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## White light emission from polystyrene under pulsed ultra violet laser irradiation

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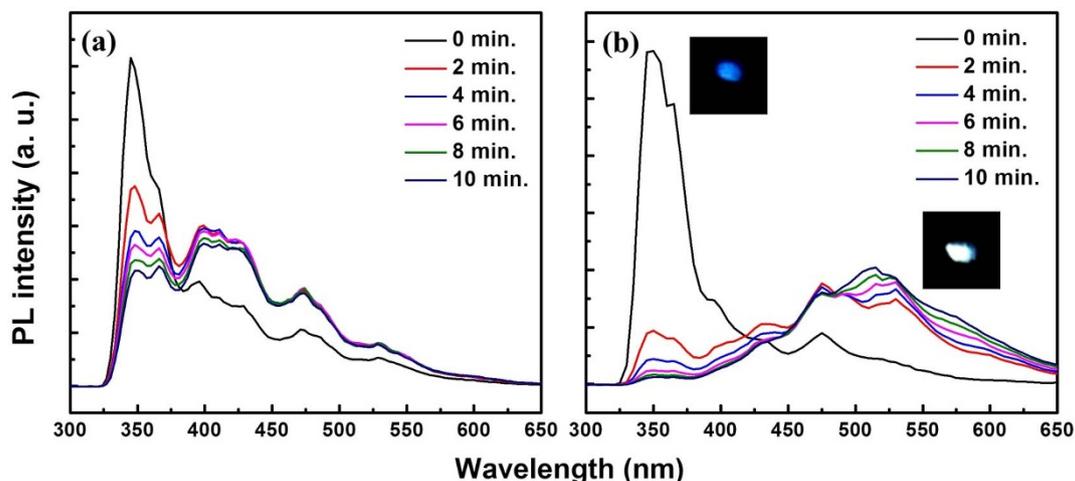
This paper reports for the first time the luminescent property of polystyrene (PS), produced by pulsed ultra violet laser irradiation. We have discovered that, in air, ultra-violet (UV) irradiated PS nanospheres emit bright white light with the dominant peak at 510 nm, while in vacuum they emit in the near-blue region. From the comparison of PS nanospheres irradiated in vacuum and air, we suggest that the white luminescence is due to the formation of carbonyl groups on the surface of PS by photochemical oxidation. Our results potentially offer a new route and strategy for white light sources.

Organic light-emitting diodes (OLEDs), particularly white OLEDs, are attracting increasing interest owing to their potential applications as illumination light sources and back light for liquid crystal displays (LCD) as well as full color displays<sup>1–5</sup>. Many methods have been developed to prepare white OLEDs, such as using multilayer structures in which each layer emits a primary color of light to achieve white-light emission<sup>6–8</sup>, using a single-layer structure into which different luminescent red–green–blue dyes are doped<sup>9,10</sup>, and using hybrid inorganic/organic composite emitters<sup>11,12</sup>. For the multilayer structure devices, a serious problem is that the Commission Internationale de l’Eclairage (CIE) coordinates vary with respect to the applied current or voltage, which may influence the color rendering or color temperature of the light source. White OLEDs based on a single-emitting component have clear advantages over those with multiple-emitting components, such as improved stability, better reproducibility, and simpler fabrication processes. However, obtaining white emission by two or three different light emitting dopants in a single layer has its own problems in that different rates of energy transfer between dopants may lead to a color imbalance. Therefore, the study for a material emitting white light without any dopants is important.

In this paper, we report that undoped polystyrene (PS) nanospheres can emit bright white light under pulsed UV laser irradiation. It is well-known that PS is composed of long hydrocarbon chains with phenyl groups and it does not emit in the visible region<sup>13</sup>. We found that visible light was emitted when the PS was irradiated in air by a pulsed UV laser. We also observed that the luminescence is a function of the irradiation time and it varied from a blue to white color as the irradiation time increased. In order to study the origin of the white luminescence, the irradiated PS nanospheres, were investigated under vacuum and air, and the change in chemical structures analyzed by Fourier transform infrared (FTIR, Nicolet 5700) spectroscopy.

