การสังเคราะห์ด้วยวิธีไฮโดรเทอร์มัลและสมบัติทางไฟฟ้าของ CeO_2 นาโนคลัสเตอร์

Hydrothermal Synthesis and Electrical Properties of CeO_2 Nanoclusters

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Received: Jul 09, 2023

Revised: Aug 05, 2023

Accepted: Aug 08, 2023

บทคัดย่อ

ในงานวิจัยนี้ใช้วิธีไฮโดรเทอร์มัลที่ไม่ซับซ้อนในการสังเคราะห์ซีเรียมออกไซด์ (CeO_2) นาโนคลัสเตอร์ที่อุณหภูมิต่างกันสองค่า โดยใช้ซีเรียมไนเตรตเฮกซะไฮเดรตเป็นสารตั้งต้นของซีเรียม ลักษณะทางสัณฐานวิทยาของซีเรียมออกไซด์นาโนคลัสเตอร์ที่สังเคราะห์ได้ถูกนำไปวิเคราะห์โดยเทคนิคกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดที่มีสมรรถนะสูงชนิดฟิลด์อีมิสชัน จากนั้นสารตัวอย่างถูกนำไปวิเคราะห์ด้วยรามานสเปกโทรสโกปี, สเปกโทรสโกปีของอนุภาคอิเล็กตรอนที่ถูกปลดปล่อยด้วยรังสีเอกซ์ และการเลี้ยวเบนของรังสีเอกซ์ สมบัติทางไฟฟ้าถูกวิเคราะห์โดยการศึกษากราฟความสัมพันธ์ระหว่างค่ากระแสไฟฟ้ากับแรงดันไฟฟ้า ผลการตรวจสอบแสดงให้เห็นว่าสามารถสังเคราะห์ซีเรียมออกไซด์นาโนคลัสเตอร์ภายใต้กระบวนการและเงื่อนไขเหล่านี้ได้

คำสำคัญ: ซีเรียมออกไซด์นาโนคลัสเตอร์ การสังเคราะห์ด้วยวิธีไฮโดรเทอร์มัล สมบัติทางไฟฟ้า

Abstract

In this research, the facile hydrothermal method was used to synthesize cerium oxide (CeO_2) nanoclusters at two different temperatures employing cerium nitrate hexahydrate as the initial cerium material. The morphology of the synthesized CeO_2 nanoclusters was characterized by Field emission scanning electron microscopy. The as-prepared products were examined utilizing Raman spectroscopy, X-ray photoemission spectroscopy and X-ray diffraction. The electrical properties were investigated by measuring the IV curves. The findings from all the examinations clearly indicated the successful synthesis of CeO_2 nanoclusters under the specified conditions.

Keywords: Cerium oxide nanoclusters, Hydrothermal synthesis, Electrical properties

1. Introduction

In the past few decades, metal and metal oxides nanostructures have drawn much attention due to their unique and excellent properties that different than bulk counterparts. It is also well known that shape, size, composition and morphology of nanostructures play an important role in physical, chemical and electronic properties of the materials. Cerium element is known for its abundance in the rare earth element family and its ability to release oxygen in Ce^{3+} to Ce^{4+} oxidation reaction [1].

Cerium oxide (CeO_2, Ceria) is one of the most active rare earth oxides with a wide band energy gap of 3.2 eV. It has been widely utilized in the fields of materials science, electrochemistry, catalysts,

optical devices, and energy storage [2]-[6]. Many approaches have been employed to synthesis nanosized CeO_2, for examples, sol-gel process, chemical vapor deposition (CVD), electrochemical deposition, microemulsion method, thermal decomposition and hydrothermal method [7]-[11]. However, the hydrothermal method is considered as one of the most effective and economical approaches because it can be done in one step and at low temperature [12]-[20]. The method offers good quality nanostructures in large amount. The synthesis can be done in an equipment called autoclave which is a corrosion-resistant metal cylinder with a thick wall. The disadvantages of the hydrothermal method include inability to observe nucleation and growth during the formation and the autoclave itself can be costly. It has been demonstrated that the properties of CeO_2 are related to different shapes, sizes and morphologies of CeO_2 [21]-[25]. In this work, CeO_2 nanoclusters were synthesized at two different temperatures. The nanoclusters were then characterized by several techniques to confirm the composition, morphology, and properties.

