

Optical Properties Characterization of Gamma Irradiated CeO₂ Nanoparticles Solution

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Abstract. Optical properties of CeO₂ nanoparticles solution have been studied to explore the possibility of CeO₂ nanoparticles as a liquid chemical dosimeter to measure gamma radiation in radiotherapy. CeO₂ nanoparticles were synthesized by ultrasound irradiation of cerium nitrate solution. The CeO₂ nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). CeO₂ nanoparticles solution with concentration of 2.5×10^{-4} g/ml was irradiated by 1.3 MV ⁶⁰Co gamma rays with a dose of 1.0 to 2.5 Gy. The UV absorbance spectrum of unirradiated and irradiated CeO₂ nanoparticles solution was measured by using UV-Vis spectrophotometer. The UV absorbance of CeO₂ nanoparticles solution increased with increasing radiation dose and caused a change in the band gap. The change in optical properties of CeO₂ nanoparticles solution is correlated to chemical reactions induced by gamma radiation. The obtained chemical yield was in the order of 10^3 mol/J indicates the sensitivity of CeO₂ nanoparticles to gamma radiation. The results show the possibility of CeO₂ nanoparticles for use as gamma radiation dosimeter.

Keywords: Optical properties, Gamma, irradiation, CeO₂, nanoparticle.

1. Introductions

Measurement of gamma rays is important in radiotherapy, medical diagnosis, and environmental monitoring. Gamma rays interact with materials through ionization and excitation. Ionization is the key process to detect gamma rays, where part or all of the gamma rays energy give up to an electron in materials. The materials used to detect gamma rays are gas, solid or liquid. Irradiation of gamma rays to the system of an aqueous solution of the solid materials generates free radicals by radiolysis process. The free radicals recombine or interact with other species present in the solution produce the chemical changes and induce optical property changes of the solution. That phenomenon is used as a basis for developing of the chemical dosimeter to determine the amount of energy absorbed from ionizing radiation. The degree of chemical change associated with the absorbed dose is called as *G*-value and determines the sensitivity of chemical dosimeter.

Dosimeters based aqueous chemical system (such as ferrous sulfate and iodide/iodate solution) have been used in radiation dosimetry. The most widely use of chemical dosimeter is ferrous sulfate or Fricke dosimeter due to high sensitivity and high accuracy to X-ray and γ -ray irradiation for high absorbed dose level [1, 2]. This level of detection is not sufficient to be used in radiotherapy. Consequently, some efforts have been made to improve sensitivity and develop standard Fricke dosimeter by adding various organic solutes including benzoic acid, xlenol and sorbitol [2-5]. Those



efforts successfully improved the sensitivity of Fricke dosimeter. However, its capability to measure Co-60 γ -ray with the precision of 0,1% is limited for doses range of 5 - 25 Gy [6]. Meanwhile, the daily dose of γ -ray used in radiotherapy is in the range of 1.8 – 2.0 Gy. Therefore, there is interest to find dosimeter for dose level radiotherapy application. Nanoparticles can be used to detect the high radiation energy like as: X-rays, gamma rays, and other particles (β -particles, α -particles) with high sensitivity because of large surface area. CeO₂ nanoparticles have attracted attention due to two oxidation states of Ce (Ce⁺⁴ and Ce⁺³) and potential to be developed for medical application [7-10]. Both oxidation states are associated with optical properties and have two characteristics spectrophotometric UV absorbance peaks. In the 230–260 nm range corresponding to Ce⁺³ absorbance and in the 300–400 nm range corresponding to Ce⁺⁴ absorbance. Similar to ferric ion in Fricke dosimeter, the property of those CeO₂ nanoparticles can be explored as sensitive materials for chemical dosimeter.

In this paper, the optical property of CeO₂ nanoparticles solution was studied to explore the potential CeO₂ nanoparticles for chemical dosimeter. CeO₂ nanoparticles were used in this study produced by ultrasonic radiation as we have reported, previously [11]. The absorbance spectrum of CeO₂ nanoparticles solution unirradiated and irradiated by gamma rays with doses range 1 to 2.5 Gy was measured by using UV-Vis spectrophotometer.

2. Experimental Method

2.1. Synthesize of CeO₂ nanoparticles and preparation of CeO₂ solution

To synthesize CeO₂ nanoparticles, Cerium (III) nitrate (Sigma Aldrich, Germany) was dissolved in a mixed solvent of aqua demineralized and isopropanol with a volume ratio of 1:6. Ammonium hydroxide (3M) was added drop by drop to solution until pH 10. The solution was irradiated by ultrasound wave with a frequency of 40 kHz for 60 minutes. The product of irradiated solution was then washed and calcined at 100°C for 3 hours. CeO₂ nanoparticles solution was prepared by dispersing CeO₂ nanoparticles in distilled water with a concentration of 0.25×10^{-4} g/ml and then placed into the glass tube.

