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The Effect of Temperature Treatment on Structural and Optical Properties of Cr^{3+} doped Alumina Nanocrystals

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Cr^{3+} doped alumina nanocrystals have been successfully prepared using combustion method. The chemicals used in this preparation are aluminium nitrate, chromium nitrate, urea and glucose. All these chemicals were thoroughly mixed then heated in a furnace. The mixture was heated at 600 °C for 1 hour then heated at 700, 800 and 900 °C for 30 minutes. At the final stage the mixture was heated at the temperature of 1000 °C for 30, 60, and 120 minutes. At every different temperature and heating time, some of the sample was taken for analysis. The samples were analysed in terms of their structure and optical properties by using X-ray diffraction (XRD) and spectrofluorometer, respectively. From the analysis, it is found that the structure and optical properties were strongly affected with the temperature and heating time. The sample heated at 1000 °C for 30 minutes contains gamma and alpha phases structures. The structure fully transformed to alpha phase after 1 hour of heating at 1000 °C. From the X-ray diffractogram, crystallite size was estimated using Scherrer equation, which shows increasing trend from 21 nm to 33 nm as the heating time prolonged from 30 minutes to 120 minutes at 1000 °C. The fluorescence spectra at 694 nm observed for the samples annealed at 1000 °C. The intensity of fluorescence increases with longer heating time. Based on the result, it shows that the temperature and heating time significantly influence the structure and fluorescence intensity.

Keywords: alumina; chromium; fluorescence; nanocrystal; structure; temperature

I. INTRODUCTION

Nowadays, there are many types of nanomaterials have been used as fluorescent probe for bioimaging application such as semiconductor nanocrystals (NCs), nanodiamonds, upconversion NCs and dye doped silica NCs (Chen *et al.*, 2016). For biological application, the NCs should have excellent photoluminescence properties and brings no harm to the cell (non-toxic). Current fluorescent probes frequently experience toxicity and photostability issues. Edmonds *et al.* (2013) proposed a new type of fluorescent probe known as nanoruby (Cr^{3+} doped Al_2O_3 NCs). In their study, nanoruby has been demonstrated as a probe for cellular imaging (Edmonds *et al.*, 2013). Cr^{3+} doped Al_2O_3 NCs have an attractive photo physical property including excellent photo stability, high quantum yield and millisecond-range of fluorescence lifetime make it suitable for complete background suppression using time-gated imaging system (Razali *et al.*, 2016).

There are several methods which can be used to synthesis NCs such as laser ablation, co-precipitation, sol-gel and combustion method (Mi *et al.*, 2009). Baranov *et al.* (2016) used laser ablation to produce ruby NCs with stable aqueous/buffer colloid which allows facile conjugation to

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proteins (Baranov *et al.*, 2016). However, this method requires expensive instrument. In this study, combustion method is preferred because it uses simple equipment, forms high-purity product and the produced powder has great sinterability with a homogeneous arrangement (Salunkhe *et al.*, 2014). Using this method, the characteristics of the NCs can be controlled by modifiying the parameter of the reaction including temperature, concentration and pH (Alvarado *et. al.*, 2013; Kakooei *et al.*, 2012).

II. MATERIALS AND METHOD

In the preparation of Cr^{3+} doped alumina NCs using combustion method, the chemicals involved were chromium nitrate-9-hydrate, ($Cr(NO_3)_3{\cdot}9H_2O$), aluminium nitrate-9-hydrate (Al(NO3)3·9H2O), urea ($CO(NH_2)_2$) and glucose ($C_6H_{12}O_6$). 36.793 g of aluminium nitrate nonahydrate, 0.263 g of chromium nitrate, 14.826 g of urea and 0.534 g of glucose were mixed together. To obtain homogenous mixture, the mixed sample was transferred into a milling jar and milled at 180 rpm for 24 hours. As a result, cream-like paste was obtained and then transferred into alumina crucible for the heating process. Firstly, the sample was heated at 600 °C in the furnace for an hour until the sample turns into brown powder. The produced powder was equally distributed into several batches for further temperature treatment process. The distributed powder was heated at 700, 800, and 900 °C for 30 minutes. In the next stage, the sample was heated at 1000 °C for 30, 60, and 120 minutes.