2. Materials and methods

A standard straightforward hydrothermal process was employed here in this work. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) was dissolved in 5 mL decanoic acid ($CH_3(CH_2)_8COOH$), 3 mL ammonia solution ($NH_3.H_2O$), 30 mL ethanol and deionized (DI) water. The mixture was stirred for 1 h. After that, it was poured in an alumina crucible and put in an aluminum autoclave. The alumina autoclave was placed in the oven chamber at temperature of 80°C for 52 h. After the alumina autoclave was cool down to room temperature, colloid gel was collected in a beaker and filled with 10 mL ethanol, then stirred for 10 min. The mixture was filled in the crucible then put back in the autoclave. The autoclave was placed in the furnace chamber with temperature set at 120°C for 12 h. The autoclave was taken out after the furnace cooled down to room temperature. The yellowish sediment was collected in a beaker in which 40 mL of DI water was added. After ultrasonication for 30 min, the sediment was filtered and stirred for 10 min with 40 mL of ethanol. The sediment was filtered again and stirred with 20 mL of acetone for 10 min. The yellowish sediment was filtered and dried in an oven at 60°C for 20 h. The sediment was separated and labelled as 2 samples. Sample 1 was heated at 120°C for 12 h and sample 2 was heated at 300°C for 6 h. After the furnace cooled down to room temperature, it was clearly seen that the sample 2 appeared more yellow than sample 1.

The morphology of the synthesized CeO_2 nanoclusters was characterized by Field emission scanning electron microscopy (FESEM). The synthesized products were examined by Raman spectroscopy, X-ray photoemission spectroscopy and X-ray diffraction. The electrical properties were investigated by measuring the IV curves.

3. Results and discussion

3.1. Field emission scanning electron microscopy

The surface morphology of the prepared samples was investigated by Field emission scanning electron microscope (FESEM). Figure 1 and Figure 2 are the images of the synthesized CeO_2 prepared at 120°C and 300°C respectively.

It was found that the materials were formed in agglomerated clusters and the conformations in both cases were similar. However, CeO_2 prepared at 300°C exhibited higher density, smaller cluster size and more uniformly formed compared to the one prepared at lower temperature.