2.2. Material characterization

X-ray Diffraction (*Phillips PW 1710*) measurement was used to analyze the structure of nanoparticles. Morphology of the synthesized nanoparticles was observed by scanning electron microscope (JEOL JSM-6360LA). Optical properties of nanoparticles were measured by using ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu 1420).

2.3. Irradiation of CeO₂ nanoparticles solution

The CeO₂ nanoparticles solution in the glass tube was irradiated by Gamma rays by using Co-60 teletherapy air FCC8000F Series with the energy of 1.30 MV. The irradiation dose was varied at 1, 1.5, 2 Gy, and 2.5 Gy. The absorbance of unirradiated and irradiated CeO₂ nanoparticles solutions were measured by using UV-Vis spectrophotometer over the wavelength in the range of 200 nm – 400 nm to observe absorption peak. The absorption peak was further used to analyze response and sensitivity of CeO₂ nanoparticles solution.

3. Results and Discussion

3.1. Structure and morphology of CeO₂ nanoparticles

The diffraction pattern of CeO₂ nanoparticle is shown in Figure 1(a). Certain of diffraction peaks were observed which indicate that CeO₂ nanoparticles are polycrystalline in nature. The (111), (200), (220), (311) dominant diffraction peaks corresponded to a pure fluorite cubic structure of CeO₂ (JPDS 43-1002). The sharp of those peaks is indicating that CeO₂ is well crystallized. To confirm the synthesized nanoparticles composed of a single phase with the cubic structure of CeO₂, the

Rietveld refinement yielded the agreement factors are $wRp = 13.95\%$ and $R_p = 10.82\%$ with the goodness of fit (χ^2) of 1.02 and the refined cell parameter is $5.4218 \text{ \AA}$. Figure 1(b) shows the Rietveld refinement plot of XRD pattern of CeO_2 nanoparticles.

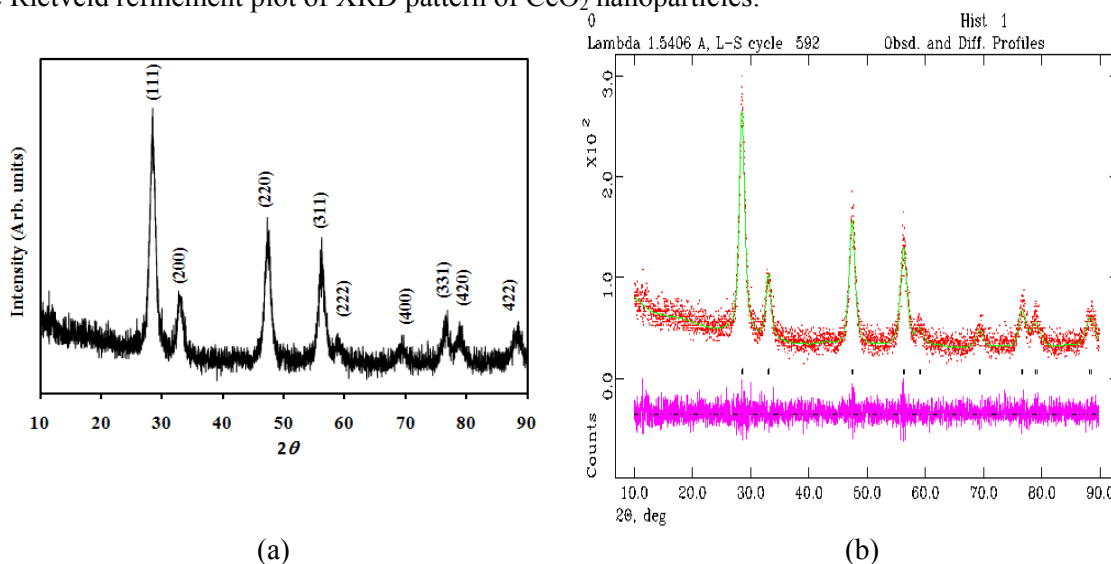


Figure 1. (a) XRD pattern and (b) Rietveld refinement plot of CeO_2 nanoparticles. Experimental data is indicated by red tick marks, while calculated curve obtained after refinement is indicated by green solid line. The rose-colored of continuous curve represents the difference between the experimental data and the calculated curve.

The morphology and particles size of CeO_2 nanoparticles were analyzed by using SEM image as depicted in Figure 2. The surface morphology of CeO_2 appears to be rough and generally spherical in shape with estimated average particle size of 37 nm .

