Improved Optical Degradation Characteristics of Eu Complex Encapsulated by High-Pressure Annealing

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The instability of Eu complexes against ultraviolet (UV) light irradiation is an important problem to solve before they can be practically applied in white light-emitting diodes. A novel technique of encapsulating tris(2-thenoyltrifluoroacetonato)(1,10-phenanthroline)europium(III) [Eu(TTA)$_3$phen] was investigated using high-pressure annealing (solvothermal process) as a final process in the sol-gel synthesis. The photoluminescence and excitation spectra of encapsulated Eu(TTA)$_3$phen samples synthesized by solvothermal and conventional annealing processes were almost the same. A half brightness time of 589 min was achieved while irradiating with UV light of 360 nm and 5 mW/cm^2 by optimization of ammonia concentration and annealing temperature. The longest half brightness time was longer than that of encapsulated Eu(TTA)$_3$phen synthesized by conventional thermal treatment. One possible reason for this result is that the chemical reaction of the sol-gel based glass network occurs more efficiently with high-pressure annealing. As a result, a high encapsulating efficiency was achieved owing to the small amount of organic component in the sol-gel derived glass network.

1. Introduction

Recently, organic-inorganic hybrid light-emitting materials and devices have attracted interest for several applications.[1–3] In particular, lanthanide-complex-based organic-inorganic hybrid materials are expected to be used as phosphors for white light-emitting diodes (LEDs)[4,5] and wavelength conversion films for photovoltaic cells,[6] owing to their high photoluminescence (PL) quantum efficiency, a large absorption coefficient in the near violet region, and long-term stability compared with organic materials. White LEDs in combination with blue LEDs and fluorescent phosphors have been already in a practical use for general lighting and backlights of liquid crystal displays. Trichromatic or quadchromatic white LEDs that employ blended phosphors have also been reported for improvement of the color rendering index of white LEDs. The practical realization of red light-emitting phosphors is an important challenge that is presently under investigation by many researchers. Several Eu^{3+} complexes

exhibit high PL quantum efficiency with ultraviolet (UV) excitation; however, the long-term stability is much lower than that of inorganic phosphors, owing to the weak bonding energy of organic ligands.[7,8] An organic ligand absorbs UV light and the photoinduced exciton moves to an Eu^{3+} ion. Red light is then generated from the Eu^{3+} ion. Therefore, the change in the molecular structure of the organic ligand causes the lowering of the PL quantum efficiency of the Eu complex.

Recently, several studies have demonstrated a method to encapsulate the Eu complex,[9,10] and an improved long-term stability was achieved by encapsulation with a sol-gel-derived glass network.[11–13] The encapsulating glass layer protects the reaction of the Eu complex with oxygen and/or moisture; therefore, the molecular structure of the Eu complex is not easily changed, even when it is irradiated with UV light. The encapsulating glass layer is fabricated at a low temperature of approximately 100 °C, ownig to the low heat resistance of the Eu complex, so that many organic components remain. Therefore, the encapsulating efficiency of the sol-gel-derived glass network is lower than that of a conventional inorganic glass network, which results in a poor long-term stability of the sol-gel-derived glass-coated Eu complex. For further improvement of such optical degradation characteristics of the sol-gel-derived glass-coated Eu complex, a novel technique of forming the dense glass network is necessary at low temperatures of less than 150 °C, because most Eu complexes are easily decomposed by high-temperature annealing at greater than 150 °C.

We have investigated a novel method to fabricate the encapsulating glass layer around tris(2-thenoyltrifluoroacetonato)(1,10-phenanthroline)europium(III) [Eu(TTA)$_3$phen] using a conventional sol-gel process and high-pressure annealing, referred to as the solvothermal process. The high-pressure annealing results in the efficient hydrolysis and condensation of silane alkoxide; therefore, the dense glass network is considered to be formed after high-pressure annealing. Eu(TTA)$_3$phen has a high PL quantum efficiency obtained by UV irradiation, and the absorption coefficient of Eu(TTA)$_3$phen is much higher than those of inorganic phosphors. Therefore, most of the incident UV light is converted to a red emission. If the long-term stability can be improved by encapsulation of Eu(TTA)$_3$phen with a glass network, it will be of practical use for white LEDs, biosensors, and wavelength conversion films for photovoltaic cells.

