Advanced Powder Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Green synthesis of ruthenium oxide nanoparticles: Characterization and its antibacterial activity

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ARTICLE INFO

Article history:
Received 16 March 2015
Received in revised form 17 July 2015
Accepted 14 August 2015
Available online xxxx

Keywords:
Ruthenium oxide
Green synthesis
Nanostructure
Acalypha indica
Antibacterial activity

ABSTRACT

Recently, biosynthesis of nanoparticles has attracted scientists' attention because of the necessity to develop new clean, cost-effective and efficient synthesis techniques. In particular, metal oxide nanoparticles are receiving considerable attention in a large variety of applications. However, up to now, the reports on the green synthesis and characterization of nanocrystalline Ruthenium oxide (RuO_2) are relatively few compared to some other metal oxides. In this paper, we report for the use of plant extract (*Acalypha indica*) in the biosynthesis of ruthenium oxide nanoparticles of dimensions 6–25 nm. The synthesized nanomaterials were characterized by Fourier transform infrared (FT-IR) spectrum analysis to confirm Ru–O symmetric stretching. X-ray diffraction (XRD) confirms the formation and the crystalline nature of ruthenium oxide nanomaterial. Further, these nanoparticles were found to exhibit high antibacterial activity against four different strains of the bacteria like *Escherichia coli*, *Pseudomonas aeruginosa*, *Serratia marcescens* and *Staphylococcus aureus*.

1. Introduction

The development of green processes for the synthesis of nanoparticles is evolving into an important branch of nanotechnology. An important area of research in nanotechnology deals with the synthesis of nanoparticles of different chemical compositions, sizes and controlled monodispersity. Indeed, nanoparticle shape control is a recent addition to the list of demands being made of newly emerging synthesis methods. Currently, there is a growing need to develop environmentally benign nanoparticle synthesis processes that do not use toxic chemicals in the synthesis protocol. As a result, researchers in the field of nanoparticle synthesis and assembly have turned to biological systems for inspiration. This is not surprising given that many plant sources like *Moringa oleifera* [1], *Syzygium cumini* [2], and *Ocimum sanctum* [3]. Currently, the people of Asia and India are utilizing plants as part of their routine health management [4]. *Acalypha indica* is a weed widely distributed throughout the plains of India. It has been reported to be useful in treating pneumonia, asthma, rheumatism and several other ailments. The dried leaves of *A. indica* were made into a poultice to treat bedsores and wounds. The juice of *A. indica* is added to oil or lime and used to treat a variety of skin disorders.

Ruthenium oxide (RuO_2) attracts both scientific and technological importance because of a combination of characteristics such as high thermal and chemical stability, low resistivity and remarkable redox properties [5,6]. For example, hydrous RuO_2 has been exploited as a well-known electrode for supercapacitors not only due to its excellent specific capacitance but for the long cycle life also [7]. Further, they are of great interest for their applications in a variety of fields such as catalysis, microelectronics and electrochemical capacitor [8]. For instance, RuO_2 is the main active component in dimensionally stable anodes in the Chlor alkali industry, while many other applications CO oxidation in sensors and CO_2 reduction in photocatalysis. Recently, research has been directed to develop more efficient and reliable methods for the generation of RuO_2 nanomaterials so that particle size, shape and crystal structure can be tailor made for devices with excellent thermal and chemical stability, very low resistivity as well as enhanced electrocatalytic activity.

The aim of this work is to study the processes taking place in the precipitation of ruthenium hydroxide from chloride solutions using *A. indica* leaf extracts as a precipitant, the thermal decomposition of precipitates with the production of RuO_2, and the evolution of particle ensembles in the processes of thermal processing. The synthesized RuO_2 nanoparticles were characterized by XRD, SEM, TEM, EDX, FT-IR, DLS and TGA–DSC analysis. In addition, the RuO_2 nanoparticle was tested for its antibacterial activity using four different pathogens.

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http://dx.doi.org/10.1016/j.apt.2015.08.009
0921-8831/

2. Experimental details

2.1. Materials

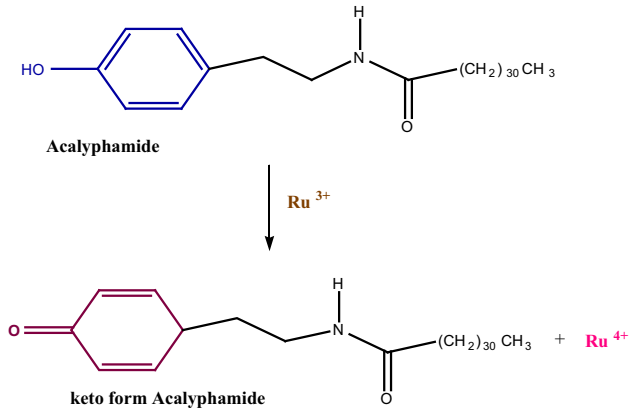
Ruthenium chloride [$RuCl_3 \cdot xH_2O$] purchased from Sigma–Aldrich was directly used without further purification. The leaves of *A. indica* were collected in the Alagappa University campus, Karaikudi, India. Then these leaves were washed thoroughly with double distilled water and dried for a week at room temperature.

2.2. Preparation of plant extract

The dried and finely cutted leaves (20 g) were boiled in a 250 ml Erlenmeyer flask with 100 ml of double distilled water for 30 min. Then the extract was filtered through ordinary filter paper and through Whatman No. 1 filter paper. The filtrate was collected and it was kept in a refrigerator at 4 °C for further experiments.