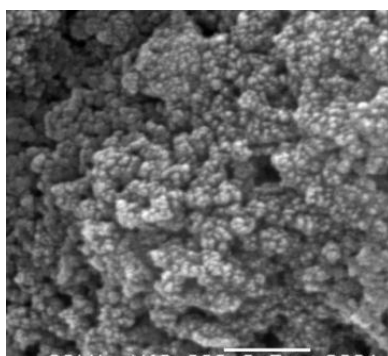


Figure 2. SEM image of CeO_2 nanoparticles

3.2. Optical properties of CeO_2 nanoparticles solution

The absorbance spectrum of un-irradiated and gamma irradiated CeO_2 nanoparticles solution under 1, 1.5, 2, and 2.5 Gy dose of gamma rays are shown in Figure 3. When CeO_2 nanoparticles solution was exposed to gamma radiation, the absorbance increased with increasing the gamma radiation dose and the optical absorption edge shifted to a shorter wavelength. Gamma irradiation with a dose of 1 to 2 Gy increased the absorbance slightly and the absorbance increased sharply at gamma irradiation dose of 2.5 Gy. The maximum absorbance was observed at a wavelength of 304 nm and became strong by increasing the dose. The wavelength of 304 nm was then used as a sensitive wavelength reference for further analysis of UV absorbance spectrum.

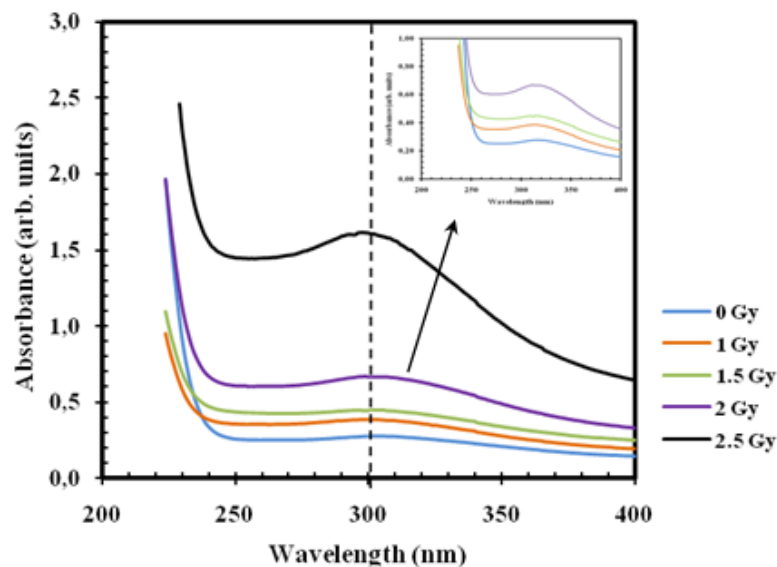


Figure 3. UV absorbance spectrum of the irradiated CeO_2 nanoparticles solution under gamma rays with different doses. The insert represents the UV absorbance spectrum of CeO_2 nanoparticles irradiated with dose 0, 1, 1.5, and 2 Gy.

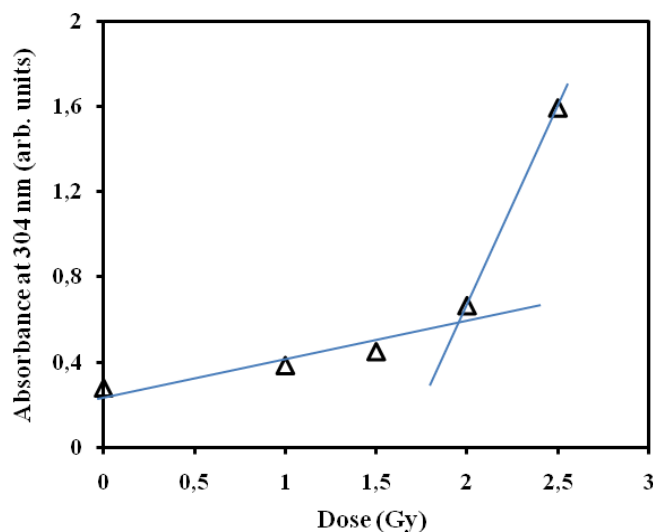


Figure 4. UV absorbance at 304 nm of irradiated CeO_2 nanoparticles solutions under gamma rays as function of radiation dose.

