Infiltration of VOPcPhO into porous alumina template grown by in-situ method

Muhammad Zharfan Mohd Halizan1, Abdullah Haaziq Ahmad Makinudin3 and Azzuliani Supangatb,*

In this study, the fabrication of in-situ anodic alumina template (AAO) directly onto glass substrate is realized by varying the stirring speeds and molarity of phosphoric acid. Porous alumina template will then be used to infiltrate vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO) prior to the formation of alumina:VOPcPhO nanocomposite. VOPcPhO has been seen to fully infiltrate the template with the excess formation of VOPcPhO layer on top of the porous due to the lengthy immersion time of 6 hours. Uniformity and density of pore size, and available pore, can be respectively tuned by varying the stirring speeds (0 – 300 rpm) and molarity of pore widening agent (0 – 10 % of phosphoric acid). Rounded-sphere shape of pores has been observed with higher transparency template is dominated by stirring the speed between 100 and 200 rpm. At these speeds, the template’s pore size and pore density are highly homogeneous. Different molarity of phosphoric acid as a pore widening agent has an effect on the pore size and pore density. Occurrence of merging pores is observed by increasing the molarity of agent to 10% which unlikely to happen in the lower molarity of 5% phosphoric acid. Optical properties of alumina:VOPcPhO nanocomposites that identified from the characterization of UV-vis, photoluminescence (PL) and Raman spectroscopies, support the successful infiltration of VOPcPhO. Alumina:VOPcPhO nanocomposite has ability to absorb light at the longer wavelength and photon can be emitted by the nanocomposite at the respective energies.

Introduction

For a decade, the various methods to fabricate a high-quality porous template such as anodic aluminium oxide (AAO) have been comprehensively studied in order to generate the diverse dimensions of nanomaterials that employed in optoelectronic devices. AAO template is widely exploited due to its potential to produce the high quality nanochannel and its capability in producing the nanoscale composite. It is proven that the templating method is able to garner a low cost nanoscale fabrication, a highly uniform nanoscale production, a facile control of production process and a high aspect ratio structures of pore size over its length. Templating method has an advantage over the other techniques when it’s come to the production of high aspect ratio structure in the larger area.

AAO template can be commercially or traditionally obtained depending on the utilization of the final product. Commercial template has been extensively used in producing the novel nanostructured materials. However, its suitability only applies for the standalone formation. It is rather discouraging fabrication with the commercial template due to its poor structure controllability. Pertaining to the problem, researchers have initiated the home-made AAO template via anodization process. To date, three types of electrolyte (sulfuric acid, phosphoric acid and oxalic acid) have been used under the different conditions of voltage, temperature, etching and anodization time in fabricating the home-made template. Home-made template can be either fabricated from the aluminium foil or aluminium film which integrates the use of no substrate or with substrate, respectively. In-situ template growth would have to integrate the use of substrate in order to produce the standing porous template of good adhesion properties. In-situ grown template could benefit the bottom-up fabrication of devices with no transferring process is involving during the fabrication. Unlike the commercial template or home-made template synthesized from aluminium foil, template that grown directly on substrate has a hassle-free process.

Substrates such as glass, indium tin oxide (ITO) and silicon have been used as an excellent base due to their abilities to tune their adhesion properties with the evaporated aluminium film. Highly usage of these substrate is due to the capability of being use as an electrode in optoelectronic devices such as light emitting diode, solar cell and laser diode. In addition, the integration of substrate in the template fabrication may ease the deposition of desired aluminium thickness which indicate the final length and diameter of the nanostructured materials. To deposit aluminium layer onto these substrates, thermal evaporation technique has been used with aluminium film prepared via this technique ranging from 100 nm to 5.5 µm of thickness. Thermal evaporation technique has advantage over the DC sputtering method when it comes to metal deposition. Thermal evaporation technique can have affordable cost and deposit less damage film if compared to the latter technique. In previous works, thicker aluminium layer (1 µm - 0.25 mm) have been deposited and anodized to produce AAO template.
In-situ template growth may assist to the production of nanocomposite by infiltrating the guest material into the nanoporous. Dissolution of template by chemical etching can be done if porous template is solely used for replication purposes. However, porous template (host) can be incorporated with the infiltrated guest materials for the production of nanocomposite and further bottom-up fabrication of optoelectronic devices. Infiltrating a guest material such as vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO) into a porous template would direct to the formation of nanocomposite which can be employed in organic optoelectronics devices. VOPcPhO is highly soluble in various types of organic solvents which make it the most reliable metal phthalocyanine organic solution among its families. Various nanostructures based organic and inorganic materials such as nanowires, nanoparticles, nanorods, nanotubes, nanopods, nanoflowers, and nanocomposites have been synthesized via a templating method. In the present study, nanocomposite containing porous alumina template and VOPcPhO was fabricated onto the glass substrate and its optical properties of infiltrated VOPcPhO were elaborated to study the uniformity of nanocomposites.

Study of anodization using stirring done in previous works while application of pore widening technique by using 5 wt.% H$_3$PO$_4$ established before. To our knowledge, the deeper study effect of stirring on AAO template in sulfuric acid and the usage of other molarity H$_3$PO$_4$ of is still not studied yet. Therefore, the different fabrication parameters of porous alumina template in particular stirring speed and pore widening molarity are documented in this work. In ensuring the achievement of desired template structure, various anodization techniques involving two-and four-steps technique are introduced, while to complement the thickness of aluminium in our study, single step method is employed.