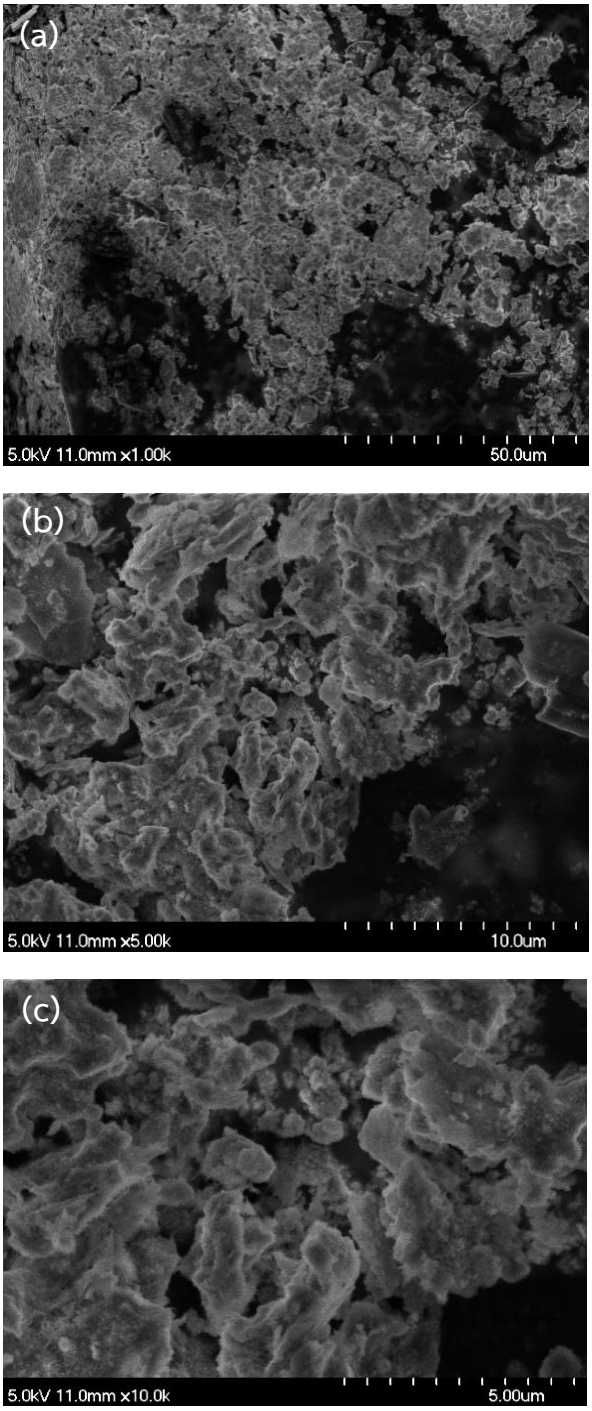

Figure 1 (a) to (c) FESEM images of CeO_2 prepared at 120°C at different magnifications

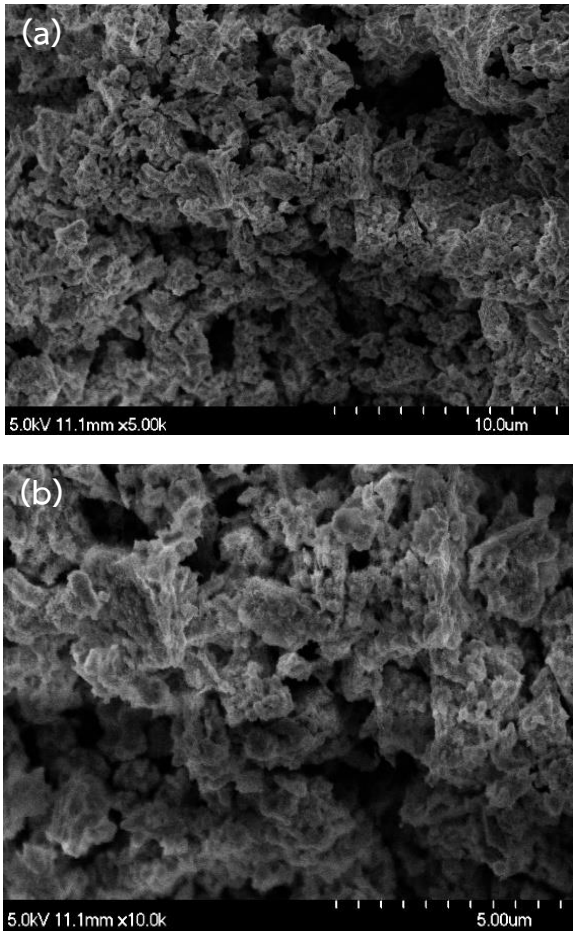

Figure 2 (a) and (b) FESEM images of CeO_2 prepared at 300°C at different magnifications

3.2. Raman spectroscopy

The sample prepared at 120°C exhibited multiple Raman shift peaks as seen in Figure 3(a). The most intense peaks were found at 462.92 cm^{-1} and 476.41 cm^{-1}. Additionally, peaks at ~ 246, 316, 391 and 622 cm^{-1} were also be observed. These peaks possibly attributed to short-range structural defects that took place during the synthesis.

The second sample prepared at 300°C exhibited a single peak at 462.92 cm^{-1} which was at the same location as the previous sample Figure 3(b) and 3(c). This peak is a confirmation of the CeO_2 cubic structure. The higher intensity reflects higher orderly organized structure of CeO_2. Moreover, no additional peaks were found indicating that CeO_2 prepared at higher temperature had less structural defects than that prepared at lower temperature.

3.3. X-ray photoelectron spectroscopy

Further investigation by X-ray photoelectron spectroscopy (XPS) was performed on the CeO_2 prepared by hydrothermal method at 300°C (sample 2). Figure 4(a) is the survey spectrum showing peaks corresponding to C1s, O1s and Ce3d structures. The result indicated that during the hydrothermal process, there was no other contaminants. No other elements were found except cerium.

Figure 4(b) shows multiple peaks from 875 to 925 eV binding energy. These peaks corresponded to different sub-orbitals in Ce3d structure. Raman spectroscopy and XPS results confirmed that the nanostructure was composed of Ce without any impurity and exhibited common characteristics of CeO_2.

