The precipitation synthesis of broad-spectrum UV absorber nanoceria

by Iis Nurhasanah

RESEARCH ARTICLE | SEPTEMBER 09 2013

The precipitation synthesis of broad-spectrum UV absorber nanoceria

Iis Nurhasanah; Heri Sutanto; Nurul Wahyu Puspaningrum

AIP Conference Proceedings 1554, 54–57 (2013)
https://doi.org/10.1063/1.4820282

The Precipitation Synthesis of Broad-spectrum UV Absorber Nanoceria

Iis Nurhasanah*, Heri Sutanto and Nurul Wahyu Puspaningrum

Department of Physics, Faculty of Science and Mathematics, Universitas Diponegoro
Jl. Prof. Soedarto, S.H, Tembalang Semarang 50275, Indonesia
*iisphysics@gmail.com

Abstract. In this paper the possibility of nanoceria as broad-spectrum UV absorber was evaluated. Nanoceria were synthesized by precipitation process from cerium nitrate solution and ammonium hydroxide as precipitant agent. Isopropanol was mixed with water as solvent to prevent hard agglomeration. The structure of resulting nanoceria was characterized by x-ray diffractometer (XRD). The transparency in the visible light and efficiency of protection in UV A region were studied using ultraviolet-visible (UV – Vis) spectrophotometer. The results show that nanoceria possess good tranparency in visible light and high UV light absorption. The critical absorption wavelenght of 368 nm was obtained which is desirable for excellent broad-spectrum protection absorbers. Moreover, analysis of photodegradation nanoceria to methylene blue solution shows poor photocatalytic activity. It indicates that nanoceria suitable for used as UV absorber in personal care products.

Keywords: Nanoceria, Optical properties, UV absorbers, Precipitation.
PACS: 78.67.Bf

INTRODUCTION

The ultraviolet (UV) radiation reaching the earth surface consists of UV B (290 nm – 320 nm) for about 1 – 10 % and 90 % of UV A (320 – 400 nm), while UV C (100 – 290 nm) is totally absorbed by atmospheric ozone. It is well known, that excessive exposure to UV radiation in sunlight causes harmful damage to human body such as aging of skin, skin cancer and cataract. In line with an increased understanding of damage cause by UVA radiation, the protection of skin from UV radiation has been great concern. FDA recommends for protection skin by applying sunscreen which contains broad spectrum UV absorbers to provide high protective in both UV A and UV B range. The efficiency of protection in UV A region is determined by critical wavelength (λ_c). The critical wavelength of 370 nm or greater is classified as excellent broad-spectrum protection [1].

Curently, ultrafine TiO_2 and ZnO are the main compound widely used as inorganic UV absorber in sunscreen cosmetics. However, sunscreen cosmetics incorporating TiO_2/ZnO nanoparticle give the skin an unnatural pale white look because high refractive index. In addition, TiO_2/ZnO shows high photocatalytic activity. Under UV light irradiation, that compound present catalysing the formation of superoxide and hydroxyl radicals. Those radicals not only can initiate oxidation and degradation other ingredients in the formulation but also can damage DNA of skin cells. Such photo-oxidation raising safety concern in the toxicity of illuminated TiO_2/ZnO [2].

Nanoceria more prominent as broad spectrum UV absorbers for cosmetics due to wide band gap of 3,2 eV, lower refractive index is relatively transparent to visible light, and the photocatalytic activity is lower than that of TiO_2/ZnO [3-5]. Moreover, nanoceria shows ability to serve as free-radical scavenger or antioxidant to protection of normal cell from radiation-induced cell damage. Therefore, nanoceria is non-toxic, biocompatible and safety for used as personal care product [6,7].

In the present study, we investigate the possibility of nanoceria as broad-spectrum UV absorbers with low photocatalytic activity and safer than that of TiO_2/ZnO nanoparticle. Nanoceria was synthesized by precipitation process in water/isopropanol mixed solvent. Since, the nanomaterials exhibit size-dependent optical properties, therefore the pH precipitaion process was adjusted to controll particle size. The efficiency of protection in UV A region and photocatalytic properties of that nanoceria were studied.

