Electrospinning of decorated nanofibers with active cerium oxide nanoparticles

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ABSTRACT

Cerium oxide nanoparticles (ceria NPs) attract a great research and commercial interests due to its observable capability to capture radicals and dissolved oxygen molecules. Keeping ceria NPs in active form; containing Ce^{+3} ions with O-vacancies, is a big challenge to be fitted into wide variety of applications such as free radical scavengers in bio-medicine, bacteria filters in water waste treatment, and oxygen sensing in environmental monitoring. This novel work presents active ceria NPs on nanofibers host. It is suggested to decorate the surface of electrospun nanofibers of PVA and PEO, as host media, with the active ceria NPs. To achieve this aim, PVA and PEO nanofibers containing active ceria NPs were electrospun by a conventional needle electrospinning and Nanospider machine for producing commercial scale nanofibers. SEM image shows that the ceria NPs are successfully located at the surface of nanofibers. Optical characterizations, absorbance spectroscopy and band gap measurements, show that there is reasonable activity of ceria NPs after electrospinning. Therefore, it is concluded that there is a possibility to host active ceria NPs over the electrospun nanofibers which can be helpful for different applications in green chemistry and Materials.

Keywords: ceria nanoparticles, electrospinning, nanofibers, oxygen vacancies.

1 INTRODUCTION

Cerium oxide nanoparticles (ceria NPs) attract a great research and commercial interests due to its observable capability to capture radicals and dissolved oxygen [1,2].These promising properties are applicable in many applications related to medical, environmental, and sustainable energy fields [3]. Depending on the oxidation state of cerium ions, ceria could exist in two forms: active with associated charged oxygen vacancies (Ce^{+3}) and non-active with no formed O-vacancies (Ce^{+4}) [4]. The formed O-vacancies act as probes to scavenge some charged objects such as radicals and dissolved [1,5]. The conversion of solid oxide from lower oxidation state (Ce^{+3}) to a higher one (Ce^{+4}) occurs in a fast manner while the opposite reaction is hard to happen [6]. Therefore, it is challenge to keep ceria NPs in active form; containing Ce^{+3} ions, to be fitted into the mentioned applications.

In this novel work, we aim to produce active ceria NPs in nanofibers host. In a research work done by Xinghua Yang et.al., it is showed that the ceria formed on the nanofibers has non-active form (Ce^{+4}; CeO_2) [7]. However, this paper suggests the surface decoration of electrospun nanofibers made from poly-vinyl alchohol (PVA) and poly-ethylene oxide (PEO) as host media, with the active ceria NPs. PVA and PEO polymers are considered one of the well known polymers as a non-toxic biodegradable water soluble polymer [8–10]. These important characters make them feasible for many applications as in nano-agriculture, tissue engineering and biomedical applications [11,12]. To achieve this aim, PVA and PEO nanofibers containing active ceria NPs are electrospun by a conventional needle electrospinning for lab scale, and Nanospider machine from Elmarco Inc. for producing commercial scale nanofibers. The electrospinning conditions are controlled to keep the ceria NPs in active form within all processing steps starting from polymer solution preparation up to electrospinning process.

2 EXPERIMENTAL PROCEDURE

2.1 Nanoparticles synthesis

Undoped ceria nanoparticles are prepared using a modification of a chemical precipitation technique documented in [13]. First, 0.5 gm of cerium (III) chloride heptahydrate, (99.9%, Aldrich Chemicals) is added in 40 mL of de-ionized water. The solution is stirred at rate of 500 rpm during the 24 hour synthesis process. After the reagents have dissolved, the solution is heated to 50 °C in a hot water bath. After stirring for approximately 60 seconds to ensure that the solution is homogenous, 1.6 mL of ammonia (30%) is added to the solution. The ammonia immediately reacts with the cerium chloride to form cerium hydroxide nanorods. The color of the nanorods in solution is initially a pale purple and, over a period of an hour, the solution turns into yellowish in color; indicating the

formation of $Ce(OH)_3$ nanoparticles. In an atmosphere of air and with continued heating, the dispersion of nanoparticles turn into white color, indicating that the $Ce(OH)_3$ has converted to CeO_2. The heating stage is important because it helps in the conversion of $Ce(OH)_3$ to CeO_2 (Ce^{+4} ions) and then to Ce_2O_3 (Ce^{+3} ions) [14]. However, the synthesis temperature is not high to prevent the agglomeration of the nanoparticles. The continuously stirred solution is kept in the heated water bath for a total of 1.5 hours. In the second stage of the synthesis process, the temperature of the water bath is allowed to cool and the solution is stirred for additional 22.5 hours in room temperature. The long period of stirring fractures any remaining nanorods into small, relatively spherical nanoparticles. The solution is then centrifuged, washed with de-ionized water and ethanol twice to remove any unreacted cerium chloride and ammonia. Between centrifuging, the solution is sonicated to break apart the ceria nanoparticle agglomerates.

