

A Simple New Method to Synthesize Nanocrystalline Ruthenium Dioxide in the Presence of Octanoic Acid As Organic Surfactant

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Abstract:

Ruthenium dioxide nanoparticles (RuO_2) with an average particle size of 50 nm are readily synthesized from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ via the precipitation process in the presence of in-situ sodium octanoate as anionic surfactant. The phase composition, morphology, lattice parameters and size of nanoparticles in these products are characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM).

Keywords: Ruthenium dioxide, Nanoparticles, Co-precipitation, X-ray diffraction, SEM, Octanoic acid.

1. INTRODUCTION

Amongst the various transition metal oxides, RuO_2 is one of the most versatile materials due to its excellent diffusion barrier properties, high thermal stability and low temperature resistivity [1]. It is known to have very high capacitance at low resistance, possibly making it suitable for construction of high energy, high power supercapacitors [2]. It has been used in resistors, electrochemical capacitors, electrode material for supercapacitor application either as single oxide or mixed oxide, gas sensors as well as catalysts [3-5]. RuO_2 with high surface area and partially ordered structure shows high catalytic activity for the oxidation of CO to CO_2 at relatively low temperature [6]. Nanometric RuO_2 confined in a zeolite framework has recently been reported as an efficient catalyst for alcohol oxidation under mild aerobic conditions [5]. It is also found to be an effective co-catalyst for overall water splitting [7]. The catalytic propensity of RuO_2 nanomaterial can be adequately exploited in oxidation reactions

owing to its coordinatively unsaturated but reactive Ru center [8].

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 [9].

The preparation of nanomaterials has been achieved by many methods, such as thermal synthesis, combustion synthesis, sol-gel and precipitation. Precipitation method can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. Furthermore, if process conditions such as solution pH, reaction temperature, stirring rate, metal salts concentration and surfactant concentration are carefully controlled, oxide particles of the desired shape and sizes can be produced. One of the main advantages of precipitation method is that it does not require sophisticated equipment. In this work, a simple and novel method was developed for preparation of

Table 1. Lattice parameters and size of RuO₂ nanoparticles synthesized using Co-precipitation method.

| Cell parameters (Å) | | Cell volume (Å ³) | average size (nm) | |
|---------------------|----------|-------------------------------|-------------------|------------|
| <i>a=b</i> | <i>c</i> | | <i>XRD</i> | <i>SEM</i> |
| 4.4934 | 3.0913 | 62.4153 | 46 | 48 |

RuO₂ nanoparticles by precipitation method in the presence of sodium octanoate as anionic surfactant. The synthesized materials have been characterized by FT-IR, SEM and XRD techniques.

2. EXPERIMENTAL

2.1. Material and characterization

All reagents used were obtained from Merck and Aldrich Chem. Co. SEM images of the samples were produced on Philips XL30 equipped with an EDX microanalysis (Tarbiat Modares Uni.). XRD analysis was conducted on a Philips analytical PC-APD X-ray diffractometer with graphite monochromatic Cu K α radiation ($\lambda = 1.54056$ Å). FT-IR spectra were recorded on a JACSO (model 640 plus) infrared spectrophotometer with KBr pellets in the range of 400-4000 cm⁻¹.

2.2. Synthesis of RuO₂ nanoparticles

Ruthenium dioxide nanoparticles were synthesized from RuCl₃.xH₂O by chemical method. In this process, RuCl₃.xH₂O (0.28 g) was first dissolved into appropriate quantities doubled distilled, deionized water. 2 ml of octanoic acid was added as a pro-surfactant. A 1.5 M solution of NaOH was dropped slowly in the solution to form precipitate and under constant stirring maintaining pH to about 8. The contents of the reaction were then heated to a temperature of 80°C. The reaction was maintained at 80°C under constant stirring for 1 hour. The reaction was cooled to room temperature. The precipitate formed was centrifuged and washed with deionized water till there was no trace of Cl ions in the filtrate and the filtrate became neutral. The neutral chloride free product was then washed with ethanol for several times. The precipitated solid was

dried in pre-heated oven at 100°C for 3 h and finally calcinated at 950°C for 4 h, Yield 90%, (Scheme 1).