X-ray diffraction (XRD) analysis was done using PANalytical X'Pert PRO system. From the analysis, the crystal structure formation can be monitored. 2 g of each sample were weighed and put on the instrument sample holder. The crystallite size, *d* was calculated using Scherrer's formula as shown below (Monshi *et al.*, 2012)

$$d = \frac{0.89\,\lambda}{\beta cos\theta} \qquad (1)$$

where λ is X-ray source wavelength, β is full width at half maximum (FWHM) in radians and θ is Braggs diffraction angle.

Fluorescence spectroscopy analysis was carried out using Horiba Fluoromax-3 spectrofluorometer. For the analysis, the samples were firstly ground using mortar and pestle. 1 mg of each sample was added into 1 ml of distilled water followed by sonication to ensure the sample was well dispersed. From the data obtained, graph of normalised fluorescence intensity as a function of wavelength was plotted.

III. RESULTS AND DISCUSSION

The physical properties of Cr^{3+} doped Al_2O_3 NCs can be observed based on the colour of the sample. The colour of the samples heated at 600 and 700 °C are brown, at 800 and 900 °C light brown and at 1000 °C white colour. The colours of the samples are shown in Figure 1. The structure of the samples analysed using XRD is shown in Figure 2. This figure illustrates the XRD pattern for the sample heated at 600, 700, 800, 900, and 1000 °C. Based on this result, the sample heated at 600 to 900 °C shows broad peaks which are identified as γ-phase alumina. The α-phase alumina started to form in the sample heated at 1000 °C.

Figure 1. Pictures of samples heated at 600, 700, 800, 900, and 1000 °C (from right to left)

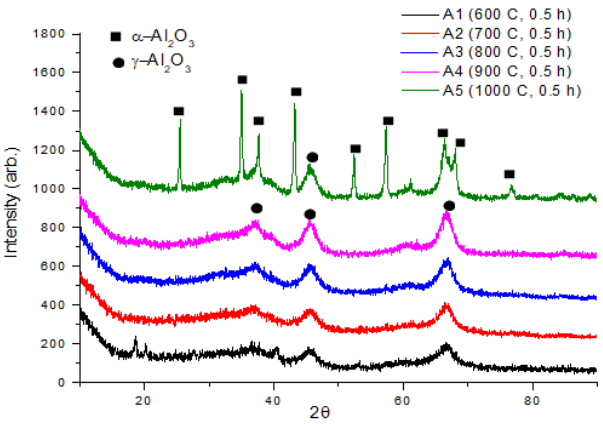

Figure 2. X-ray diffraction (XRD) spectra of Cr^{3+} doped Al_2O_3 sample heated for 30 minutes at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. Black dots show the γ-phase structure. Black squares show α -phase structure.

The sample heated at 1000 °C for 30 minutes has α-phase alumina with small portion of γ-phase alumina (marked by black dot in Figure 3). As the heating time extended to 60, 90 and 120 minutes, stable α-phase alumina fully formed showing that longer heating time is not required. From XRD pattern identification, it is shown that the NCs produced have a rhombohedral crystal structure. The colour of these samples is light pink as depicted in Figure 4.

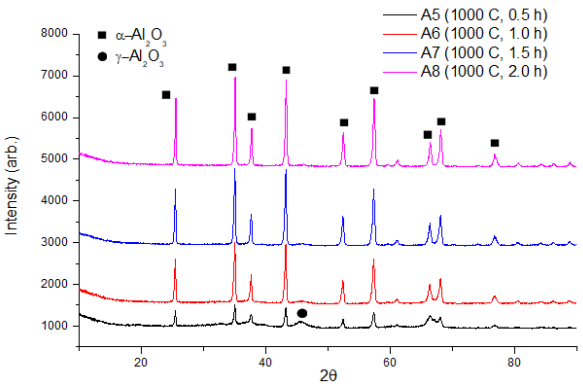

Figure 3. X-ray diffraction (XRD) spectra of Cr^{3+} doped Al_2O_3 sample heated at 1000 °C for 30, 60, 90 and 120 minutes. Black dots show the γ-phase structure. Black squares show α - phase structure.