2. Experimental Procedure

The conventional sol-gel synthesis is based on the hydrolysis and condensation of organo alkoxide starting materials with the aid of a catalyst, water, and alcohol. Figure 1 shows the process for encapsulation of Eu(TTA)$_3$phen with the sol-gel-derived glass network. The starting solution was composed of tetraethoxysilane (TEOS), deionized water, ethanol, *N,N*-dimethoxyformamide (DMF), ammonia, and Eu(TTA)$_3$phen mixed in a Teflon beaker. The solution was stirred with a magnetic stirrer for 10 min at room temperature and was then cast

on a glass substrate. The sample was then annealed at 100, 120, and 150 °C for 3 h in an auto-clave container under a high pressure to investigate the influence of the annealing pressure on the optical degradation characteristics. 1 μL of the sol-gel solution was placed into the 25 mL autoclave container. The measured pressure was approximately 100 kPa. A reference sample was also prepared by annealing in an electric furnace under the same annealing conditions. The concentration of the sol-gel starting solution and the mixing condition were the same as the sample to be encapsulated by the solvothermal process.

PL and PL excitation (PLE) spectra were measured using a spectrofluorometer (Horiba Jobin Yvon, Fluoromax-3). The excitation wavelength of the PL spectrum was 360 nm, and the PLE spectrum was monitored at 612 nm. PL quantum efficiency was measured with a luminance quantum yield measurement system (Systems Engineering, QEMS-2000), which consists of an integrated sphere and a UV LED with a center wavelength of 375 nm as the excitation source. PL quantum efficiency was determined using a method based on that originally developed by de Mello et al.[15] In this approach, quantum efficiency is given by the integrated PL intensity of the sample excited by the UV LED divided by the decrease in excitation intensity caused by inserting the sample into the integrated sphere. In addition, normalized PL intensity was also recorded as a function of time under UV irradiation using a spectrofluorometer. The center wavelength and the optical intensity of the excitation UV light were 360 nm and 5 mW/cm^2, respectively.

3. Results and Discussion

Figure 2 shows the relative PL intensity changes at 612 nm for irradiation with UV light at 360 nm and 5 mW/cm^2. The molar ratio of TEOS, deionized water, ethanol, DMF, ammonia, and Eu(TTA)$_3$phen was 1:4:4:4:0.01:0.05, and the annealing temperatures of 100, 120, and 150 °C were applied to estimate the optimal annealing temperature for Eu(TTA)$_3$phen. The relative PL intensities of all the samples decreased with increasing UV irradiation time, because the molecular structure of Eu(TTA)$_3$phen was changed by UV irradiation,[11] which resulted in a low exciton transfer efficiency from the organic ligand to Eu^{3+} ions. Figure 2 shows that the PL intensity change was suppressed by encapsulation of Eu(TTA)$_3$phen for both the solvothermal (high pressure) and conventional annealing processes. This result indicates that the encapsulating layer of sol-gel-derived glass prevents Eu^{3+} ions from reacting with moisture and oxygen in the atmosphere.[5] In addition, the PL intensity change was reduced by annealing using the solvothermal process; the long-term stability of sol-gel-derived glass-coated Eu(TTA)$_3$phen was improved by annealing under high-pressure conditions.

Details of the encapsulation mechanism are now under investigation and will be published elsewhere. One possible explanation is that the efficient reaction of the sol-gel-based glass network occurs with high-pressure annealing. Organic components in the encapsulating glass layer have higher oxygen and moisture transmittances than an inorganic glass network, which

are considered to decrease after high-pressure annealing in an autoclave container.[16] The PL intensity change decreased with the increase in annealing temperature, and the optimized annealing temperature for the solvothermal process was 150 °C. In addition, only a slight red emission was observed after annealing at 200 °C. In addition, the amount of organic components remaining in the glass network generally decreased with an increase in the annealing temperature of the sol-gel process.[17–19] Therefore, the long-term stability was improved by high-temperature annealing, as shown in Fig. 2(a). In contrast, the optimal temperature for the conventional annealing process was 120 °C.

