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Article

Temperature-dependent Photoluminescence Properties of Eu^{2+}-doped $CaMgSi_2O_6$ Phosphors

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Abstract: The solid-state reaction method was used to synthesize $0.025Eu^{2+}$-doped $CaMgSi_2O_6$ (Eu-$CaMgSi_2O_6$) powder in the reduction atmosphere of 5% H_2 + 95% N_2 at 1300ºC with a duration of 4 h. The reduction atmosphere was removed when the temperature was down to 800ºC. The XRD pattern showed that only the $CaMgSi_2O_6$ phase was observed in synthesized $0.025Eu^{2+}$-doped $CaMgSi_2O_6$ powder. Room-temperature photoluminescence excitation (PLE) and photoluminescence (PL) spectra of Eu-$CaMgSi_2O_6$ phosphors were recorded by using the Hitachi F-4500 fluorescence spectrophotometer at wavelength ranges of 200–430 and 350–600 nm, respectively. A new important finding is that the synthesized Eu-$CaMgSi_2O_6$ phosphor has three important PLE wavelengths. Therefore, Eu-$CaMgSi_2O_6$ phosphors are measured from 25ºC (room temperature) to 200ºC under three different PLE wavelengths to find the effect of temperature on the variations of maximum photoluminescence intensities (PLmax). All the PL spectra show that only one emission band with a central wavelength of 449 nm is found, which is independent of the PLE wavelengths and is caused by the transition of $4f^7 \rightarrow 4f^65d^1$. Another important finding is that the different PLE wavelengths have an apparent effect on the PLmax value of the Eu-$CaMgSi_2O_6$ phosphor. Finally, the decay-time curves of Eu-$CaMgSi_2O_6$ phosphor under three PLE wavelengths are also investigated.

Keywords: Photoluminescence properties, $CaMgSi_2O_6$, Phosphor, Reduction atmosphere

1. Introduction

Because white light-emitting diodes (WLEDs) have the advantages of high brightness, a long lifetime, light extraction efficiency, and environmental friendliness, they have attracted research attention and are recognized as next-generation lighting sources. When different Ca-Mg-Si-O compositions are used as raw materials, many different compounds can be formed such as $Ca_3MgSi_2O_8$ [1], $Ca_2MgSi_2O_7$ [1,2], and $CaMgSi_2O_6$ [3,4]. $Ca_3MgSi_2O_8$- and $Ca_2MgSi_2O_7$-, and $CaMgSi_2O_6$-based phosphors have good chemical and thermal stabilizations, so they are known as high-efficiency phosphors. When the compounds are investigated as phosphors, several transition elements are usually added as an activator to enhance the emission properties of the synthesized phosphors. Eu_2O_3 is a useful activator material because it can be added to the host materials to enhance the maximum photoluminescence intensities (PLmax) of the synthesized phosphors. Eu_2O_3 has Eu^{2+} and Eu^{3+} ions and causes the synthesized phosphors to produce different emission colors. For example, as Eu_2O_3 is used as an activator and the prepared powders are synthesized in a non-reduction atmosphere, the synthesized phosphors emit near-infrared light [5] or red light [6, 7]. If the prepared compounds are calcined in a reduction atmosphere, the synthesized phosphors emit blue light [1] or green light [1,8-10]. Therefore, the Eu_2O_3 is used as the activator, and $CaMgSi_2O_6$ is used as the main composition to prepare the $0.025Eu^{2+}$-doped $CaMgSi_2O_6$ (abbreviated Eu-$CaMgSi_2O_6$) as the main composition, which is synthesized in a reduction atmosphere to prepare the phosphor with blue light.

The novelty of this study is the finding that Eu-$CaMgSi_2O_6$ phosphor has three important photoluminescence excitation (PLE) wavelengths, namely 276, 313, and 342 nm. We use the three PLE wavelengths to excite Eu-$CaMgSi_2O_6$ phosphor and compare their optical properties, including photoluminescence (PL), PLE, and decay-time curve. Thermal stabilization was an important factor for the further applications of synthesized Eu-$CaMgSi_2O_6$ phosphor. Therefore, we use three PLE wavelengths to excite the Eu-$CaMgSi_2O_6$ phosphor. Another important purpose is to measure the variations of maximum photoluminescence intensities

(PLmax) from 25 to 200°C for finding the relationship between the temperature and PLmax of Eu-$CaMgSi_2O_6$ phosphor. The other novelty lies in the finding that all PL spectra of the Eu-$CaMgSi_2O_6$ phosphor show only one emission band with a central wavelength of 449 nm, which is caused by the transition of $4f^7 \rightarrow 4f^65d^1$. The wavelength to show the PLmax value is independent of the PLE wavelengths and the measured temperature.

