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Green synthesis of Ce^{3+} rich CeO_2 nanoparticles and its antimicrobial studies

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ABSTRACT

Cerium oxide nanoparticles (CeO_2-np) with Ce^{3+} rich surfaces were synthesized by ecofriendly route using tannic acid. XRD and SAED patterns confirm the cubic structure of CeO_2-np. A semi-quantitative XPS analysis revealed the presence of 34 % Ce^{3+} ions. Tannic acid not only mediates the CeO_2-np synthesis, but also helps in reduction of surface states from Ce^{4+} to Ce^{3+}. Oxygen vacancies were evidenced from XPS and photoluminescence studies. The synthesized nanoparticles showed good antimicrobial activity towards both gram positive (*Bacillus subtilis*) and gram negative (*Escherichia coli*) bacteria. The toxicity of CeO_2-np towards tested bacteria is due to production of Reactive oxygen species (ROS). The presence of Ce^{3+} ions and rich surface oxygen vacancies may lead to excellent production of ROS and simultaneously causing cell wall damage. Present findings show that tannic acid assisted CeO_2-np with obtained properties acts as good antibacterial agent.

1. Introduction

Among rare earths, cerium the first element of lanthanide group with *4f* electrons has tremendous attention in all research fields including physics, chemistry and biology [1,2]. Upon its combination with oxygen during the formulation of nanomaterial, cerium oxide takes on crystalline fluorite structure that comes into sight as an interesting material with wide range of applications.

The general synthesis strategies in preparing CeO_2-np includes chemical and physical methods which are complex, time consuming and uses expensive and hazardous chemicals. Hence, green chemistry approaches for the production of CeO_2-np was adopted successfully using natural resources such as *Gloriosa superba L.* leaf extract [3] and honey [4]. There are difficulties to bring out the mechanism of formation of CeO_2-np when using crude extracts and other natural resources.

Only few reports are available on the antimicrobial activity of CeO_2-np. Kannan et al. [5] reported the antibacterial effect of CeO_2-np synthesized using *Acalypha indica* leaf extract against both gram positive and negative bacteria. Kuang et al. [6] provided the comparative bactericidal effect between bulk ceria and CeO_2-np. In addition to the above, reports are available with polymer coated CeO_2-np on bactericidal activity [7]. A contradictory exists for CeO_2-np toxicity due to discrepancy of data on its bio-activity and has no clear consent about property of nanoparticle that is responsible for biological effects.

In this present work, CeO_2-np was synthesized using the secondary plant metabolite 'Tannic acid' and investigated the structural and optical properties. To best of our knowledge, there are no previous reports to synthesize Ce^{3+} rich CeO_2-np using tannic acid, and attempted to explain how high levels of Ce^{3+} and oxygen vacancies helped in achieving good antibacterial activity.

2. Materials and methods

2.1. Synthesis of CeO_2-np using tannic acid

Tannic (0.5 g) acid was dissolved in 25 mL of deionized water using ultrasonicator. The pH of the solution was brought down slightly towards basic (pH = 7.8 ± 0.2) in order to initiate the

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hydrolysis of tannic acid. Then 1.9 g of $CeCl_3{\cdot}7H_2O$ (99.9%, sigma Aldrich) was added to the above solution and sonicated further for 5 min. The solution mixture was then refluxed for about 3 h and centrifuged to obtain dark yellow precipitate. This precipitate was washed thrice with ethanol and kept in a hot air oven at 100° C for overnight, followed by calcination at 400° C for 3 h. The final obtained solid product was pale yellow in color.

2.2. Characterization

UV–Vis spectrum was recorded using HITACHI U-5100 UV–visible spectrophotometer. FT-IR spectrum was recorded using Varian 660-IR FT-IR spectrophotometer. High Resolution Transmission Electron Microscopic (HR-TEM) images were taken with JEOL JEM 2100. X-ray diffraction (XRD) was done using Bruker D8 advance eco diffractometer. X-ray photoelectron spectrum (XPS) of the sample was measured using K-Alpha spectrometer from Thermo Scientific.

2.3. Antibacterial activity of CeO_2-np

The antibacterial activity was studied against both gram positive (*B. subtilis*) and gram negative (*E. coli* XL) bacteria at different concentrations of CeO_2-np by well diffusion method. The complete experimental methodology was given in Supplementary Material S1.