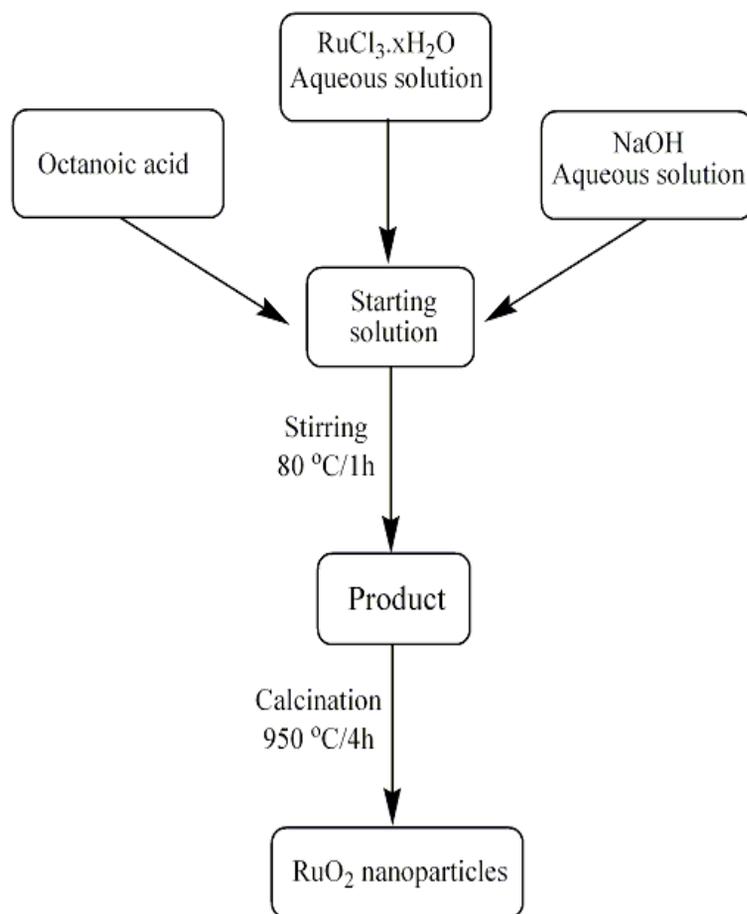
3. RESULTS AND DISCUSSION

Ruthenium dioxide nanoparticles were synthesized from RuCl₃.xH₂O by precipitation method in the presence of NaOH and octanoic acid. It is necessary to point out that the addition of NaOH solution has an important influence on the shape of the RuO₂ nanoparticles. It is assumed that when the NaOH solution was added drop-wise into the mixture solution, some small RuO₂ crystal nuclei was formed at the initial stage of the reaction. With the increase of the NaOH solution, the slowly produced RuO₂ crystallites grew along one growth direction on the basis of the initially formed RuO₂ crystal nuclei.

The shape and size of RuO₂ nanoparticles can be further tuned by adding small amounts of surfactants. The result demonstrates that the presence of small amounts of octanoic acid leads to the versatile shape of RuO₂ product. Also, the presence of octanoic acid led the particles to be well dispersed with no agglomeration, while much larger particles flocculating together were synthesized in the absent of octanoic acid. The use of a surfactant to control the morphological evolution of nanocrystals has been extensively explored. It is generally accepted that the surfactant kinetically controls the growth rates of various faces of nanocrystals by selective adsorption and desorption on these surfaces. The octanoic acid may adsorb into the fastest growth face of RuO₂ nanoparticles.

3.1. FT-IR spectroscopy

The vibration frequencies in the infrared spectrum of a molecule were considered to be a unique



Scheme 1: Synthesis of RuO₂ nanoparticles

physical property and it is common characteristic for almost every molecule. The FT-IR spectra of octanoic acid, product before heating in the furnace and RuO₂ nanoparticles are shown in Figure 1. As seen in Figure 1a, the broad bands in the region of 2600-3000 cm⁻¹ are due to the stretching vibration of OH groups in octanoic acid. The stretching vibration of C=O group can be seen in the region of 1712 cm⁻¹ and the absorption band in the region of 1459 cm⁻¹ is attributed to the bending vibration of CH₂ group. The FT-IR spectrum of the product before heating in the furnace is shown in Figure 1b. As can be clearly observed, all the peaks of the octanoic acid can be seen in FT-IR spectrum of the product but with less intensity and the little shift due to the interaction with the metal. It is demonstrated in Figure 1c that all above bands disappeared in the calcinated product. The characteristic bands of OH

groups also disappeared showing only strong bands due to the ruthenium oxide. The strong peak at 500 cm⁻¹ is due to the Ru-O vibrations, indicating formation of RuO₂.