2. Materials and Methods

First, Eu_2O_3, $MgCO_3$, $CaCO_3$, and SiO_2 were used as the precursors and wetted in the compositions of 0.025Eu^{2+}-doped $CaMgSi_2O_6$ (Eu-$CaMgSi_2O_6$) powder. The wetted Eu-$CaMgSi_2O_6$ powder was ball-milled for 2h in a solution of absolute alcohol, and then, the wetted powder was dried and ground. In order to deoxidize the Eu^{3+} ions into Eu^{2+} ions, the Eu-$CaMgSi_2O_6$ powder was synthesized at 1300°C for 4 h in a reduction atmosphere of 95% N_2 + 5% H_2. The surface morphology of Eu-$CaMgSi_2O_6$ powder was observed by using a field emission scanning electron microscope (FESEM), and the crystalline structure of Eu-$CaMgSi_2O_6$ powders was measured by using X-ray diffraction (XRD) patterns. To analyze the optical properties of the Eu-$CaMgSi_2O_6$ phosphor, the optimum PLE wavelength was found with the "3D scanning method". A Hitachi F-4500 fluorescence spectrophotometer was used to measure the PLE and PL properties of Eu-$CaMgSi_2O_6$ phosphor in the wavelength of 200–430 and 350–600 nm at room temperature. When the multiplied detecting value of the photomultiplier tube (PMT) was set to be higher than 350, the maximum emission intensities of PLE and PL spectra exceeded the displayable range of the fluorescence spectrophotometer. Therefore, the PMT was set at a value of 350. From the PLE spectrum, we found that there were three optimal exciting wavelengths in the Eu-$CaMgSi_2O_6$ phosphor, namely 276, 313, and 342 nm. Therefore, the Eu-$CaMgSi_2O_6$ phosphor was measured from 25°C (room temperature) to 200°C with a step of 25°C under three different exciting wavelengths to find the effect of measured temperature on the PLmax values.

3. Results and Discussions

SEM image and XRD pattern of 1300°C-synthesized Eu-$CaMgSi_2O_6$ phosphor are shown in Figs. 1 and 2. Figure 1 shows a special morphology for the synthesized Eu-$CaMgSi_2O_6$ powder which reveals large and small grains coexist. The SEM images present that as the synthesis temperature is lower than 1300°C, only small particles are observed, and the synthesized Eu-$CaMgSi_2O_6$ phosphor has weak PLE and PL intensities. As the synthesis temperature is higher than 1300°C, the Eu-$CaMgSi_2O_6$ phosphor melts and it also has lower diffraction intensity and weak PLE and PL intensities. Therefore, the Eu-$CaMgSi_2O_6$ powder is synthesized at 1300°C. The XRD pattern in Fig. 2 shows that all the precursor materials are not observed in synthesized Eu-$CaMgSi_2O_6$ powder and only the monoclinic $CaMgSi_2O_6$ phase is observed in synthesized powder, and the crystalline phase has a good match with the standard JCPDS File of No 01-070-3482.