2.2 Polymers preparation

PVA and PEO solutions of weight concentration 13 wt% and 8%, respectively, are prepared by mixing 13 g PVA with 87 mL of distilled water or 8 g PEO with 92 mL of water. Both solutions are containing 0.03 g of the synthesized cerium oxide overnight. After that the polymer solution containing cerium oxide nanoparticles is electrospun without any further modifications.

2.3 Nanofibers electrospinning

The electrospinning setup shown in Figure 1, consists of two high voltage power supplies, a syringe pump (New Era Pump, Inc. model NE-300), a 10 mL plastic syringe with 18 gauge metallic needle and a metallic target covered with aluminum foil. The first voltage power supply (single polarity, Gamma High Voltage Research, Inc. model ES40) is connected to the needle, while the second one (dual polarity, Spellman High Voltage Electronics Corporation model CZE1000R) is connected to the target. The distance between the needle tip and the target is fixed at 15 cm. The difference in voltage between the needle and target is selected at 25 kV. The flow rate of the polymer solution supplied to the syringe is fixed at 1 mL/hr. The polarities of the two voltage generators are controlled to guide the polymer jet aroused from the needle directly towards the target. The samples are collected on a flat metallic surface covered with aluminum foil. The deposition of electrospun fibers is run for 30 minutes.

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2.4 Characterization

The decorated nanofibers with embedded nanoparticles are characterized through measuring optical absorbance dispersion curves. Spectra are collected from 300 nm to 800 nm using Shimadzu UV-3101PC UV-Vis-NIR spectrometer. The dimensions of the electrospun fibers are characterized using a Zeiss LEO 1550 field emission scanning electron microscopy (FESEM) to determine the morphology of the fiber web and the diameter and homogeneity of the individual fibers. The fiber diameters are measured by Image-J software

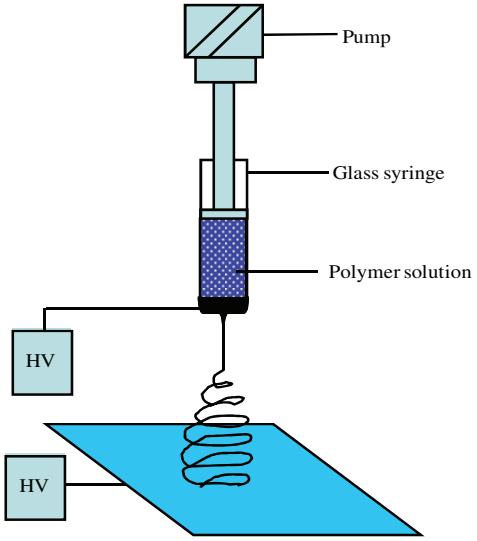

Figure 1: Needle electrospinning setup

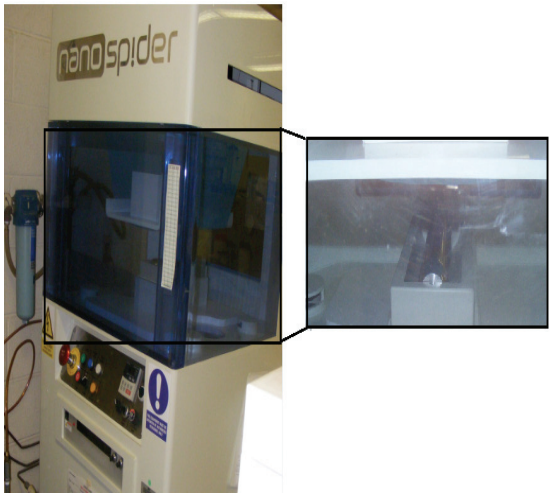

Figure 2: Nanospider machine for commercial scale of electrospun nanofibers

3 RESULTS & DISUCCIONS

SEM image, Fig.3, shows that the synthesized ceria NPs are successfully located on the surface of nanofibers, as pointed by the arrows in the SEM image. The mean diameter of the nanofibers is found to be around 300 nm. The mean grain size of ceria nanoparticles, over the nanofibers surface, is measured to be approximately 60 nm .