Padjadjaran International Physics Symposium 2013 (PIPS-2013)
AIP Conf. Proc. 1554, 54-57 (2013); doi: 10.1063/1.4820282

EXPERIMENTAL

Precipitation process was carried out by adding 3M Ammonium hydroxide solution to 0.08 M solution of cerium nitrate under stirring and controlling pH of 7 and 10. The resulting precipitate washed three time with water and finally isopropanol. The precipitate was then dried at 60°C and followed by calcination at 300°C for 2 hours in air atmosphere.

Crystal structure of as-precipitated samples was characterized by X-ray diffraction (XRD, Phillips PW 1710) using Cu Kα radiation (λ = 1.54056 A). The samples were analyzed in the 2θ range 20 – 90°. According to full width half-maximum (FWHM) of all observed diffraction peaks, the average crystallite size was estimated by Scherrer equation. Optical transmission response was investigated by UV-vis spectrophotometer (Agilent 8453) in the range of 200-800 nm using quartz cells 1 cm in length. The samples were dispersed in methanol at a concentration of 0.2 g/L by ultrasonication for 5 min. Photocatalytic activity was studied through photodegradation of 10 ppm methylene blue (MB) solution under sunlight irradiation for 120 min. Absorbance of the sample was measured to evaluate the appearance photodegradation.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of samples is shown in Fig. 1. The main diffraction peaks were observed corresponding to (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes. All the peaks can be identified as ceria with fluorite structure (JCPDS card no.43-0394). The broadening of diffraction peaks for both samples indicates that small nanocrystals are present in the samples. Crystallite sizes obtained from Scherrer equation as expressed by Eq. (1) are to be 8.3 nm and 9.7 nm for sample prepared at pH 7 and 10, respectively. The sample prepared at pH 10 shows higher intensity and sharper diffraction peaks than that prepared at pH 7 indicating higher crystallinity. There is correlation between crystallinity and crystallite size, crystallinity is reduced as crystallite size decreases.

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where, k = 0,89 (for spherical nanoparticle), β is full width half-maximum (FWHM), λ is wavelenght of x-ray irradiation and θ is diffraction angle.

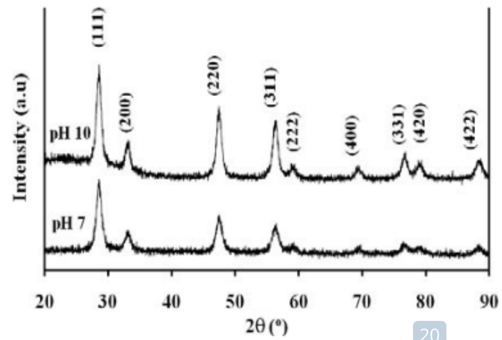

FIGURE 1. Diffraction pattern of the samples prepared at pH 7 and 10.

The UV-Vis transmittance spectra of nanoceria is depicted in Fig. 2. The spectra exhibits the low transparency below 400 nm and relatively transparent in the visible light region. The transparency of nanoceria prepared at pH 7 is lower than that of nanoceria prepared at pH 10. It means that precipitation process at pH 7 results in nanoceria with stronger UV absorption. Since the optical properties of nanoparticle related to particle size and agglomeration behaviour of particle, therefore the low transparency of that nanoceria might be caused by agglomeration of small primary crystallite forming large particle. There is relation between particle size and effective band gap of nanoparticle, where the band gap increases with decreasing particle size as described in Eq. (2).

$$E_{g,n} = E_{g,b} + \frac{h^2}{8R^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] - \frac{1.8e^2}{\varepsilon R} \qquad (2)$$

where, $E_{g,b}$ is the bulk band gap (3,19 eV), R is radius particle, m_e* and m_h* are the effective mass of the electron and hole, respectively with $m_e^* = m_h^* = 0,4\ m_o$, where m_o is the mass of free electron, h is Planck's constant, ε is the bulk optical dielectric constant.