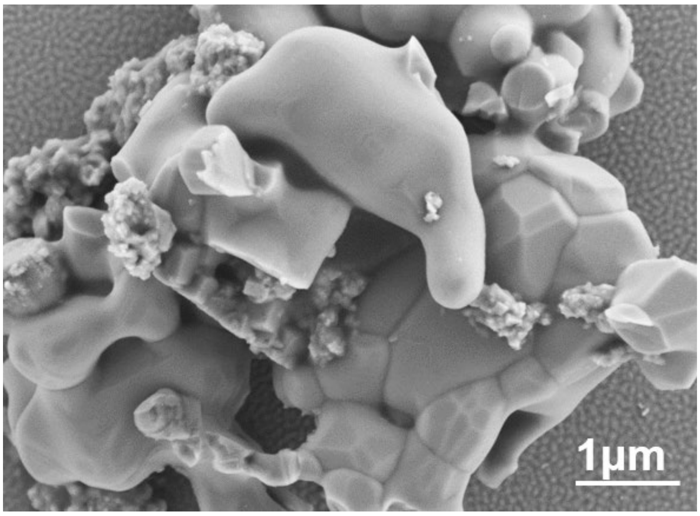


Fig. 1. SEM image of Eu-$CaMgSi_2O_6$ phosphor.

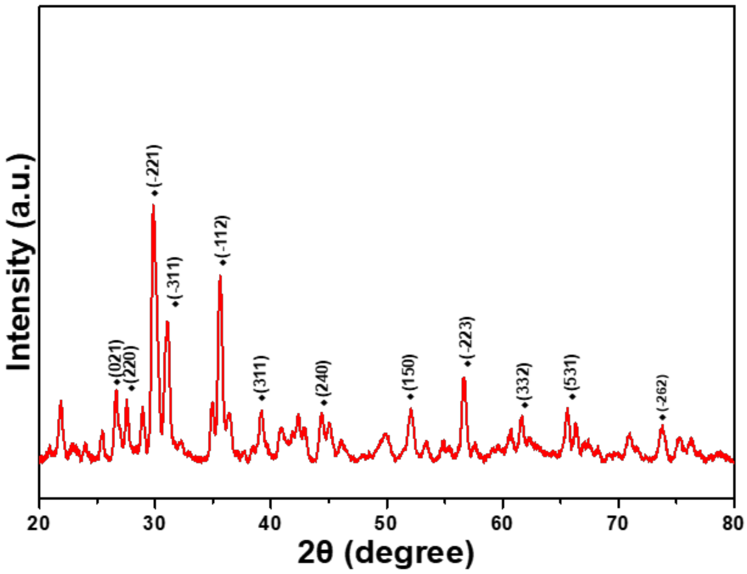


Fig. 2. XRD pattern of Eu-$CaMgSi_2O_6$ phosphor.

Figure 3 shows the PLE spectrum of Eu-$CaMgSi_2O_6$ phosphor synthesized in a reduction atmosphere, which is recorded at room temperature and is monitored by 449 nm. Another important result is that the Eu-$CaMgSi_2O_6$ phosphor has one broad band with three apparent peaks which center at 276, 313, and 342 nm. The emission intensity of 276 nm is approximately equal to that of 313 nm and the emission intensity of 342 nm is higher than those of 276 and 313 nm. Therefore, the three wavelengths are used to excite the Eu-$CaMgSi_2O_6$ phosphor, and we believe that the PLmax values under the three excited wavelengths become different.