Figures 3(a) and 3(b) show PLE and PL spectra of the encapsulated sample prepared by the solvothermal process at 150 °C and the reference sample prepared by the conventional annealing process at 120 °C. The PLE spectrum of the encapsulated sample was shifted toward the shorter-wavelength region compared with the reference sample. However, a large excitation spectrum was observed in the near-UV-wavelength region, which indicates that encapsulated $Eu(TTA)_3phen$ could be applicable to red-emitting phosphors of UV-LED excited white LEDs. In addition, our previous experimental result showed that the PLE spectrum of the encapsulated Eu complex shifts toward the shorter-wavelength region owing to the change in the molecular structure.[14] Therefore, the shift of the PLE spectrum in Fig. 3 is due to a change in the molecular structure of $Eu(TTA)_3phen$ caused by high-pressure annealing. On the other hand, all the samples showed a sharp red emission at the center wavelength of 612 nm, which corresponds to the $^5D_0 \rightarrow {^7F_2}$ transition in the Eu^{3+} ion.[20,21] A sharp red emission was obtained for $Eu(TTA)_3phen$ even after encapsulation by the solvothermal process without degradation of $Eu(TTA)_3phen$ by the chemical reaction.

The relationship between the ammonia concentration and the PL quantum efficiency of prepared samples is shown in Fig. 4. The molar ratio of TEOS, deionized water, ethanol, DMF, ammonia, and $Eu(TTA)_3phen$ was 1:35:30:4:x:0.02 to suppress the influence of ammonia, and the annealing temperature was fixed at 150 °C for the solvothermal process and 120 °C for the conventional annealing process. Ammonia concentrations (x) of 0.1, 0.5, 1, and 2 mol% were used. Ammonia generally acts as a catalyst in the condensation and hydrolysis processes during the sol-gel process. The PL quantum efficiency decreased linearly with the increase in the ammonia concentration of the sol-gel starting solution. The organic ligand of $Eu(TTA)_3phen$ is easily decomposed by the addition of excess ammonia; therefore, a low PL quantum efficiency was observed by the addition of large amounts of ammonia, as shown in Fig. 4.

The PL quantum efficiency of $Eu(TTA)_3phen$ powder without encapsulation was 67%, whereas some of the encapsulated samples exhibited a higher PL quantum efficiency when $Eu(TTA)_3phen$ was encapsulated at ammonia concentrations of less than 0.5 mol%. The most likely reason for this result is that the vibration-induced exciton loss is reduced by en-

capsulating Eu(TTA)$_3$phen with the glass layer. As a result, photoinduced excitons can be efficiently transferred from the organic ligands to the Eu^{3+} ions, and a bright red emission is observed from Eu(TTA)$_3$phen. The sample encapsulated by the solvothermal process exhibited a higher PL quantum efficiency than the reference sample for synthesis with all ammonia concentrations used. The reason for this is not clear; however, a dense glass network is considered to be formed by annealing under the high-pressure conditions.[22] The dense glass network suppresses vibration-induced exciton loss in Eu(TTA)$_3$phen under UV light irradiation, which results in a high PL quantum efficiency.

Figure 5 shows the optical degradation characteristics of Eu(TTA)$_3$phen encapsulated by the sol-gel-derived glass network. The initial PL intensity, which corresponds to the starting point of measurement, is equal to the measured PL quantum efficiency of the encapsulated sample shown in Fig. 4. This is because the initial PL intensity was changed by changing the ammonia concentration in the sol-gel starting solution. The relative PL intensity decreased with increasing UV irradiation time due to the oxidation of the organic ligand.[19] The most important finding is that the relative PL intensity change was suppressed owing to improvement in the encapsulating efficiency of the glass network by annealing under high pressure. The longest stability of the encapsulated sample was at a relative PL intensity of 42 after 800 min of emission; however, that of the non encapsulated Eu(TTA)$_3$phen powder was at 14. This result can also be explained by the density of the glass network and the remnant organic components in the sol-gel derived glass. The dense encapsulation glass layer results in the long-term stability of Eu(TTA)$_3$phen against UV light irradiation. In addition, the PL intensity change was reduced with the decrease in the ammonia concentration in the sol-gel starting solution. The PL quantum efficiency of encapsulated Eu(TTA)$_3$phen is reduced by the addition of excess ammonia, owing to the change in the molecular structure of Eu(TTA)$_3$phen by reaction between the organic ligand and ammonia. This suggests that the initial molecular structural change of the organic ligand accelerates the oxidation of Eu(TTA)$_3$phen by UV light irradiation in air.