## Results

Figure 1 shows the PL spectra with various irradiation times in vacuum and air. Figure 1 (a) shows the results obtained under vacuum. A peak at 350 nm is clearly observed. The peak becomes quickly depressed as the irradiation time increases while the side band emission over the blue range becomes dominant. This phenomenon is analogous to that of the previous report<sup>14</sup>. They reported that the blue-emission by electron irradiation of PS nanospheres could be possible and the emission was associated with the generation of polycyclic aromatic hydrocarbons (PAHs). Accordingly, we believe that the band emission over the blue range is due to the generation of polycyclic aromatic hydrocarbons (PAHs)<sup>15,16</sup>. In detail, the PAHs can be generated as a result of the photochemical reaction of PS, leading to the emission of near-blue luminescence. While the PS nanospheres are irradiated with pulsed laser light at 266 nm, the photon energy is initially absorbed by the benzene rings, then subsequently transferred to the C-H bonds. Various reactive radicals are then formed due to the hydrogen elimination process. These chemically reactive radicals can be easily recombined when two active points are close to each other. As a result of these cross-linking processes, the number of various PAHs in the nanospheres



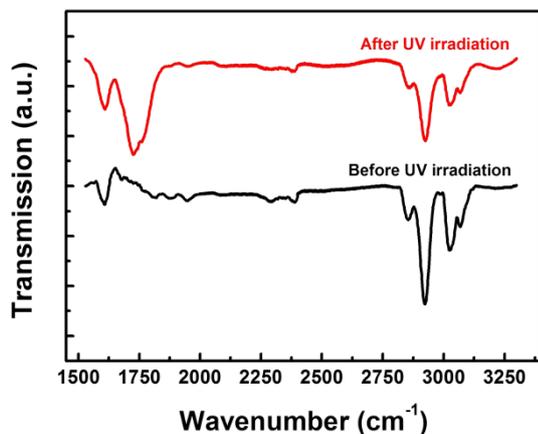
**Figure 1** | Photoluminescence spectra of PS nanospheres during 266 nm pulsed laser irradiation in (a) vacuum and (b) air. The inset shows luminescence spectra before and after UV irradiation in the presence of oxygen.

increase considerably, similar to that reported by<sup>14</sup>. A broad emission extending from 350 nm to 500 nm is observed, meaning that the PAHs with different cluster sizes are simultaneously formed with irradiation time.

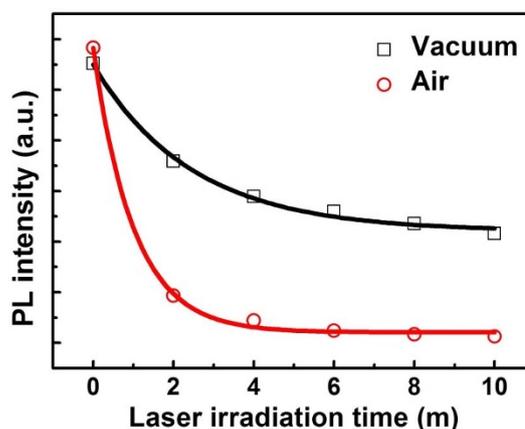
In comparison, the PL spectra of the nanospheres irradiated in air are shown in Figure 1 (b). It is clearly seen that the main peak of emission sharply decreases and disappears within 10 min. Meanwhile, we observed the bright white emission, not the near-blue. This indicates that the emission wavelength and rate in air is different from that in vacuum, and therefore, the phenomenon of the white emission in air cannot be explained by the creation of PAHs. We suggest that the origin is associated with photochemical oxidation, since no white emission was observed in the absence of oxygen as shown in Figure 1 (a). Photochemical oxidation of polystyrene has been studied by Geuskens et al.<sup>17</sup>, who proposed that the products of photo-oxidation were acetophenone and hydroperoxides. According to previous reports<sup>17,18</sup>, the photochemical oxidation of UV-irradiated PS is explained briefly by the following mechanism. First, the hydroperoxides groups are produced by acquiring hydrogen atoms from other polymer molecules. Secondly, the photolysis of the hydroperoxides produces alkoxy radicals, and eventually, carbonyl groups are formed by the fragmentation of the alkoxy radicals. Therefore, we deduce that the photochemical reaction generates the white emission due to the formation of the carbonyl groups on the surface of the nanospheres.