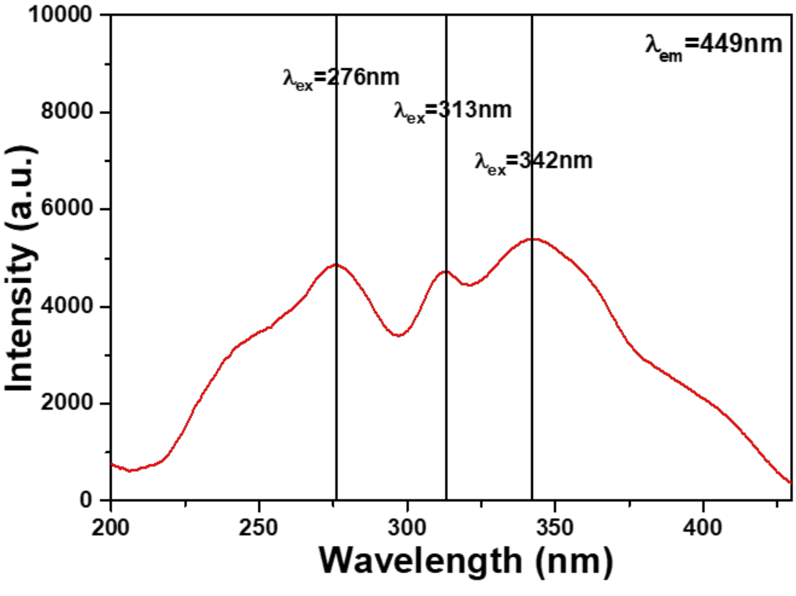
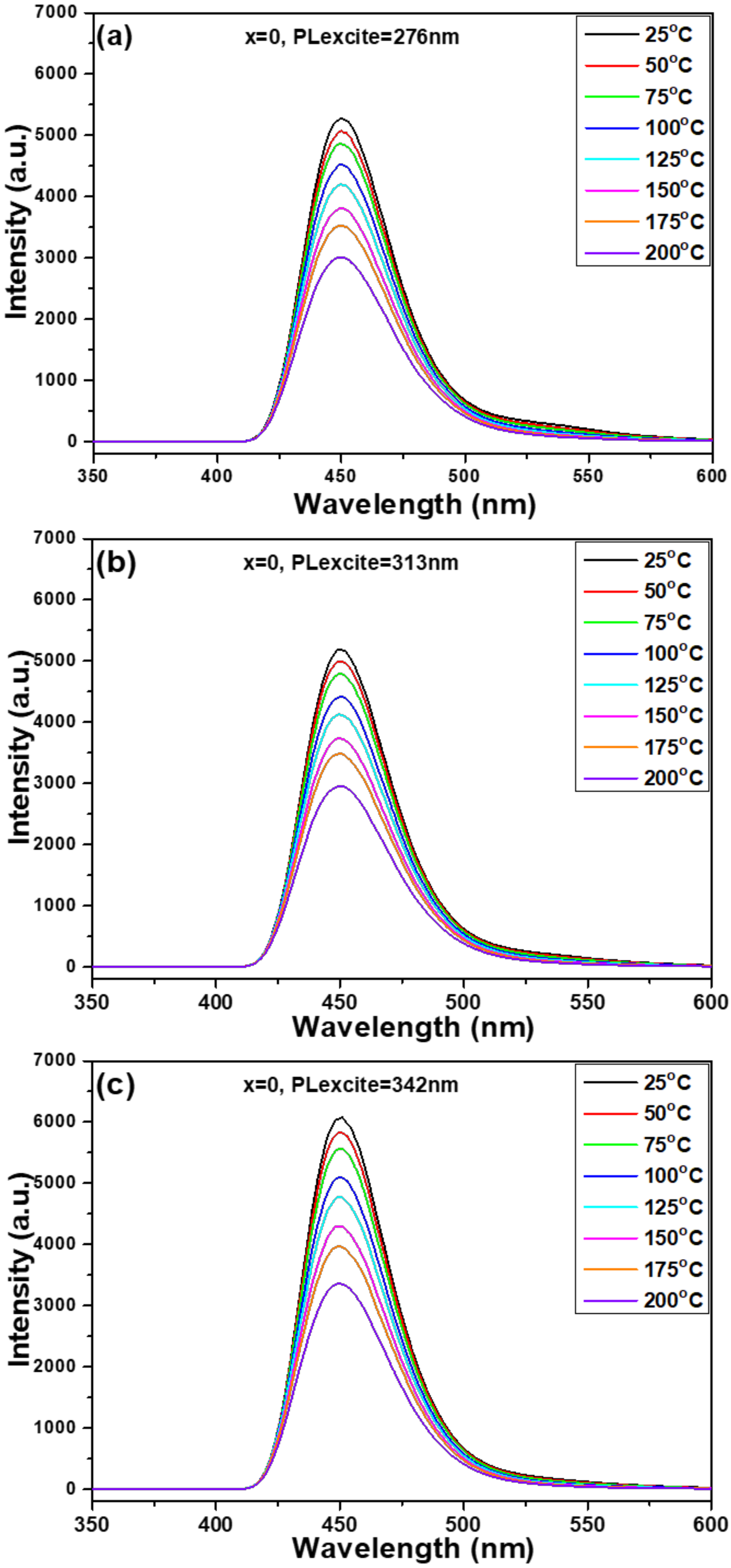


Fig. 3. PLE spectrum of Eu-$CaMgSi_2O_6$ phosphor measured at room temperature.