3.2. X-ray diffraction

The crystal structure confirmation analysis was carried out by the X-ray diffraction patterns. The XRD patterns of RuO₂ nanoparticles have been displayed in Figure 2. The sharp intense peaks confirm the crystalline nature of the synthesized RuO₂ nanoparticles. The observed *d*-lines patterns for RuO₂ nanoparticles (observed plan diffractions: 110, 101, 200, 211, 220, 002, 310, 112, 301, 202) can be well indexed to the tetragonal RuO₂ (JCPDS Card Number 21-1172) with a main diffraction peak at *d* = 3.178 Å ((1 1 0) plane).

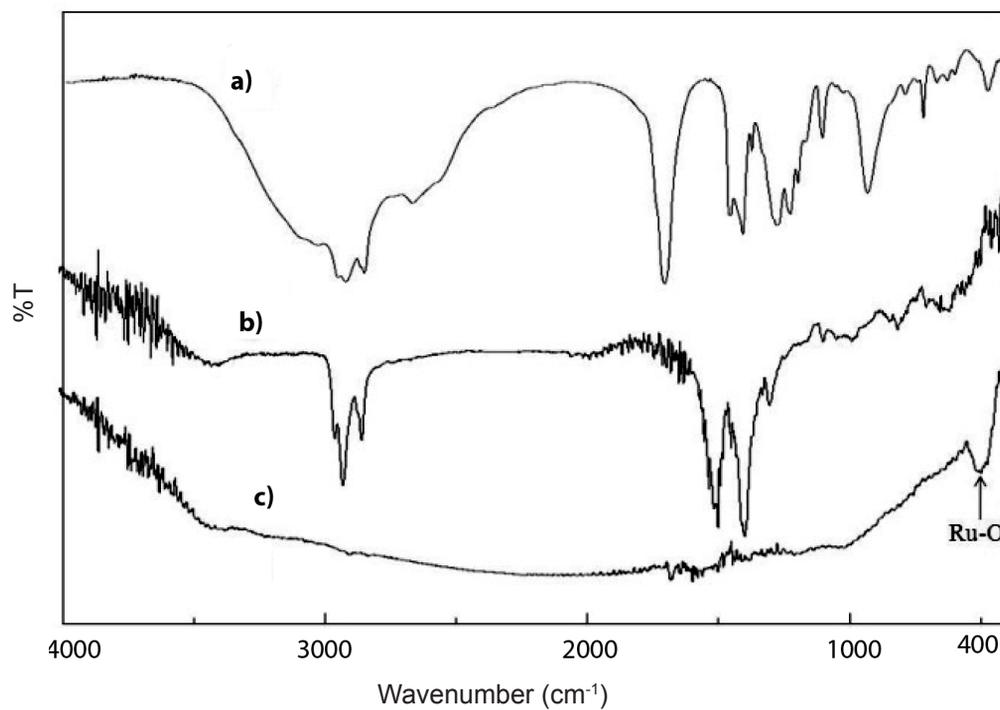


Figure 1: FT-IR of (a) surfactant, (b) product before heating in the furnace, (c) product after heating in the furnace.

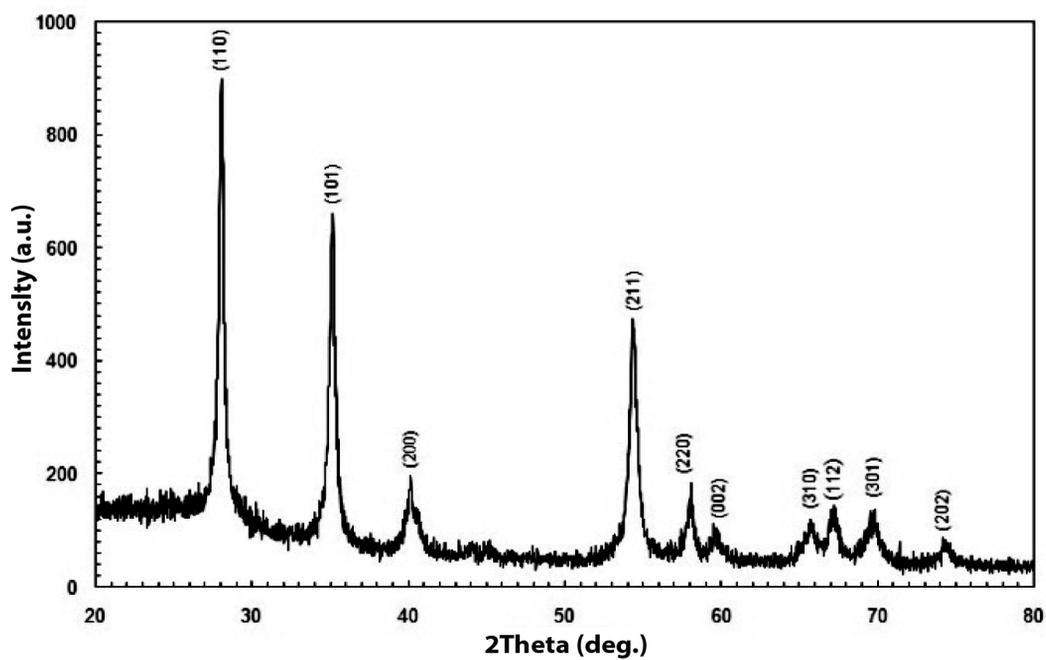


Figure 2: XRD pattern of RuO₂ nanoparticles by precipitation method.