To demonstrate the formation of the carbonyl groups, the FTIR spectra of the nanospheres before and after UV irradiation under air was analyzed, as shown in Figure 2. Before the irradiation, one can observe three main peaks appearing at  $1600\text{ cm}^{-1}$ ,  $2800\text{--}3000\text{ cm}^{-1}$ , and  $3000\text{--}3100\text{ cm}^{-1}$ , corresponding to the C=C stretching of aromatic ring, C-H stretching of aliphatic ring, and C-H stretching of aromatic ring, respectively<sup>14</sup>. During irradiation in air, it is clearly shown that a broad peak at  $1720\text{ cm}^{-1}$  is created in addition to the three main peaks. This indicates that the carbonyl groups were formed on the nanospheres by UV irradiation in air. We also observe that the intensity of the peaks for C-H bonds of aliphatic ring and aromatic ring are reduced after irradiation while the intensity of the peak for C=C bonds remains constant. The new small peaks at  $3200\text{--}3500\text{ cm}^{-1}$  resulting from the hydroperoxides were also observed. This verifies that UV irradiation in air leads to the decomposition of C-H bonds with the subsequent formation of the carbonyl groups. Therefore, the white emission (around 510 nm) can be clearly attributed to the formation of the carbonyl groups on the surface of the nanospheres.

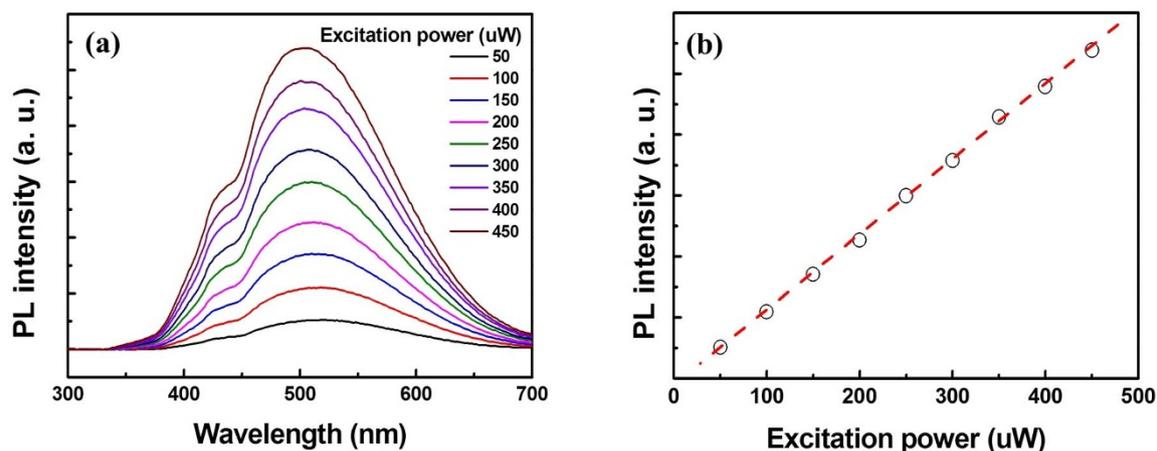
We carried out the same UV irradiation in vacuum and air for PS nanospheres and found a decrease in the 350 nm PL peak intensity with the generation of several PL peaks in the visible range. That means the decrease of the 350 nm PL peak intensity should be related to the creation of new luminophores, which are formed by photochemical reactions<sup>19</sup>. Correlation between the decrease of the 350 nm



**Figure 2** | FTIR spectra before (black line) and after (red line) UV irradiation in the air.



**Figure 3** | The experimental data of the 350 nm peak intensity as a function of UV irradiation time in with and without oxygen. The curve is fitted resulted by equation.



**Figure 4** | Excitation power dependent PL spectra of PS nanospheres (a) and linear fitting at PL peak (b) after fully complete photochemical oxidation process.

PL peak and generation of new luminophores is described by the following equation:

$$y = A(1 - e^{-Bt})$$

where  $A$  and  $B$  are constants,  $y$  is the yield of luminescence, and  $t$  is the irradiation time. The  $B$  values could be considered to be a decay rate of luminescence intensity.