The PL spectra of synthesized Eu-$CaMgSi_2O_6$ phosphor are revealed in Figs. 4(a), 4(b), and 4(c), in which 276, 313, and 342 nm are the exciting wavelengths, and the wavelength range of 350–600 nm is used to record room-temperature PL spectra. However, as presented in the same figures, the PLmax value with an exciting wavelength of 276 nm is approximately equal to that of 313 nm, but the PLmax value with an exciting wavelength of 342 nm is higher than that of 276 and 313 nm. The emission band with a central wavelength of 449 nm is caused by the transition of $4f^7 \rightarrow 4f^6 5d^1$, and we believe that the difference in the PLmax value is caused by the difference in the emission intensity of the PLE value. The figures also show that when Eu-$CaMgSi_2O_6$ phosphor is measured in the range of 25°C to 200°C, the wavelengths of PLmax are almost unchanged with the variations of the exciting wavelength and measured temperature.


(a)
x=0, PLexcite=276nm
(b)
x=0, PLexcite=313nm
(c)
x=0, PLexcite=342nm
25°C
50°C
75°C
100°C
125°C
150°C
175°C
200°C
Intensity (a.u.)
Wavelength (nm)
0
1000
2000
3000
4000
5000
6000
7000
350
400
450
500
550
600

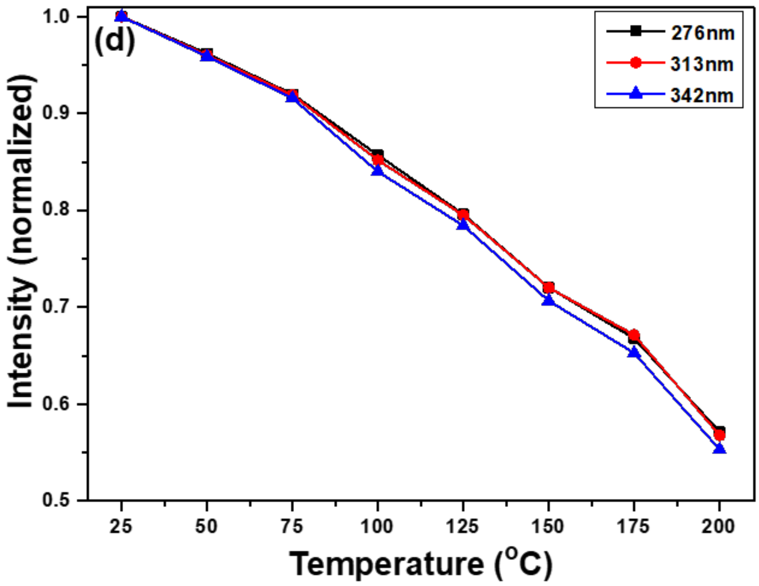


Fig. 5. PL spectra of Eu-$CaMgSi_2O_6$ phosphor measured from 25°C to 200°C with exciting wavelengths of (a) 276 nm, (b) 313 nm, and (c) 342 nm. (d) The variations of the normalized PLmax.

The PLmax values of Eu-$CaMgSi_2O_6$ phosphor measured at 25°C and different exciting wavelengths are used as the standard values to normalize the PLmax values at the temperature range of 25–200°C. The variations for the relative PLmax are shown in Fig. 4(d). For Eu-$CaMgSi_2O_6$ phosphor with different exciting wavelengths, the PLmax value decreases from an initial 100% to 84.0–85.7% at 100°C and 55.3–57.1% at 200°C. These results (Fig. 4(d)) prove that Eu-$CaMgSi_2O_6$ phosphor has a low thermal quenching effect. Figure 3(a) shows that the decay rates of PLmax for three different exciting wavelengths are almost the same, which also proves again that even though the exciting wavelength is different, the Eu-$CaMgSi_2O_6$ phosphor has the same emission mechanism.