Figure 6 shows scanning electron microscopy (SEM) images of encapsulated Eu(TTA)$_3$phen prepared by the solvothermal process at ammonia concentrations of 0.1 and 0.5 mol%. Stable Eu(TTA)$_3$phen was obtained under both these reaction conditions. Larger particles were obtained for an ammonia concentration of 0.5 mol%. Ammonia acts as a catalyst in the sol-gel process; therefore, the particle size increased with the addition of a larger amount of catalyst (ammonia). The particles in the prepared samples aggregated with each other; however, the primary particle size was less than 1 μm in the case of encapsulation with the sol-gel derived glass.

4. Conclusions

The prevention of optical degradation using an encapsulation technique by the solvothermal process proved to be useful for improvement of the long-term stability of Eu(TTA)$_3$phen against UV irradiation. The relative PL intensity of Eu(TTA)$_3$phen encapsulated via the solvothermal process after 800 min of UV irradiation was 3 times higher than that of the original Eu(TTA)$_3$phen powder. The solvothermal process was found to be a useful technique for improvement of the long-term stability of the sol-gel glass-encapsulated Eu complex under UV irradiation.

Acknowledgment

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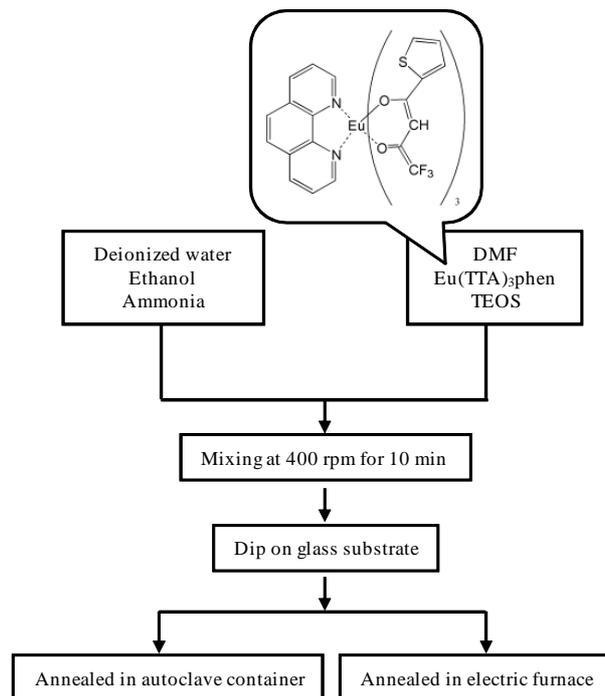
Figure captions

Figure 1. Process for the encapsulation of Eu(TTA)$_3$phen by the sol-gel process. The final annealing process is high-pressure annealing in an autoclave container or conventional annealing in an electric furnace (reference sample).

Figure 2. Relative PL intensity as a function of UV light irradiation time for Eu(TTA)$_3$phen encapsulated by (a) the solvothermal and (b) conventional annealing processes. Temperatures of 100, 120, and 150 °C were examined for optimization of annealing temperature.

Figure 3. PL and PLE spectra of Eu(TTA)$_3$phen encapsulated by the solvothermal process and the reference sample encapsulated by conventional annealing process. Optimal annealing temperatures were 150 and 120 °C for solvothermal and conventional annealing processes, respectively. The excitation wavelength for the PL spectrum was 360 nm, and the PLE spectrum was monitored at 612 nm.

Figure 4. PL quantum efficiency of sol-gel glass-encapsulated Eu(TTA)$_3$phen annealed under high pressure (solvothermal process) and annealed by conventional thermal treatment. The ammonia concentration in the sol-gel starting solution was changed from 0.1 to 2 mol% for both annealing processes.