To compare the photochemical reactions that occur in vacuum and air, we calculated the decay rate of the 350 nm PL peak intensity with the same UV irradiation. Figure 3 shows the change of the peak intensity during laser irradiation under vacuum and air. The symbols are experimental data and the curves are fitted. The yield of luminescence is described by the following equation:

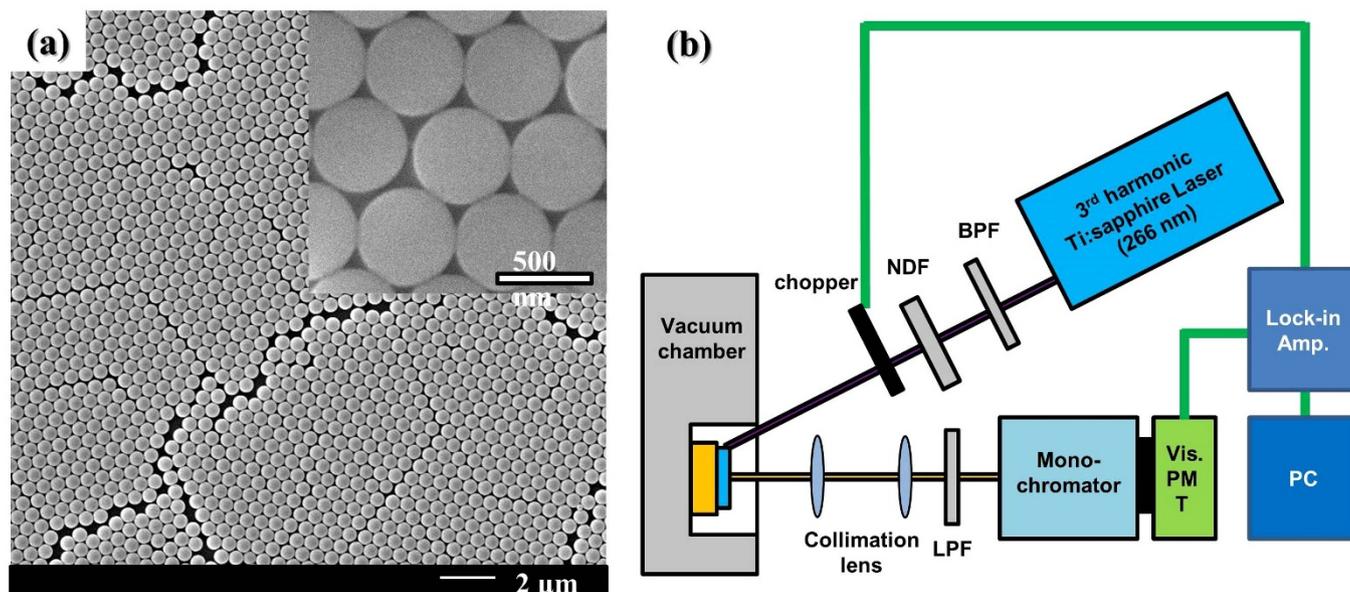
$$y = \frac{I_i - I_t}{I_i - I_f}$$

where  $I_i$ ,  $I_t$ , and  $I_f$  are the intensity of luminescence at initial time, time  $t$ , and final time, respectively. The function of PL intensity is defined by:

$$I_t = A \left\{ \left( \frac{I_i}{A} - I_i + I_f \right) + (I_i - I_f) e^{-Bt} \right\}$$

From the fitted results, the values of  $A$  in vacuum and air have a very similar value of 1. The values of  $B$  in vacuum and air are determined to be 0.41 and 0.99, respectively. With these results, we confirm that photochemical reactions in vacuum and air are different. The reaction with oxygen is twice faster than without oxygen.

Figure 4 shows the effect of the excitation power on the PL spectra of the irradiated nanospheres in the presence of oxygen. It should be noted that the luminescence by optical excitation at 266 nm is a complex process because the photo oxidation and radiative recombination process occur simultaneously. Thus, in order to simplify the simultaneous processes for the luminescence, we irradiated the nanospheres for 2 h, followed by measuring the luminescence of the full visible spectral region. Since the PL peak was centered at 510 nm under excitation of 266 nm, regardless of the excitation power, it is believed that the photochemical oxidation was completed by the 2 h irradiation. It is also clearly shown that PL intensity ( $I_{PL}$ ) is linearly proportional to the intensity of excitation source ( $I_{ex}$ ), thus, it



**Figure 5** | (a) SEM images of a self-assembled PS nanospheres monolayer. (b) Schematic diagram illustrating the pulsed UV laser irradiation system.



can be described by  $I_{PL} = \eta \alpha I_{ex}$ , where  $\eta$  is the quantum efficiency and  $\alpha$  is the absorption coefficient, under steady state in monomolecular luminescence. Therefore, this means that the surface of PS is chemically stabilized so that the luminescence is controllable by the applied power without the shift of peak wavelength.