Figure 4. Pictures of Cr^{3+} doped Al_2O_3 samples heated at 1000 °C for 30, 60, 90 and 120 minutes

The samples heated at 1000 °C for 30, 60, 90 and 120 minutes were analysed in term of their crystallite size. The calculated crystallite sizes are 24, 28, 31 and 33 nm for the sample heated at 1000 °C for 30, 60, 90 and 120 minutes, respectively. From the graph of crystallite size versus heating time (Figure 5), it is found that the crystallite size increases proportionally to the heating time. A similar trend has been found by previous researcher (Antolini *et al.*, 2012). The increase might be due to the agglomeration of particles at higher temperature, which resulted in the increase of crystallite size.

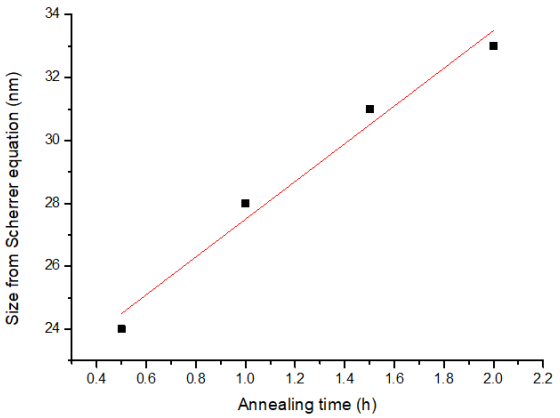

Figure 5. Graph of crystallite size of Cr^{3+} doped Al_2O_3 sample heated at 1000 °C as a function of heating time

The optical properties of the samples were analysed by using fluorescence spectroscopy. The normalised fluorescence intensity is plotted against the wavelength as shown in Figure 6. The sample was excited at 405 nm due to strong absorption of Cr^{3+} doped Al_2O_3 NCs at this wavelength (Razali *et al.*, 2018). The fluorescence peak was observed at 694 nm which is due the $^2E_g \rightarrow {}^4A_{2g}$ transition (Marchenko and Kiselev, 2017). The samples heated at temperature below 1000 °C shows very low fluorescence intensity which is due to the existence of γ-phase structure in the sample (Cheng *et al.*, 2006). In this state, the Cr^{3+} ions are likely to be distributed independently, which interrupt the fluorescence intensity. The intensity of fluorescence intensity increases drastically in the sample heated at 1000 °C for 90 minutes. This is due to Cr^{3+} ions have replaced the Al^{3+} ions at most of the lattice position and therefore all α-phases structures have fully formed (Mi *et al.*, 2009). After further 30 minutes of heating process, a small increase in fluorescence intensity was observed. This might be due to higher number of Cr^{3+} ions located in the alumina lattice.

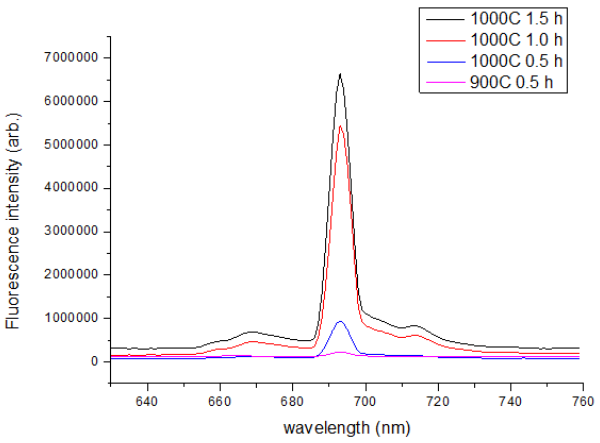

Figure 6. Fluorescence spectra of Cr^{3+} doped Al_2O_3 samples heated at 1000 °C for 30, 60, 90 and 120 minutes

IV. CONCLUSION

The Cr^{3+} doped Al_2O_3 NCs have been successfully prepared using combustion method. The structural and optical properties were characterised using XRD and spectrofluorometer, respectively. From the results obtained, it is shown that the temperature and period of heating influence the structural and optical properties. XRD analysis suggested that the sample heated at 1000 °C for 1 hour obtains high crystallinity sample. The sample heated at 1000 °C for longer heating time yield higher fluorescence intensity centred at 694 nm. Heating at 1000 °C longer than 2 hours is not suggested because it would increase further the crystallite size

V. ACKNOWLEDGEMENT

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