The lattice parameters were calculated by equation (1):

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Where d is the distance between crystalline planes with Miller indices $(h\ k\ l)$, a and c are the lattice parameters. From this expression, it is evident that the position of two XRD peaks must be determined in order to assess the parameters of tetragonal structure. Peaks belonging only to one signal and with a significant diffracted intensity were selected, corresponding to crystalline planes indexed as $(1\ 1\ 0)$ and $(1\ 0\ 1)$. The lattice parameters for sample are reported in Table 1. These patterns are in good agreement with the literature values [9]. Also, the average crystallite size, d , was measured

from the XRD data based on Debye–Scherrer’s equation:

$$D_c = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

Where K is the shape factor, which usually takes a value about 0.9, λ is the wavelength of the X-rays (1.54056 Å), β is the full width at half maximum (FWHM) and θ is the diffraction angle. The average crystallite size of the RuO₂ nanoparticles is tabulated in Table 1. Also, for comparison, the particle size of RuO₂ prepared by several methods was reported in Table 2.

3.3. Surface morphology

Figure 3 represents the scanning electron micrograph of RuO₂ nanoparticles. This micrograph reveals that RuO₂ nanoparticles have uniformity in shape

Table 2: The comparison of particle size of RuO₂ prepared by several methods.

| Preparation method | Average particle size (nm) | Reference |
|-----------------------|----------------------------|-----------|
| Co-precipitation | 48 | This work |
| Thermal decomposition | 54 | 9 |
| Sol-gel | 15 | 11 |
| Microwave assisted | 23 | 12 |

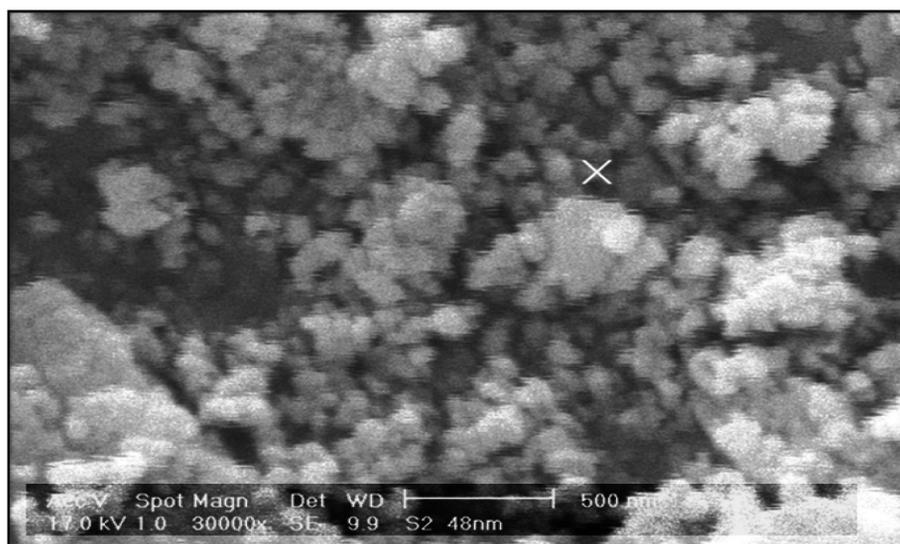


Figure 3. Scanning electron micrograph showing the morphology of RuO₂ nanoparticles prepared by co-precipitation method.

and size, also spherical shaped morphology have been observed for RuO₂ nanoparticles. Since the reaction was conducted under constant agitation the nanoparticles randomly aggregated to form almost spherical morphology.

4. CONCLUSIONS

The RuO₂ nanoparticles were successfully synthesized by precipitation process in the presence of sodium octanoate as surfactant. The pure phase (tetragonal) of RuO₂ has been obtained in this method and the particles have an average size in the nanoscale range about 50 nm. Morphology of the RuO₂ nanoparticles was sphere-like nanoparticles in this method. Co-precipitation method is convenient, environment friendly and low-cost method.

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