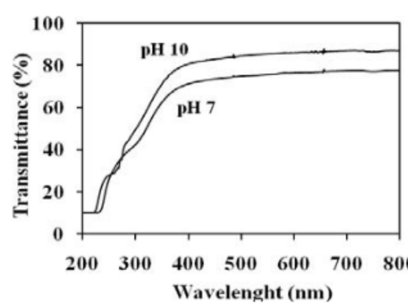

FIGURE 2. UV-Vis transmittance spectra of nanoceria.

The direct band gap of nanoceria was obtained by fitting the absorption data to the direct transition equation:

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (3)$$

where α is absorption coefficient, $h\nu$ the photon energy, E_g direct band gap and A constant. The absorption coefficient is defined as:

$$\alpha = \frac{2.303 Abs\rho}{Lc} \quad (4)$$

where Abs is absorbance, ρ, c concentration (gL^{-1}), L is path lenght (1 cm). The plots of equation (2) is shown in Fig. 3. The linier extrapolation of the curve to the absorption equal to zero gives E_g of about 3.31 eV and 3.38 eV for nanoceria prepared at pH 7 and pH 10, respectively. They are larger than band gap of bulk ceria (3.19 eV) suggesting there is blue shift phenomenon due to decrease particle size as expressed by Eq. (2). The absorption edge of nanoceria shifts towards the shorter wavelenght. The band gap of nanoceria prepared at pH 7 smaller than that of nanoceria prepared at pH 10 indicating the larger particle size. Generally, the larger particles are better light scatterer. Therefore, a possible explanation for the low transparancy of nanoceria prepared at pH 7 is due to absorption and light scattering by large particle.

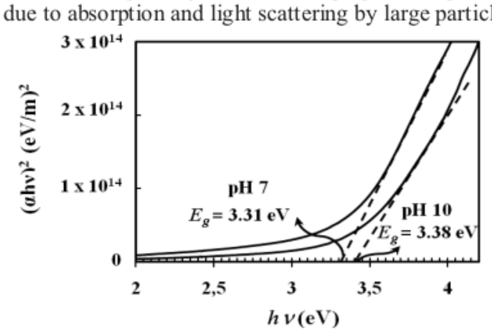

FIGURE 3. Plot of $(\alpha h\nu)^2$ versus photon energy.

The UV absorber ability of nanoceria can be identified by transparency of UV light range 200- 400 nm. Low transparency in UV range refers to high UV absorber ability indicating that nanoceria can blocked most of the UV light (200 – 350 nm). The efficiency of protection in UV range of nanoceria was identified using critical absorption length which is proposed by Diffey as follow [8]:

$$\int_{290}^{\lambda_c} \lg[1/T(\lambda)]d\lambda = 0.9\int_{290}^{400} \lg[1/T(\lambda)]d\lambda \quad (5)$$

The critical absorption wavelength were 368 nm and 367 nm for nanoceria prepared at pH 7 and pH 10, respectively which is almost closed to the critical absorption wavelength for excellent broad-spectrum protection. The result exhibits that nanoceria is promising for broad-spectrum UV absorber material. In order to evaluate that potential, the photocatalytic performance of nanoceria was investigated.

Fig. 4 shows photodegradation of methylene blue (MB) under sunlight irradiation without nanoceria and with addition nanoceria prepared at pH 7 and pH 10. The degradation of MB solution was calculated by following expession:

$$\text{Degradation } (\%) = \frac{A_o - A_t}{A_o} \times 100\% \quad (6)$$

where A_o and A_t are absorbance of MB solution before irradiation (t = 0 min) and after irradiation for t = 120 min, respectively.