3. Results and discussion

The mechanism of formation of CeO_2-np can be explained as follows: Under mild acidic/basic conditions, tannic acid hydrolyses and produce gallic acid and glucose moieties. On addition of $CeCl_3.7H_20$ into the hydrolyzed tannic acid solution, cerium forms stable complex with abundantly available gallic acid. This cerium-gallic acid complex formation can be explained on the basis of Hard Soft Acid Base (HSAB) principle [8]. The hydroxyl groups of gallic acid behaves as hard ligands and cerium as hard metal ion and when this ligand comes in contact to the metal ion, complexation favors. Then, the cerium-gallic acid complex upon hydrolysis produces colloidal sol of cerium hydroxide growth units covered with gallic acid and glucose, and the solution appears to be in dark yellow color [9]. And so, released polyphenols helps in reducing surface Ce^{4+} to Ce^{3+}. The obtained cerium hydroxide after calcination at 400 °C yields CeO_2-np. An illustrative mechanism was given in Supplementary Material S2.

X-ray diffraction pattern of CeO_2-np synthesized using tannic acid is shown in Fig. 1a. and all peaks in agreement with JCPDS. No.00-034-0394, which indicates the cubic structure of CeO_2-np. To understand the surface chemistry of the synthesized CeO_2-np, XPS was carried out. Fig. 1b and c shows the O(*1s*) and Ce(*3d*) XPS spectra respectively. A complete detail of XPS analysis is given in Supplementary Material S3. Since the role of surface valence states of CeO_2-np play important role in biological effects [10], the concentration of Ce^{3+} was calculated using the method described elsewhere [11] which involves calculation of area under each individual deconvoluted peak. The concentration of Ce^{3+} was found to be 34% in the present case (Supplementary Material S3).

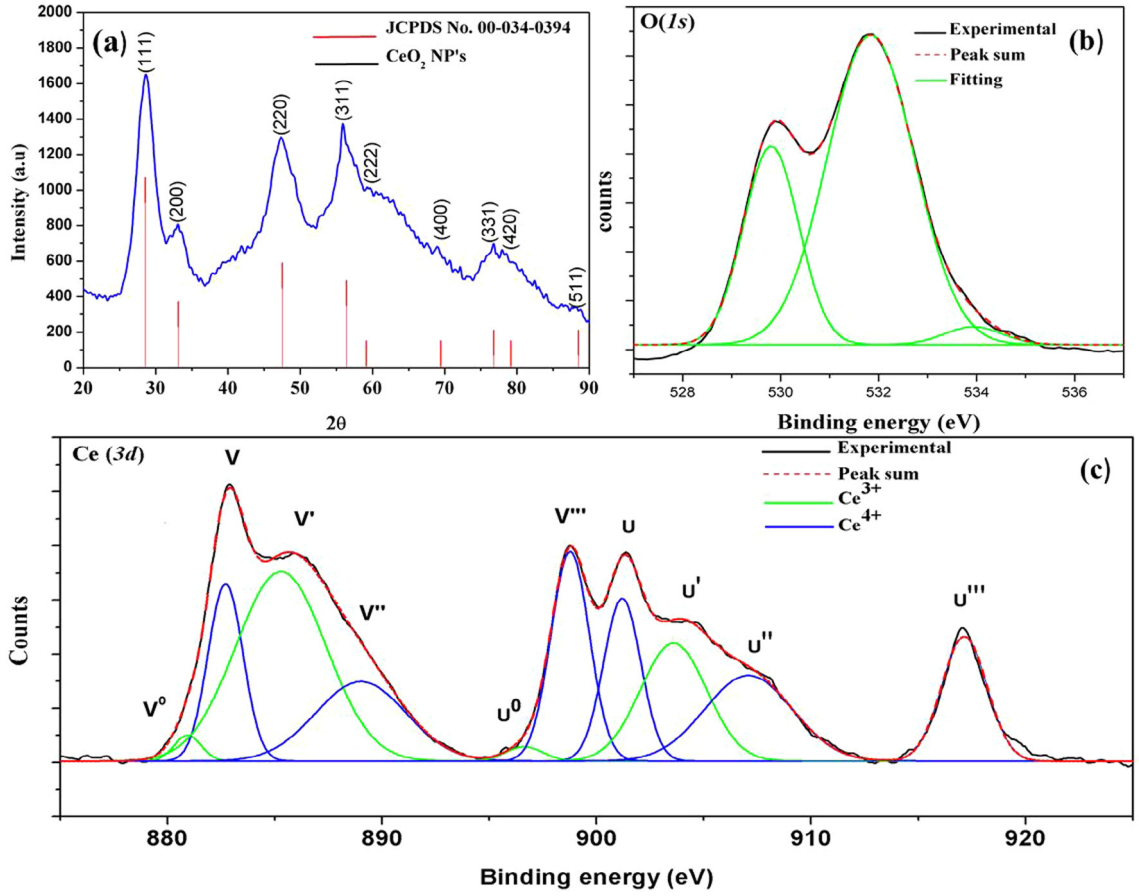

Fig. 1. (a) XRD pattern of synthesized CeO_2-np, (b) and (c) deconvoluted XPS spectra of O(*1s*) and Ce(*3d*) respectively.