Journal of Molecular Liquids 241 (2017) 772–781

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Controlled green synthesis and characterization of CeO_2 nanostructures as materials for the determination of ascorbic acid

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ARTICLE INFO

Article history:
Received 26 March 2017
Received in revised form 12 June 2017
Accepted 16 June 2017
Available online 20 June 2017

Keywords:
CeO_2
Nanostructures
Hydrothermal
Mesoporous
Ascorbic acid
Electrochemical sensors

ABSTRACT

In this work, we studied a new sensor to determine the ascorbic acid (AA) based on CeO_2 nanostructures and multi-walled carbon nanotube on the pencil graphite electrode. For this purpose, different morphologies of CeO_2 nanostructures were synthesized via a simple hydrothermal method and their applications in the biosensors were investigated. Different parameters such as capping agent kind, hydrothermal time, and temperature on the product size and morphology were studied. The products were characterized via different analysis such as X-ray diffraction pattern (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Photoluminescence (PL), Fourier transform infrared (FT-IR), N2 adsorption (BET) and Cyclic Voltammetry (CV). The results showed that each parameter has a significant effect on the product size and morphology. This method showed appropriate responses to a trace amount of AA and the limit of detection was found to be 8 nmol L^{-1} for AA.

1. Introduction

Cerium (IV) oxide nanostructure have been the subject of many studies due to their great potential in various fields of applications like electrochemical devices, catalysis, optoelectronics, environmentally friendly pigments, catalysis, microelectronics, gas sensors, gamma radiation dosimetry, biocompatibility, hybrid solar cells, H_2S removal [1–4], using as an inorganic UV filter in sunscreens [5]. Also, the antioxidants properties of Ceria make it a promising biomaterial [6]. CeO_2 has high oxygen storage capacity and high oxygen mobility due to the variation of the oxidation state of cerium between +3 and +4, under different reductive or oxidizing conditions. For example, the catalytic activity of CeO_2 structures is relevant to their capability of providing adsorbent oxygen species at their surfaces and simple extraction of their lattice oxygen forming oxygen vacancies [7–10]. Furthermore, the particle morphology has also an important role in the catalyst activity. Also, CeO_2 nanoparticles have received substantial attention due to their unique properties in the development of biosensors. CeO_2 nanostructures have a high isoelectric point (IEP) of 9.2 at pH 7.0. It may be that positively charged surface of nano-CeO_2 can be employed for binding of negatively charged biosensing molecules. In addition, high chemical stability, high electron transfer capability, and non-toxicity make cerium oxide a promising material for immobilization of desired biomolecules. Mehta et al. fabricated a novel multivalent CeO_2 based hydrogen peroxide biosensor for application as a 3-terminal amperometric sensor [11]. Feng et al. have reported a nanoporous CeO_2/chitosan composite for immobilization of single-stranded DNA probe for tracing of cancer gene [12]. Crystalline CeO_2 nanoparticles have been synthesized in a wide range of synthesis techniques such as ultrasonication [11], phase transformation [12], hydrothermal [13], the solid state reaction method [14], surfactant-assisted [15], liquid–liquid interface [16], sol-gel method [17], thermal decompose method [18], and co-precipitation [19]. These approaches are mainly based on salt-solvent mediated high temperature, or high pressure, or surface capping agent. CeO_2 nanostructures have unique properties like UV absorbing ability [20], facile electrical conductivity, diffusivity, quick and expedient mutation of the oxidation state of cerium between Ce (III) and Ce (IV) [21], high hardness, specific chemical reactivity [22], high thermal stability [23], ability to store and transport oxygen as large oxygen storage capacity [24] and high refractive index. The activity of cerium (IV) oxide has been explained on the basis of its capability to store and mobility oxygen. In this paper, we reported a Hydrothermal method for the prepare of CeO_2 nanoparticles using the cerium salts and investigated the effect of different temperatures, reaction times and capping agents on the product size and morphology. The hydrothermal method has been regarded as one of the effective routes due to one step low-temperature synthesis, shape control, and powder reactivity. The obtained nanoparticles were utilized as modified electrode in the electrochemical measurement of ascorbic acid (AA). Ascorbic acid is another molecule of

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http://dx.doi.org/10.1016/j.molliq.2017.06.078
0167-7322/

Table 1
Samples preparation conditions.

Sample no.	Capping agent	Time (h)	Temperature (°C)
1	–	12	100
1	Glucose	12	100
2	Glucose	12	140
3	Glucose	12	180
4	Fructose	12	100
5	Fructose	12	140
6	Fructose	12	180
7	Fructose	24	180
8	Lactose	12	180
9	Gelatin	12	180

biological importance and necessary for human health that found in many fruits. Ascorbic acid used as a cofactor in various enzymatic reactions and plays an important role in metabolic reactions of both human and animals. It is a completely natural combination with antioxidant properties, essential in immunity development and cancer prevention. Ascorbic acid deficiency is associated with cardiovascular diseases, cancer, Parkinson's disease and severe symptoms of scurvy. Therefore, detection of ascorbic acid is essential in pharmaceutical, clinical and food industry. Therefore, our main objective in this work is the production of CeO_2 nanoparticles by hydrothermal method and investigation the effect of CeO_2 nanoparticles to determine the ascorbic acid (AA). Also the other novelty of this work is investigation of different parameters such as hydrothermal time and temperature, capping agent and etc. on the product size and morphology. We have introduced a new sensor to determine the ascorbic acid. Based on our knowledge, this is the first work that used carbohydrate sugars as capping agent for synthesis of the CeO_2 nanoparticles.