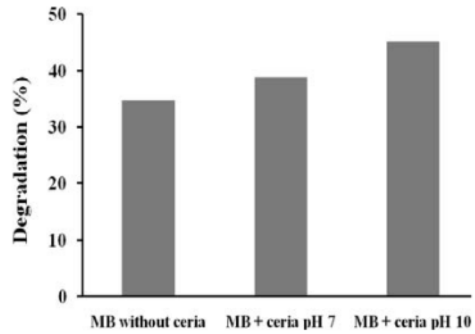

FIGURE 4. Photodegradation of methylene blue under sunlight irradiation for 120 min.

It is observed that MB solution can be degraded until 35% even though no addition of nanoceria. The addition of nanoceria to MB solution improved degradation rate, but not significant. The degradation of about 38% and 45% was observed for nanoceria prepared at pH 7 and pH 10 respectively. By comparison to degradation of MB without nanoceria, the improvement degradation of about 3% and 10% were achived by adding nanoceria prepared at pH 7 and pH 10. It refers that nanoceria possesses poor photocatalytic ability. It also found that nanoceria prepared at pH 7 had lower photocatalytic activity than that of nanoceria prepared at pH 10. Finally, nanoceria prepared at pH 7 had good UV absorber ability and almost do not indicate photocatalytic activity. However, that nanoceria transparency at visible light still needs to be improved, in order to gives natural look when applied on the skin.

CONCLUSION

Nanoceria were synthesized by precipitation process at pH 7 and pH 10. The prepared nanoceria had highly crystalline structure of cubic fluorite. pH of precipitation influences on crystalynity, crystallite size and optical properties of nanoceria. The UV-Vis spectra indicates the blue shift phenomenon occured due to decrease particle size. The transparency in UV-Vis range of nanoceria prepared at pH 10 is higher than that nanoceria prepared at pH 7. The efficiency of protection in UV range of both nanoceria did not show significant differences because that critical absorption wavelenght are closer to 370 nm which is characterized as excellent broad-spectrum protection. Due to poor photocatalytic activity, nanoceria prepared at pH 7 more suitable for used as UV absorbers in personal care products.

REFERENCES

1. Department of Health and Human Services. Food US, Drug Administration Sunscreen drug products for over-the-counter human use, proposed amendment of final monograph, proposed rule, 21CRF Parts 347 and 352. *Federal Register*. 2007;72:49070-49122.
2. N. Serpone, D. Dondi and A. Albini, *Inorg. Chim. Acta* **360**, 794-802 (2007).
3. S. Yabe and T. Sato, *J. Solid State Chem.* **171**, 7-11 (2003).
4. J. F. Lima, R. F. Martins, C. R. Neri and O. A. Serra, *Appl. Surf. Sci.* **255**, 9006-9009 (2009).
5. N. M. Zholobak, V. K. Ivanov, A. B. Scherbakov, A. S. Shaporev, O. S. Polezhaeva, A. Y. Baranchikov, N. Y. Spivak and Y. D. Tretyakov, *J. Photochem. Photobiol. B: Biology* **102**, 32-38 (2011).
6. J. Colon, L. Herrera, J. Smith, S. Patil, C. Komanski, P. Kupelian, S. Seal, D. W. Jenkins and C. H. Baker, *Nanomedicine: Nanotech. Biology and Medicine* **5**, 225-231 (2009).
7. A. S. Karakoti, N. A. Monteiro-Riviere, R. Aggarwal, J. P. Davis, R. J. Narayan, W. T. Self, J. McGinnis and S. Seal, *J. Mineral. Metal & Mater. Soc.* **60(3)**, 33-37 (2008).
8. B. I. Diffey, *Int. J. Cosmet. Sci.* **16**, 47-52 (1994).