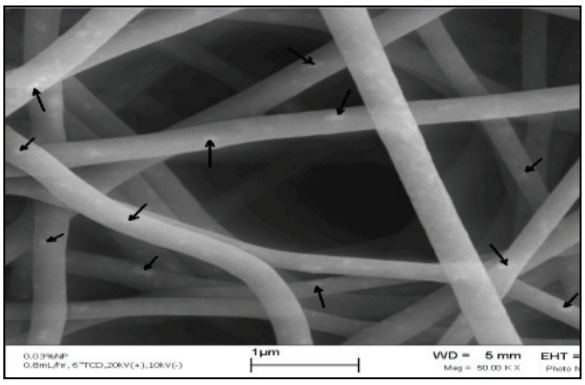

Fig.3: SEM image of electrospun PVA nanofibers embedded with ceria NPs.

The absorbance dispersion obtained from the formed nanofibers is shown in Figure 4a. Based on the absorbance measurements, the allowed optical direct bandgap of the decorated ceria on the electrospun fibers can be calculated using the following equation [15]

$$\alpha(E) = A(E - E_g)^{1/2} \qquad (1)$$

where α is the absorbance coefficient, A is a constant that depends on the effective masses of electrons and holes in the material, E is the absorbed photon energy, and E_g is the allowed direct bandgap. In Fig. 4b, $(\alpha E)^2$ versus E is plotted. The intersection of the extrapolation of the linear portion of the $(\alpha E)^2$ curve with x-axis is equal to the allowed direct bandgap that particular composition of ceria nanoparticles.

The measured The band gap measurements, in Fig.4b, show that there is reasonable activity of ceria NPs after electrospinning. In more details, the bandgaps of both cerium ionization states are reported to be 3eV for Ce^{+3}; Ce_2O_3, and 4eV for Ce^{+4}; CeO_2 [16]. As shown in Fig. 4b, the bandgap of ceria NPs is found to be 3.46 eV, which is intermediate between both bandgaps of both cerium ionization states which indicates that there are already formed active Ce^{+3} states on the electrospun fibers [4,17]. PEO nanofibers with ceria show exactly the same absorbance and bandgap curves obtained from PVA nanofibers. Both polymers have no impact on the activity of ceria nanoparticles on their surfaces.
Our experimental work shows also that there is a possibility to integrate PVA/PEO solutions with ceria nanoparticles into Nanospider machine suggesting that there is a good opportunity to scale up the process into pilot and industrial scales. Same characterizations are obtained whatever using needle electrospinning setup or needless electrospinning Nanospider facility. Nanospider offers the scaling-up of the obtained electrospun fibers with rate of generation up to 1-3.5 m²/min.

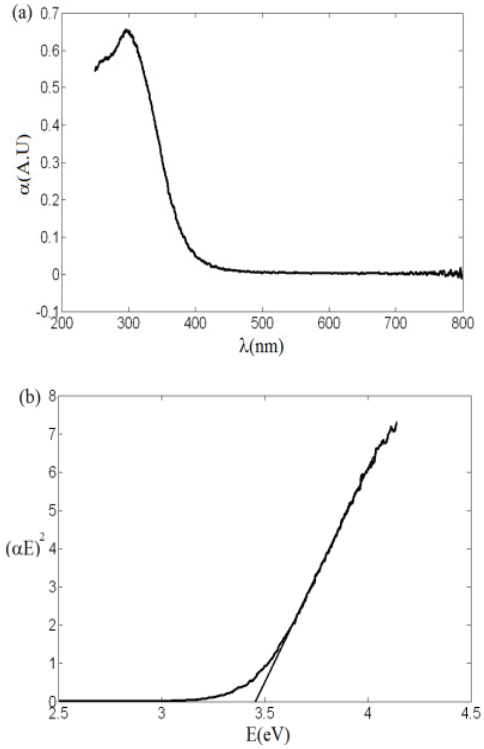

Fig.4: optical characterization of ceria NPs in nanofibers: a) absorbance dispersion and b) allowed direct bandgap calculation.