2.3. Synthesis of ruthenium oxide nanoparticles

Aqueous solution of 0.1 M ruthenium chloride [$RuCl_3 \cdot xH_2O$] was used for the synthesis of ruthenium oxide nanoparticles. 10 ml of *A. indica* leaf extract was added to 50 ml of 0.1 M $RuCl_3 \cdot xH_2O$ in a 250 ml Erlenmeyer flask and stirred at 80 °C for two hours. The particles formed after adequate time of stirring and it was collected by centrifugation at 10,000 rpm for 10 min. The centrifuged particles were washed with deionised water and again subjected to centrifugation at 1500 rpm for 30 min. The centrifuged sample, dried in an air oven, was powdered using mortar and pestle. This powdered sample was calcined in a muffle furnace at 600 °C to get ruthenium oxide nanoparticles [9,10]. The plant extract contains mainly the alkaloid like acalyphamide [11], which may be reduced by the oxidation of Ru^{3+} to Ru^{4+}. The suggested mechanism is given below for the synthesis of ruthenium oxide nanoparticle.



2.4. Characterization

SEM images were obtained using HITACHI Model S-3000H at various magnifications to study the surface morphology of RuO_2 nanoparticles. X-ray diffraction data sets were recorded at room temperature on a PANalytical X'PERT PRO system in Bragg–Brentano geometry using Cu Kα1 (1.540 Å) radiation. The powder diffraction covered the $20° < 2\theta > 80°$ range with 0.0170° steps. FT-IR spectra were obtained using BRUKER Optik GmbH FTIR spectrometer model TENSOR 27 in the diffuse reflection mode. The TEM images were recorded by using PHILIPS CM 200, operating voltage 20–200 kV with resolution ranging at 2.4 Å. Dynamic Light Scattering analysis was performed by using ZEN 3600 Malvern instrument with size range 0.3 nm–10 μm. TGA–DSC reports were collected by using TGA–DSC Perkin Elmer Instruments under nitrogen flow condition.

2.5. Antibacterial studies

2.5.1. Disk diffusion method

Escherichia coli (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Serratia marcescens* (*S. marcescens*) and *Staphylococcus aureus* (*S. aureus*) cultures were used for this study as reference strains used for antimicrobial susceptibility testing by the Kirby–Bauer diffusion method. The bacterial suspension was applied uniformly on the surface of a Muller Hinton agar (MHA) plate in the concentration range of 10^5–10^6 CFU/ml before placing ruthenium oxide nanoparticle laden disk. The strains were cultured on nutrient agar (Himedia, India) and incubated aerobically at 35 °C overnight.

2.5.2. Turbidimetric method

The antibacterial activity of the RuO_2 nanoparticles was tested by concentration dependent method like turbidimetric method. In this method, the antibacterial assay of RuO_2 nanoparticles against *E. coli*, *P. aeruginosa*, *S. marcescens* and *S. aureus* in Luria Bertani broth (LB). The 24 h old bacterial cultures were inoculated into LB Broth supplemented with various concentrations (10 μl, 15 μl, 25 μl, 50 μl, 75 μl and 100 μl) of RuO_2 nanoparticles. The RuO_2 free LB broth was used as a control. The broth containing conical flasks was incubated at room temperature under stirring for 24 h and the vulnerability of the tested organisms was observed by taking optical density at 595 nm for various time intervals.

2.5.3. Minimum inhibitory concentration (MIC)

The minimum inhibitory concentration (MIC) describes that, the lowest concentration of material that inhibits the growth of an organism was determined based on batch cultures containing varying concentration of RuO_2 nanoparticle in suspension. Different concentrations (10 μl, 15 μl, 25 μl, 50 μl, 75 μl and 100 μl) of RuO_2 nanoparticles were prepared with dimethyl sulphoxide (DMSO) and mixed with 400 μl ml^{-1} of nutrient broth and 50 μl of 24 h old bacterial inoculum and allowed to grow overnight at 35 °C for 48 h. Nutrient broth alone served as negative control. Whole setup in triplicate was incubated at 35 °C for 24 h. The MIC was the lowest concentration of the nanoparticles that did not permit any visible growth of bacteria during 24 h of incubation on the basis of turbidity.

2.5.4. Minimum bactericidal concentration (MBC)

To avoid the possibility of misinterpretations due to the turbidity of insoluble compounds if any, the MBC was determined by sub-culturing. The minimum bactericidal concentration (MBC), which describes the lowest concentration of nanoparticles that kills 99.9% of the bacteria was also determined from the batch culture studies. To test for bactericidal effect, a loopful from each flask was inoculated on nutrient agar and incubated at 35 °C for 24 h. The nanoparticle concentration causing bactericidal effect was selected based on absence of colonies on the agar plate.

3. Results and discussion

3.1. Structural confirmation

The XRD pattern was recorded in the 2θ range of 20–80°, in order to study the structural analysis of the RuO_2. Fig. 1 shows the sharp, intense peak confirms the crystalline nature of the synthesized RuO_2 nanoparticles. The XRD data clearly demonstrate

Please cite this article in press as: S.K. Kannan, M. Sundrarajan, Green synthesis of ruthenium oxide nanoparticles: Characterization and its antibacterial activity, Advanced Powder Technology (2015), http://dx.doi.org/10.1016/j.apt.2015.08.009