2. Experimental

2.1. Materials and physical measurements

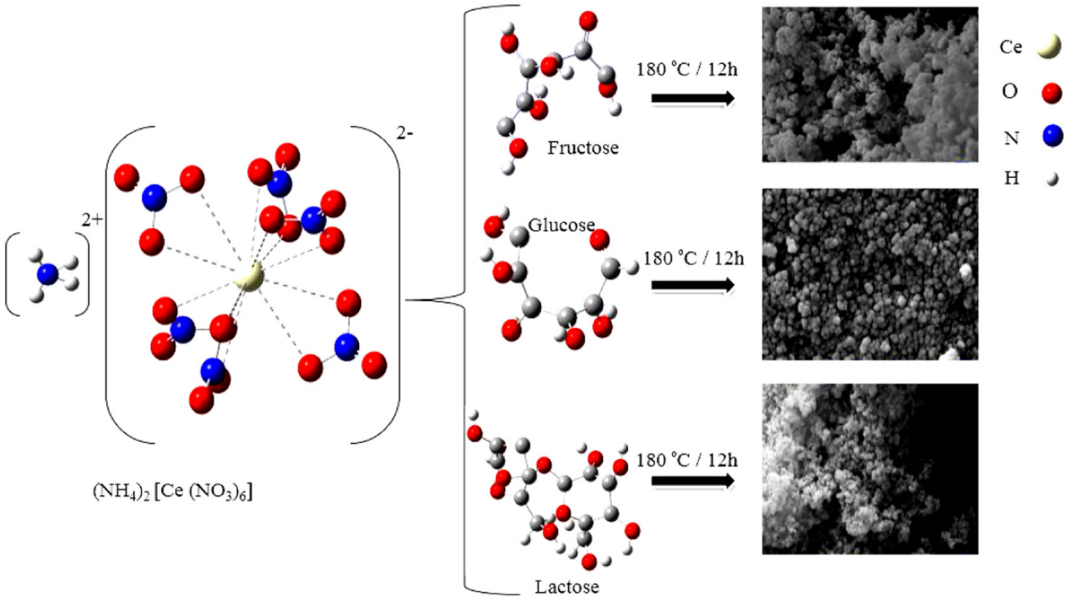
All the materials were of analytical grade purity and were used without further purification. In this investigation, $Ce(NO_3)_6(NH_4)_2$ (ammonium cerium(IV) nitrate) as Cerium precursor, Gelatin, Glucose, Lactose and Fructose as capping agent, and Sodium hydroxide as alkaline agent were purchased from Merck and were used. Also, distilled water was used for all the experiments. Product physicochemical properties were investigated by the XRD patterns were recorded via a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation, SEM (scanning electron microscopy) images were taken by on Philips XL-30ESEM equipped with an energy dispersive X-ray (EDX), TEM (Transmission electron microscopy) image was obtained on a Philips EM208 transmission electron microscope via an accelerating voltage of 200 kV equipped with a high resolution CCD Camera and FT-IR (Fourier transform infrared) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Also, the specific surface area was investigated via the BET method using N_2 adsorption at −196 °C (Tristar 3020, Micromeritics).

2.2. Preparation of the CeO_2 nanoparticles

To obtain CeO_2 nanoparticles by the hydrothermal route, a certain amount of ammonium cerium (IV) nitrate solution was added to the fructose solution. After the magnetic stirring for 20 min, sodium hydroxide solution was added to the mixed solution and pH value was adjusted to 11. Thereafter, the mixture was placed into a Teflon-lined stainless-steel autoclave for 12 h at 180 °C. The obtained precipitates were collected via centrifuged and washed via distilled water and methanol for several times, air-dried and then calcined at 500 °C for 2 h. Reaction conditions with details are shown in Table 1. The reactions pathway is shown in Scheme 1.

2.3. Preparation of the CeO_2NPs/MWCNT/PGE

Prior to the voltammetric measurements, the dissolved oxygen was removed from all solutions with pure nitrogen gas for 15 min. We modified electrode by synthesized CeO_2NPs with purified MWCNT (puMWCNT) in order to increase sensitivity in the electrochemical measurement of ascorbic acid (AA). So, the stable suspension mixture of puMWCNTs and CeO_2NPs was obtained by ultrasonication of puMWCNTs and CeO_2NPs in tetrahydrofuran (THF) solution (dispersion of 2.0 mg puMWCNTs and 2.0 mg CeO_2 nanostructures together in 4.0 mL of THF). A pencil graphite electrode (PGE) was further polished with 0.05 mm alumina powder on a polishing microcloth for several minutes. Then, it was cleaned in water and then in an ethanol/water solution (50%, v/v) in the ultrasonic bath and rinsed thoroughly with double



Scheme 1. Formation mechanism of CeO_2 nanostructures in the presence of various capping agent.