4 CONCLUSIONS

Therefore, it can be concluded that there is a possibility to host active ceria NPs over the electrospun nanofibers. That can be helpful in wide variety of applications such as free radical scavengers in bio-medicine, bacteria filters in water waste treatment, and oxygen sensing in environmental monitoring.

REFERENCES

[1] B.A. Rzigalinsk, K. Meehan, R.M. Davis, Y. Xu, C.A. Cohen, Radical Nanomedicine, Nanomedicine. 1 (2006) 300–412.

[2] N. Shehata, K. Meehan, D. Leber, Fluorescence Quenching in Ceria Nanoparticles: Dissolved Oxygen Molecular Probe with Relatively Temperature Insensitive Stern–Volmer Constant Up to 50°C, Journal of Nanophotonics. 6 (2012) 1–11.

[3] O.S. Wolfbeis, Fiber Optic Chemical Sensors and Biosensors, CRC Press, Boca Raton, 1991.

[4] N. Shehata, K. Meehan, M. Hudait, N. Jain, Control of Oxygen Vacancies and Ce^{+3} Concentrations in Doped Ceria Nanoparticles via The Selection of

Lanthanide Element, Journal of Nanoparticle Research. 14 (2012) 1173–1182.

[5] N. Shehata, K. Meehan, D. Leber, Dissolved Oxygen Sensing Using Fluorescence Quenching of Ceria Nanoparticles, in: SPIE Nanoengineering and Photonics Conference, Nanoengineering: Fabrication, Properties, Optics, and Devices IX, San Diego, CA, 2012: pp. 1–9.

[6] G.R. Rao, B.G. Mishra, Structural, Redox and Catalytic Chemistry of Ceria Based Materials, Bulletin of the Catalysis Society of India. 2 (2003) 122–134.

[7] X. Yang, C. Shao, Y. Liu, R. Mu, H. Guan, Nanofibers of CeO2 via an Electrospinning Technique, Thin Solid Films. 478 (2005) 228–231.

[8] S. Matsumura, Y. Shimura, K. Terayama, T. Kiyohara, Effects of Molecular Weight and Stereoregularity on Biodegradation of Poly(Vinyl Alcohol) by Alcaligenes Faecalis, Biotechnology Letters. 16 (1994) 1205–1210.

[9] T. Mori, M. Sakimoto, T. Kagi, T. Sakai, Isolation and Characterization of a Strain of Bacillus Megaterium That Degrades Poly(vinyl alcohol), Bioscience, Biotechnology and Biochemistry. 60 (1996) 330–332.

[10] A. Zgoła-Grześkowiak, T. Grześkowiak, J. Zembrzuska, Z. Łukaszewski, Comparison of Biodegradation of Poly(ethylene glycol)s and Poly(propylene glycol)s, Chemosphere. 64 (2006) 803–809.

[11] K. Nakamiya, Toshihiko, S. Kinoshita, Degradation of Synthetic Water-Soluble Hydroquinone Peroxidase, Journal of Fermentation and Bioengineering. 84 (1997) 213–218.

[12] S. Matsumura, H. Kurita, H. Shimokobe, Anaerobic Biodegradability of Polyvinyl Alcohol, Biotechnology Letters. 15 (1993) 749–754.

[13] H.-I. Chen, H.-Y. Chang, Homogeneous Precipitation of Cerium Dioxide Nanoparticles in Alcohol/Water Mixed Solvents, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 242 (2004) 61–69.

[14] N.J. Lawrence, K. Jiang, C.L. Cheung, Formation of a Porous Cerium Oxide Membrane by Anodization., Chemical Communications (Cambridge, England). 47 (2011) 2703–2705.

[15] J. Pankov, Optical Process of Semi Conductor, Dover Publication Inc., New York, 1971.

[16] P. Patsalas, S. Logothetidis, Structure-Dependent Electronic Properties of Nanocrystalline Cerium Oxide Films, Physical Review B. 68 (2003) 1–13.

[17] A.N. Shmyreva, A. V. Borisov, N. V. Maksimchuk, Electronic Sensors Built on Nanostructured Cerium Oxide Films, Nanotechnologies in Russia. 5 (2010) 382–389.