The precipitation synthesis of broad-spectrum UV absorber nanoceria

ORIGINALITY REPORT

17%	7%	14%	2%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	link.springer.com Internet Source	3%
2	Elaheh K. Goharshadi, Roya Mehrkhah, Paul Nancarrow. "Synthesis, characterization, and measurement of structural, optical, and phtotoluminescent properties of zinc sulfide quantum dots", Materials Science in Semiconductor Processing, 2013 Publication	2%
3	Wang, H.. "High photocatalytic activity of silver-loaded ZnO-SnO"2 coupled catalysts", Chemical Engineering Journal, 20090215 Publication	2%
4	ijirse.in Internet Source	1%
5	Elaheh K. Goharshadi, Sara Samiee, Paul Nancarrow. "Fabrication of cerium oxide nanoparticles: Characterization and optical properties", Journal of Colloid and Interface Science, 2011	1%

Publication

6	CHEN, W.. "Fabrication and ultraviolet-shielding properties of silica-coated titania-doped ceria nanoparticles", Journal of Rare Earths, 201108 Publication	1%
7	Li, Y.Q.. "Preparation and characterization of transparent ZnO/epoxy nanocomposites with high-UV shielding efficiency", Polymer, 20060308 Publication	1%
8	Takeshi Morimoto, Hiroyuki Tomonaga, Akemi Mitani. "Ultraviolet ray absorbing coatings on glass for automobiles", Thin Solid Films, 1999 Publication	1%
9	Yap, N.. "Reactivity and stability of Au in and on TS-1 for epoxidation of propylene with H"2 and O"2", Journal of Catalysis, 20040815 Publication	1%
10	www.koreascience.kr Internet Source	1%
11	suncarelab.com Internet Source	1%
12	coek.info Internet Source	<1%

13	Dominique Moyal. "Sunscreens", Cosmetic Dermatology, 03/31/2010 Publication	<1 %
14	aapt.scitation.org Internet Source	<1 %
15	core.ac.uk Internet Source	<1 %
16	C. Piccirillo, C. Rocha, D. M. Tobaldi, R. C. Pullar, J. A. Labrincha, M. O. Ferreira, P. M. L. Castro, M. M. E. Pintado. " A hydroxyapatite–Fe O based material of natural origin as an active sunscreen filter ", J. Mater. Chem. B, 2014 Publication	<1 %
17	Horng-Huey Ko, Guoli Yang, Huy-Zu Cheng, Moo-Chin Wang, XiuJian Zhao. "Growth and optical properties of cerium dioxide nanocrystallites prepared by coprecipitation routes", Ceramics International, 2014 Publication	<1 %
18	M. A. Majeed Khan, Wasi Khan, Maqusood Ahamed, Abdulaziz N. Alhazaa. "Microstructural properties and enhanced photocatalytic performance of Zn doped CeO2 nanocrystals", Scientific Reports, 2017 Publication	<1 %

19	Morlando, Alexander, Dean Cardillo, Thierry Devers, and Konstantin Konstantinov. "Titanium doped tin dioxide as potential UV filter with low photocatalytic activity for sunscreen products", Materials Letters, 2016. Publication	<1%
20	Woo-Ju Jeon, Hyunsub Kim, Song-Ho Byeon. "Ce3+ concentration control on the surface of ceria nanoparticles and the stability of surface Ce3+ in aqueous, silica, and PVA media", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022 Publication	<1%
21	Yoichi Yasaki, Noriyuki Sonoyama, Tadayoshi Sakata. "Semiconductor sensitization of colloidal In2S3 on wide gap semiconductors", Journal of Electroanalytical Chemistry, 1999 Publication	<1%
22	pure.tue.nl Internet Source	<1%
23	N.M. Zholobak, V.K. Ivanov, A.B. Shcherbakov, A.S. Shaporev, O.S. Polezhaeva, A.Ye. Baranchikov, N.Ya. Spivak, Yu.D. Tretyakov. "UV-shielding property, photocatalytic activity and photocytotoxicity of ceria colloid solutions", Journal of Photochemistry and Photobiology B: Biology, 2011 Publication	<1%

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	On		

The precipitation synthesis of broad-spectrum UV absorber nanoceria

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5