## Discussion

We have demonstrated that non-luminescent PS can emit white light by being irradiated with pulsed UV laser in the presence of oxygen. The UV irradiated polystyrene nanospheres emit bright white light with the dominant peak at a 510 nm wavelength. In the absence of oxygen, UV irradiation also produced light-emitting materials from non-luminescent PS, however, it exhibited near blue emission. From the comparison of PS nanospheres irradiated in vacuum and air, we verified that the origin of the white emission is associated with the formation of the carbonyl groups by photochemical oxidation.

In addition, we discuss the effect of the PS size on the emission characteristics. We measured PL characteristics after UV irradiation using various sizes of PS nanospheres; as a result, we observed white emission in all PS samples, indicating that the emission properties were not affected by the size of PS nanospheres (see Supplementary Figure S1). We also performed the same experiments using a variety of substrates such as Si, SiO<sub>2</sub>, Au, and Al<sub>2</sub>O<sub>3</sub>. We observed the same emission characteristics regardless of substrate, verifying that the photoluminescence from PS is not affected by substrate. (See Supplementary Figure S2).

Importantly, the peak wavelength of the luminescence reaches the steady state after the termination of the photochemical oxidation, indicating that this luminescent PS can be applied into novel applications. Therefore, our future work will extend into an electrically driven-emitting devices consisting of a PS active layer.

## Methods

**Preparation of self-assembled PS nanospheres.** All solvents and chemicals were of reagent quality and were used without further purification. The monodispersed PS nanospheres with particle size of 500 nm in diameter were purchased from Thermo Fisher Scientific (5050A). They were well dispersed in deionized (DI) water and prepared as a suspension with concentration of 10 wt.% before fabrication. Si(100) wafers of  $1 \times 1 \text{ cm}^2$  were prepared as substrates. To modify the hydrophilic surface, the wafers were chemically cleaned using acetone, methanol, buffered oxide etchant (BOE), and DI water. Then they were dipped in H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> with the ratio of 1 : 1 for 10 min. Periodic monolayer arrays of nanospheres were coated by spin coating at 4000 rpm. Figure 5 (a) shows scanning electron microscope (SEM) images with a top view of a self-assembled monolayer array of nanospheres on the substrate. The nanospheres have a regular monolayer and a hexagonally close-packed structure. SEM images of PS nanospheres before and after UV irradiation in air are shown in Supplementary Figure S3. After UV irradiation, we could not observe any obvious morphological change. However, as the irradiation time increased, the PS nanospheres contracted slightly. This was consistent with a previous report<sup>18</sup>. The reduction of the PS in size resulted from the photochemical cross-linking of PS macromolecular chains<sup>18</sup>.

**Pulsed UV laser irradiation.** Figure 5 (b) shows schematic image of experimental setup. The nanospheres were exposed to light from a frequency tripled ultrafast laser (Maitai, Spectra-Physics). The laser properties were  $\lambda = 266 \text{ nm}$ , repetition rate 80 MHz, pulse duration 100 fs and pulse energy 5 pJ. To investigate the effect of the photochemical oxidation on the white luminescence, the nanospheres were irradiated under atmosphere and vacuum ( $5 \times 10^{-3} \text{ torr}$ ). The photoluminescence (PL) spectra were measured using a photomultiplier tube (PMT) tube combined with a monochromator during expose per period.

**FTIR measurements.** To prepare samples for FTIR measurements, PS nanospheres were spin-coated on the sapphire wafers of  $1 \times 1 \text{ cm}^2$ . The FTIR spectra of the nanospheres before and after UV irradiation under air were analyzed. The FTIR spectra were recorded with a Nicolet 5700. IR spectra were obtained in the spectral range of 3300–1530 cm<sup>-1</sup> with a 2 cm<sup>-1</sup> resolution and 5 scans. The transmission mode was used for FTIR measurement.

