersion (SMAD) method in combination with digestive ripening is an efficient method which was successful for the synthesis of many reactive metal nanoparticles with uniform size and shape [17–19]. Briefly, it involves the co-evaporation of bulk metal and stabilizing solvent and their co-condensation on the walls of a reactor maintained at 77 K. Warm up of the matrix under Ar atmosphere results in a colloid of metal nanoparticles. Merits of this method include easy scale-up, high reproducibility, and avoidance of tedious purification procedures. Herein, we present our first successful synthesis of europium nanoparticles, by the SMAD method.

Surface Enhanced Raman Scattering (SERS) is an attractive spectroscopic technique to detect molecules both qualitatively and quantitatively by amplifying the vibrational signals of the probe molecules close to the vicinity of metal nanoparticles or films which even lead to the detection of single molecules [20,21]. The major contribution for this signal enhancement comes from electromagnetic mechanism, whereas charge transfer mechanism and Herzberg–Teller type transition also play important roles in the enhancement [22,23]. Most commonly used SERS substrates are nanostructures of Ag, Au, and Cu which could provide large enhancement since the SPR band in these cases fall in the visible and near infrared region. Advancement in nanotechnology made it possible to synthesize and employ several other metallic nanostructures including alkali and transition metals, as SERS substrates [24,25]. Herein, we report the synthesis of Eu nanoparticles by SMAD method; these nanoparticles show surface Plasmon resonance band in the visible region. To understand the SERS activity and biocompatibility of Eu nanoparticles, we selected 4-aminothiophenol, hemoglobin and cytochrome-*c* as probe molecules. Europium nanoparticles are unstable with respect to oxidation in an ambient atmosphere making them difficult to use for practical applications. However, if methodologies could be developed to overcome this reactivity, it will open up new possibilities in the field of metallic SERS substrates. We also anticipated that biomacromolecules like Hb or Cyt-*c* can stabilize the nanoparticles as well. Further, we investigated the binding of hemoglobin and Cyt-*c* to europium nanoparticles surface by UV–visible spectroscopy and FT-IR spectroscopy. There is no prior report on this nano-bio interaction of europium metal nanoparticles with hemoglobin or Cyt-*c*. To the best of our knowledge, this is the first instance of rare-earth metal nanoparticles demonstrated as SERS substrate. It opens up a new application area of lanthanide metal nanoparticles.

2. Experimental section

2.1. Materials

Europium metal (99.99%) was purchased from Metall Rare Earth Limited, China. Tungsten crucibles were procured from R. D. Mathis Company, California. Hexadecyl amine (HDA) and lyophilized human hemoglobin were obtained from Sigma Aldrich. Tetrahydrofuran was dried over sodium - benzophenone and degassed by several freeze pump thaw cycles. HDA was dried and degassed for 12 h at 100 °C before using in the SMAD experiment. All glasswares were kept in a hot air oven at 130 °C and evacuated in hot condition just before use.

2.2. Measurements

UV–visible spectra of europium colloids were recorded using Perkin Elmer Lambda 750 spectrometer in the range 250–800 nm. The samples for UV–visible spectral measurements were prepared inside a glove box in an air tight quartz cuvette. The TEM BF images and HRTEM images were obtained using JEOL JEM-2100F microscope operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by drop casting 2–3 μL of the colloid on a formvar coated copper grid and dried under a lamp in a nitrogen filled glove box. Raman spectral measurements were made using LabRAM HR, Horiba JobinYvon spectrometer equipped with CCD detector. SERS spectra were recorded by shining laser on different regions of the capillary using 514.5 nm, 632.8 nm, and 785 nm excitation lasers. IR spectra were recorded using Bruker alpha FT-IR spectrometer.

2.3. Synthesis of Eu–THF colloid by SMAD method

An alumina coated W crucible was assembled in a SMAD reactor which is kept in between two water-cooled copper electrodes. A glass reactor of 3000 mL was connected to the reactor head which was equipped with two water-cooled copper electrodes and the entire setup was evacuated to $1–2 \times 10^{-3}$ mbar pressure. Then the crucible was resistively heated in steps until a final pressure of $1–2 \times 10^{-3}$ mbar was reached. This curing process ensures removal of moisture and other volatile impurities from the crucible. In a particular experiment, crucible was charged with 100 mg of metal and alumina wool was wrapped around it to avoid heat dissipation during the experiment. Solvent was introduced from a solvent Schlenk tube containing dried and degassed solvent, in the vapor form through a shower head connected to the reactor head via a bridge head. The entire setup was evacuated to $1–2 \times 10^{-3}$ mbar. The reactor was immersed in a liquid nitrogen bath during the experiment. The crucible was resistively heated by applying proper voltage between the two water-cooled copper electrodes and the reactor walls were pre-coated with approximately 20 mL of THF solvent before the metal evaporation was begun. Then the crucible was heated gradually until metal vaporization began which was evident by the appearance of blue color on a white matrix. Co-condensation of metal and solvent vapors were continued for 3 h until approximately 50 mL of THF solvent was condensed. When the metal vaporization was stopped, another 20 mL of solvent was coated on this blue colored matrix. The liquid nitrogen filled dewar was removed and the matrix was allowed to melt and warm up to room temperature under Ar atmosphere. During this process, the blue colored matrix turned blackish yellow and the colloid was stirred well for half an hour. It was then siphoned into a Schlenk tube under Argon atmosphere. The as-prepared colloid was stored in a N_2 filled glove box and the