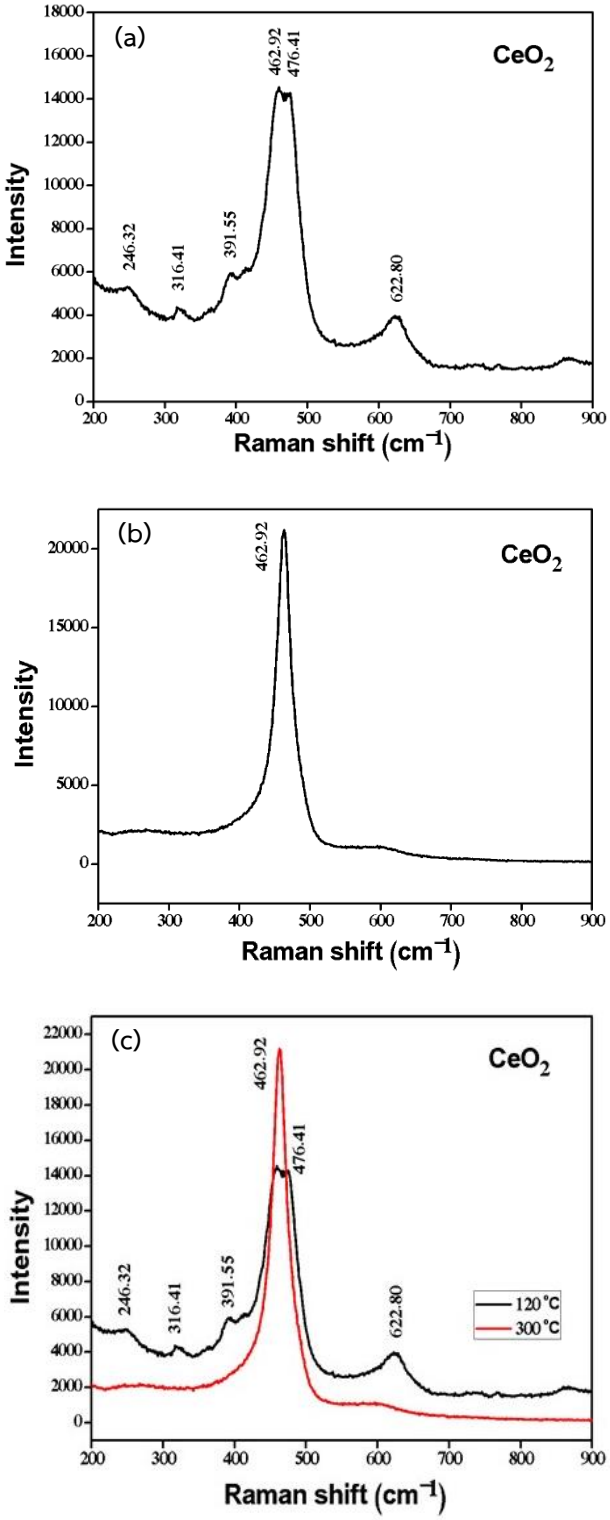

Figure 3 (a) and (b) Raman spectra of the CeO_2 samples prepared at 120°C and 300°C, respectively (c) Comparison of Raman spectra of the CeO_2 samples prepared at 120°C and 300°C