- Jordan, R. H., Dodabalapur, A., Strukjij, M. & Miller, T. M. White Organic Electroluminescence Devices. *Appl. Phys. Lett.* **68**, 1192 (1996).
- Kido, J., Hongawa, K., Okutama, K. & Nagai, K. White Light-Emitting Organic Electroluminescent Devices using the Poly(N-Vinylcarbazole) Emitter Layer Doped with Three Fluorescent Dyes. *Appl. Phys. Lett.* **64**, 815 (1994).
- Liu, S., Huang, J., Xie, Z., Wang, Y. & Chen, B. Organic White Light Electroluminescent Devices. *Thin Solid Films* **363**, 294–297 (2000).
- Gupta, D. & Katiyar, M. Deepak Various Approaches to White Organic Light Emitting Diodes and Their Recent Advancements. *Opt. Mater.* **28**, 295–301 (2006).
- Misra, A., Kumar, P., Kamalasanan, M. N. & Chandra, S. White Organic LEDs and Their Recent Advancements. *Semicond. Sci. Technol.* **21**, R35 (2006).
- D'Andrade, B. W., Holmes, R. J. & Forrest, S. R. Efficient Organic Electrophosphorescent White-Light-Emitting Device with a Triple Doped Emissive Layer. *Adv. Mater.* **16**, 624–628 (2004).
- Jiang, X. *et al.* White-Emitting Organic Diode with a Doped Blocking Layer between Hole- and Electron-Transporting Layers. *J. Phys. D: Appl. Phys.* **33**, 473 (2000).
- D'Andrade, B. W., Thomson, M. E. & Forrest, S. R. Controlling Exciton Diffusion in Multilayer White Phosphorescent Organic Light Emitting Devices. *Adv. Mater.* **14**, 147–151 (2002).
- Williams, E. L., Haavisto, K., Li, J. & Jabbour, G. H. Excimer-Based White Phosphorescent Organic Light-Emitting Diodes with Nearly 100 % Internal Quantum Efficiency. *Adv. Mater.* **19**, 197–202 (2007).
- D'Andrade, B. W., Brooks, J., Adamovich, V., Thompson, M. E. & Forrest, S. R. White Light Emission Using Triplet Excimers in Electrophosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **14**, 1032–1036 (2002).
- Feng, J. *et al.* White Light Emission from Exciplex using Tris-(8-Hydroxyquinoline)Aluminum as Chromaticity-Tuning Layer. *Appl. Phys. Lett.* **78**, 3947 (2001).
- Park, J. H. *et al.* White Emission from Polymer/Quantum Dot Ternary Nanocomposites by Incomplete Energy Transfer. *Nanotechnology* **15**, 1217 (2004).
- Wittersshaus, B. P., Baseler, T. T., Beaumont, G. T. & Zhang, Y.-Z. Excitation Energy Transfer from Polystyrene to Dye in 40-nm Diameter Microspheres. *J. Luminescence* **96**, 107–118 (2002).
- Lee, H. M., Kim, Y. N., Kim, B. H., Kim, S. O. & Cho, S. O. Fabrication of Luminescent Nanoarchitectures by Electron Irradiation of Polystyrene. *Adv. Mater.* **20**, 2094–2098 (2008).
- Nijgorodov, N. I. & Downey, W. S. The Influence of Planarity and Rigidity on the Absorption and Fluorescence Parameters and Intersystem Crossing Rate Constant in Aromatic Molecules. *J. Phys. Chem.* **98**, 5639–5643 (1994).
- Robertson, J. Diamond-Like Amorphous Carbon. *Mater. Sci. Eng. R.* **37**, 129–281 (2002).
- Geuskens, G. *et al.* A Quantitative Study of the Chemical Reactions Resulting from Irradiation of Polystyrene at 253.7 nm in the Presence of Oxygen. *Eur. Polymer J.* **14**, 291–297 (1978).
- Zhang, Y. *et al.* Touch and Hydrophilic Photonic Crystals Obtained from Direct UV Irradiation. *Macromolecular Rapid Communications* **31**, 2115–2120 (2010).
- Oldham, G. & Ware, A. R. Gamma-Radiation Damage Effects on Plastic Scintillators. *Rad. Eff.* **26**, 95–97 (1975).

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## Author contributions

E.K. and H.K. proposed, planned and supervised the project. E.K., J.H.K. and G.Y.L. performed the material preparation. E.K. and J.K. carried out the PL experiment. E.K., J.K., and G.Y.L. analyzed experimental results. E.K., D.H.K., I.K.H. and H.K. contributed to writing the manuscript.

## Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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