The measured decay curves of the Eu-$CaMgSi_2O_6$ phosphor are shown in Fig. 6 as a function of the exciting wavelength. The decay time is 0.27, 0.33, and 0.37 ms at the exciting wavelengths of 276 nm, 313 nm, and 342 nm, respectively. As the exciting wavelength increases from 276 to 342 nm, the decay time increases, which the higher PLmax value results in. All the decay curves of the Eu-$CaMgSi_2O_6$ phosphor shown in Fig. 6 are decomposed into two stages with different slopes. The stage with a larger slope is presented at shorter than about 0.5 ms, and the second stage with a smaller slope is presented at longer than about 0.5 ms. However, the variations of decay curves of Eu-$CaMgSi_2O_6$ phosphor match the results shown in Fig. 5. The decay process for the PL intensity of Eu-$CaMgSi_2O_6$ phosphor is simulated by the curve-fitting method. Even though the decay curves have two stages, they can only be fitted by one exponential component as expressed in Eqs. (1), (2), and (3) at the exciting wavelengths of 276, 313, and 342 nm.

$$y = 1.04415 \times \exp\left(-\frac{x}{0.24628}\right) + 0.000266651 \tag{1}$$

$$y = 1.06703 \times \exp\left(-\frac{x}{0.28839}\right) - 0.000836113 \tag{2}$$

$$y = 1.07833 \times \exp\left(-\frac{x}{0.32141}\right) - 0.00122 \tag{3}$$

The decay-time curves of the Eu-$CaMgSi_2O_6$ phosphor are calculated by using a curve-fitting method, and the decay curves shown in Fig. 6 are successfully fitted by Eqs. (1)-(3). Photographs of the Eu-$CaMgSi_2O_6$ phosphor with the exciting wavelength of 342 nm are shown in Fig. 7, where the Eu-$CaMgSi_2O_6$ phosphor emits blue color.

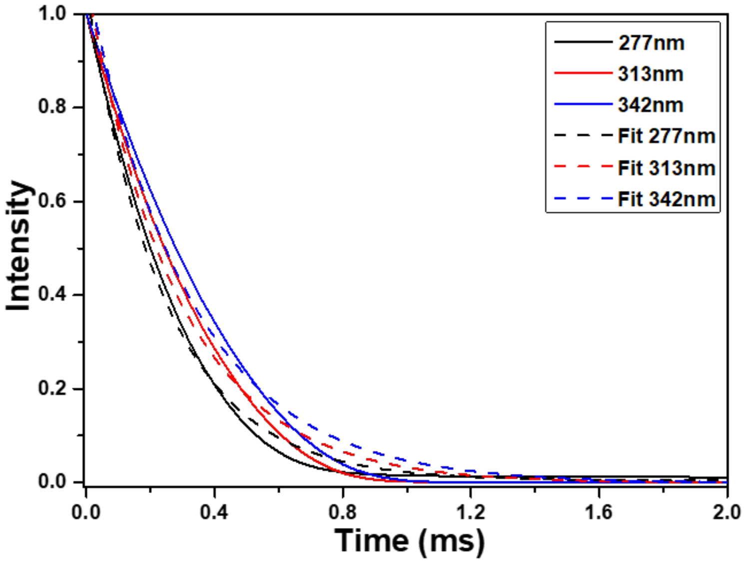


Fig. 6. Decay curves of the comparisons of measured and simulated results of Eu-$CaMgSi_2O_6$ phosphor.

Fig. 7. Photo diagram of synthesized Eu-$CaMgSi_2O_6$ phosphor.

4. Conclusions

Eu-$CaMgSi_2O_6$ phosphor has one broad band with three apparent peaks, which center at 276, 313, and 342 nm, and the emission intensity of 342 nm is higher than that of 276 and 313 nm. The Eu-$CaMgSi_2O_6$ phosphor with different exciting wavelengths shows that the PLmax value decreases from an initial 100 to 84.0–85.7% at 100ºC and to 55.3–57.1% at 200ºC, which suggests that Eu-$CaMgSi_2O_6$ be a stable phosphor for further application. Also, when 342 nm is used as the PLE wavelength, the Eu-$CaMgSi_2O_6$ phosphor has a stronger PL spectrum and longer decay time. These analysis results show that for the Eu-$CaMgSi_2O_6$ phosphor, 342 nm is the better PLE wavelength than 276 and 313 nm for the spectrum analysis.

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Conflicts of Interest: The authors declare no conflict of interest.

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