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Figure 6. SEM images of sol-gel-derived glass-encapsulated Eu(TTA)$_3$phen by annealing under high pressure. Ammonia concentrations of 0.1 and 0.5 mol% in the sol-gel starting solution were used.
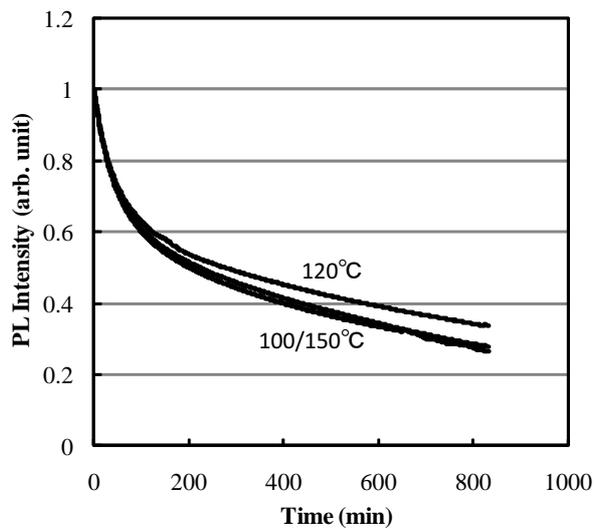
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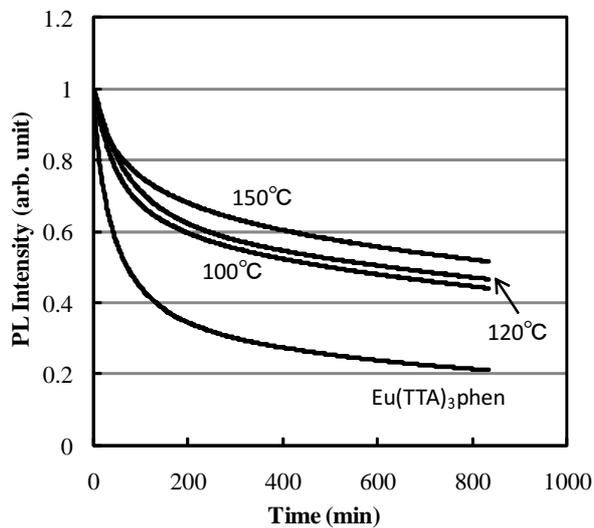