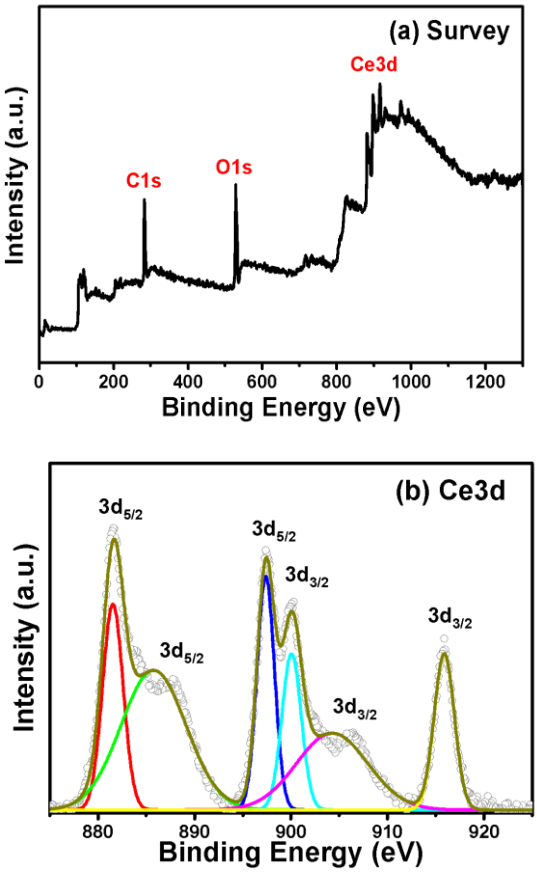

Figure 4 (a) and (b) XPS analysis of the CeO_2 sample prepared at 300°C

3.4. X-ray diffraction characterization

The crystal structure of CeO_2 nanoclusters prepared at 300°C was examined by X-ray diffraction (XRD) measurement. The most distinguished peak was at approximately 29° corresponding to (111) plane as shown in Figure 5. Crystal planes of (200) (220) (311) and (222) were also present in the X-ray diffractogram but not as intense as the first one. The XRD pattern of the sample was indexed to a face-centered cubic structure. This result is another confirmation that CeO_2 was successfully synthesized by the process.

3.5. IV curve measurements

To study electrical properties of the materials, both samples were put in an electric circuit at room temperature and under normal atmosphere. Voltages in an increment of 1V ranging from 0V to 15V were applied to the samples. Amount of current transferred according to each voltage value was recorded. The measurements were repeated after swapping the positive and negative terminals of the equipment. The voltage values were recorded as negative numbers, from 0V to -15V. Figure 6 shows IV characteristic curves of the samples. The current ranged from -0.06 to 0.05 mA. The curves were nonlinear indicating that the synthesized materials exhibited diode behavior. CeO_2 nanoclusters prepared at 300°C had higher value of current in the measurement window. Resistance of the samples could not be well determined as the diode materials had uncertain resistance values.

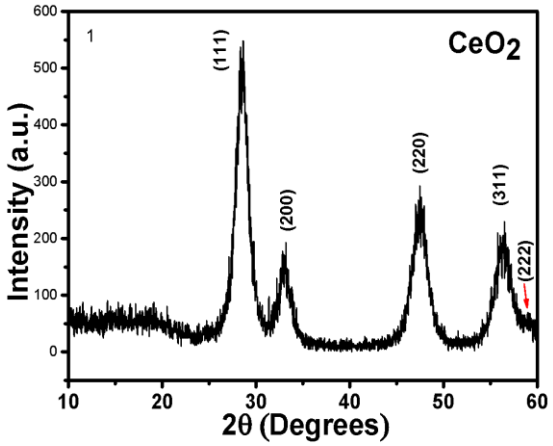

Figure 5 X-ray diffraction (XRD) measurement of the CeO_2 sample prepared at 300°C

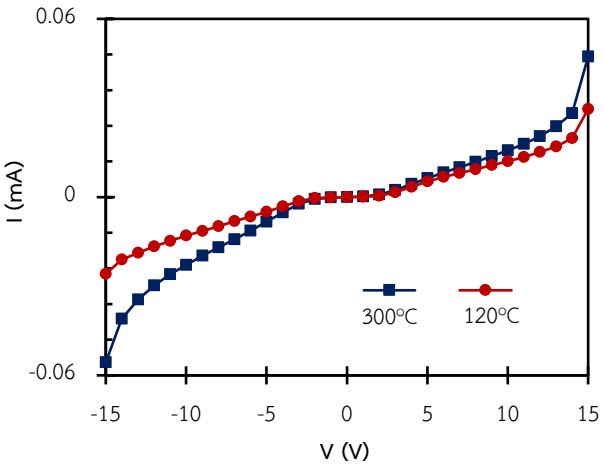

Figure 6 IV characteristic curves of the samples of the CeO_2 samples prepared at 120°C and 300°C

4. Conclusion

CeO_2 was successfully synthesized by a simple and low-cost hydrothermal method. The temperatures of 120°C and 300°C were applied in the process. The FESEM results showed that higher hydrothermal temperature resulted in denser formation of nanoclusters. Raman spectroscopy, XPS and XRD characterizations agreed that pure cubic CeO_2 was prepared. The IV characteristic measurements revealed the diode behavior of the materials. The method, therefore, can be used to synthesized contaminant-free CeO_2 for commercial applications such as polishing agents, catalysts and oxygen sensors.

5. References

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