Figure 4 shows the absorbance at the wavelength of maximum absorption ($\lambda = 304 \text{ nm}$) of irradiated CeO_2 nanoparticles solution as function of radiation dose obtained from absorption spectra in Figure 3. The absorbance increased linearly with increasing radiation dose to 2 Gy and then the absorbance increased sharply at a dose of 2.5 Gy. It indicates that CeO_2 nanoparticles solution is capable of detecting gamma radiation. Capability of CeO_2 nanoparticles solution to detect gamma radiation can be explained through basic mechanism in Fricke solution dosimeter [12-13]. When the CeO_2 nanoparticles solution irradiated, the dominant reaction is water radiolysis. Radiolysis produces

e_{aq}^- , H^* , OH , H_2 , H_2O_2 that react with CeO_2 nanoparticles led to changes in the oxidation number of Ce^{4+} into Ce^{3+} and increases the absorbance [10].

The changes in absorbance of CeO_2 nanoparticles solution due to gamma radiation and the peak absorbance at 304 nm corresponded to the CeO_2 band gap. An increase in radiation dose causes an increase in number of radical and Ce^{3+} ion formation at CeO_2 nanoparticles surface, and then change the band gap. The band gap of unirradiated and irradiated CeO_2 nanoparticles solution were determined by plotting $(\alpha h\nu)^2$ vs $(h\nu)$ for direct transition as described by Equation (1).

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

α is the optical absorption coefficient, $h\nu$ is a photon energy (eV), E_g is a band gap, A is a constant, and $n = \frac{1}{2}$ for an indirect transition or $n = 2$ for direct transition. The calculated band gap is tabulated in Table 1. An increase in band gap with gamma radiation doses is mainly caused by changes in valence state and point defect formation due to radiation. The point defect may lead blueshift in the band gap [14-18].

Table 1. Band gap of CeO_2 nanoparticles for various gamma radiation doses.

Dose (Gy)	Band gap (eV)
0	3.163
1.0	3.164
1.5	3.166
2.0	3.208
2.5	3.356

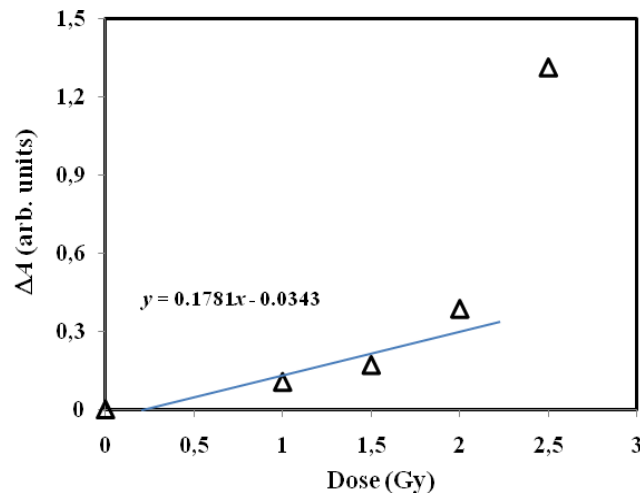


Figure 5. UV absorbance changes of CeO_2 nanoparticles solution for various doses

3.3. Sensitivity of CeO_2 nanoparticles

The sensitivity of CeO_2 nanoparticles solution to gamma radiation can be determined from the change in absorbance (ΔA) and the radiation chemical yield (G -value) as described in Equation (2) [18].

$$G = \frac{\Delta A}{D \epsilon \rho b} \quad (2)$$

ΔA is the change in absorbance at λ_{max} , D is a dose (Gy), ϵ is the linear molar extinction coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$), ρ is a density ($gr \cdot cm^{-3}$), and b is the optical path length (1 cm). The change in

absorbance of irradiated CeO₂ nanoparticles solution as function of irradiation dose is shown in Figure 5. The slope of plot of ΔA to dose in the range 0 – 2 Gy is used to calculate the G -value and the result was found to be 3.72×10^3 mol/J. The G -value obtained in this study is greater than G -value of other chemical dosimeter that is $\sim 1.6 \times 10^{-6}$ mol/J for Fricke dosimeter [6] and ~ 14 mol/J for iodide dosimeter [19]. The result shows that CeO₂ nanoparticles solution possess a high sensitivity to gamma radiation.

4. Conclusion

The optical properties of gamma irradiated CeO₂ nanoparticles have been characterized by using UV-vis spectrophotometer. The UV absorbance spectrum shows the peak absorbance at 304 nm was corresponding to the band gap of CeO₂ nanoparticles. Gamma radiation causes an increase in UV absorbance and the band gap of CeO₂ nanoparticles. High sensitivity and linear response in the range of 0 – 2 Gy indicate the possibility of CeO₂ nanoparticles to be developed as a chemical dosimeter for radiotherapy application.

5. References

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