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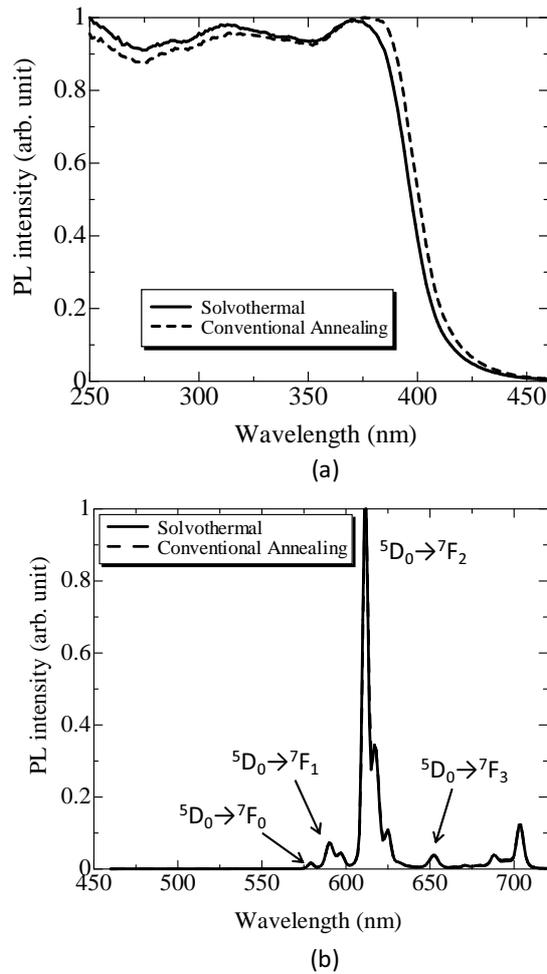
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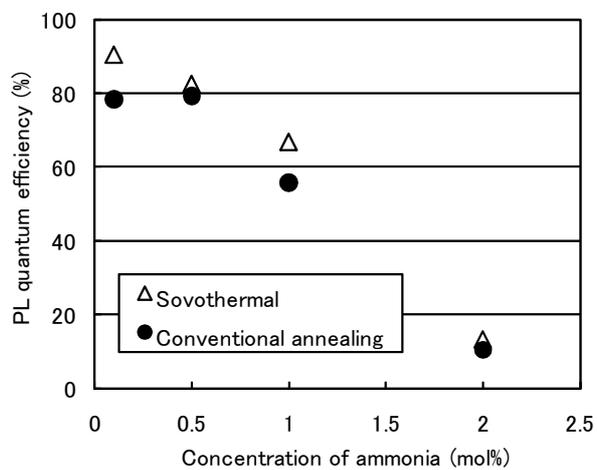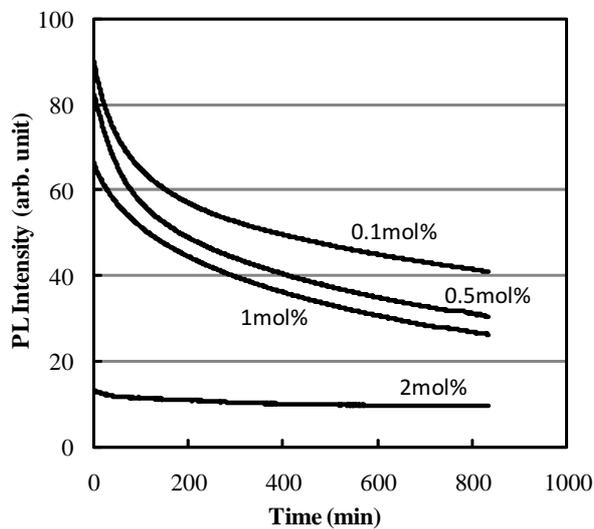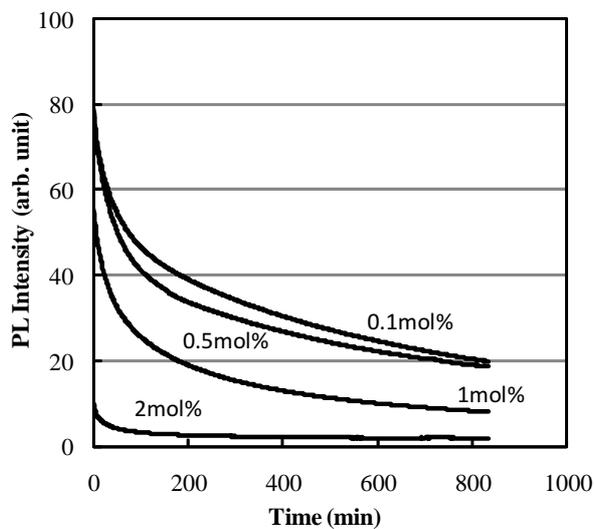
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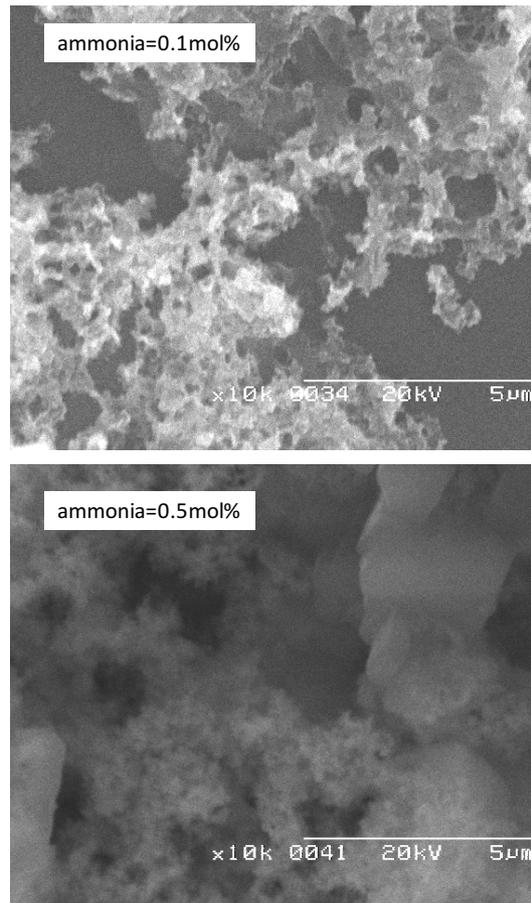
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