**Experimental**

Prior to the evaporation of aluminium film, the glass substrate was first cleaned with liquid soap and put in ultrasonic cleaner. Then, acetone and ethanol used for further cleaning before it being rinsed in distilled water. Glass substrate is then used for aluminium deposition process with the deployment of 20 V in voltage. In anodization process, platinum mesh and aluminium coated glass acted as a counter electrode and anode, respectively. One-step anodization technique with pore enlargement method was applied to construct anodic aluminium oxide (AAO) template (Fig. 1). Anodization process was performed at the temperature of 10°C with 0.3 M sulfuric acid (electrolyte) was placed within the bath circulator. Different stirring speeds of 0, 50, 100, 200 and 300 rpm were applied during the anodization process. The anodized samples were then immersed for 15 mins in 5% of phosphoric acid at 30°C for the pores widening. For the further morphological study, AAO templates that undergone 100 rpm of stirring speed will undergo the additional pore widening treatment by varying the molarity of phosphoric acid (0, 5 and 10 wt. %).

Vanadyl 2, 9, 16, 23-tetraphenoxy-29H, 31H-phthalocyanine (VOPcPhO) was purchased and used without further purification. VOPcPhO was dissolved in chloroform to make a 5 mg/ml solution concentration before it being used to infiltrate the AAO template. Infiltration was done by the wetting process of 6 hours immersion. Morphological properties of porous alumina template and AAO:VOPcPhO nanocomposite were characterized by field emission scanning electron microscopy (FESEM) (SU 8000, Hitachi, Japan), while the optical properties were done by UV-vis spectroscopy (Lambda 750, Perkin Elmer, Waltham, USA), photoluminescence and Raman spectroscopy (Renishaw, Gloucestershire, UK).

**Results and discussion**

**Anodization process**

Fig. 2(a) and (b) show the current (mA) versus time (s) graph during anodization of stirring and no stirring, respectively. The similar shape of graph obtained during the stirring process is reported by Taşaltın et. al. except that sulphuric acid is used in this work instead of oxalic acid. Besides, this graph is occurred in the less period of time. This could be due to the thinner aluminium used in the present work which enable the anodization to occur rapidly. Initially, current is rapidly decreased due to the formation of aluminium oxide barrier on aluminium surface. Small increase in current indicates the production of pores at random locations. Self-organizing of pores can be indicated from the constant current while decrease in current can be due to the penetration of pores to the glass substrate. Fig. 2(b) shows that the current is gradually decreased between 0 and 5 s of anodization until it achieved its steady decrement in current at 3 mA. Current has started to decrease which may have been due to the oxidation of aluminium film. An individual crack may have been formed during this stage, and gradually move through the barrier layer randomly. These cracks then acted as nucleation sites for the pores construction. Formation of self-organized pores is initiated where their structure’s composition is dominated by alumina (Al$_2$O$_3$). The steady reduction of current has supported the steady penetration process of pores into the alumina layer most likely facilitated by stirring process. Anodizing current is highly related to the movement of oxygen molecules (originated from acid) which processes ions with oxygen (O$^-$ or OH$^-$. These ions move through the barrier layer (situated at the bottom of pores) into the interface of oxide layer with the occurrence of outward drift by Al$^{3+}$ ions across the oxide structure. When the formation of oxide layer is sufficient enough, diffusion of ions start to be limited and diffusion path become longer along the porous layer.
Comparing these four different stirring speeds with the one nanocomposite undergone pore widening in 5% phosphoric acid at different stirring speeds of 0, 50, 100, 200 and 300 rpm, respectively. AAO template without stirring has a bigger pores size if compared with template that has undergone stirring process. Although, AAO template without stirring has produced a bigger pores size, its homogeneity is inconsistent. Throughout the template surfaces, pores are likely to enlarge which lead to the formation of thin-walled porous. Some of the pores become larger than the others due to the recombination of two or more pores. Stirring process could assist to the better dispersion of electrolyte by disturbing the static solution. However, the speed of stirring has a significant effect to the formation of nanopores.

Between the speed of 50 and 200 rpm, uniform formation of pores of smaller diameter and thicker wall are observed. As shown by the plot profile (inset), stirring speed between 50 and 200 rpm recorded the improvement in homogeneity and pores density with the decrement in pores size. This observation has led to the assumption that at the certain point (saturated), the pore will have to stop its expansion to avoid any recombination of two or more pores during anodization, which latter create a thinner wall. Despite of having a better homogeneity porous growth at higher stirring speed, increase the speed even higher to 300 rpm has resulted in adverse formation. Plot profile of 300 rpm has shown the non-well-arranged pores across the template. Instead of forming the uniform pores size, AAO template has only experienced the elongated-like pore shape of incomplete anodization on its surface. The elongated-like shape is a gap between the cracked alumina layers of poor transformation from its film to porous structure.

In a closed system of only the small volume of heat is allowed to escape, the stirring effect could provide exceptional temperature uniformity. The excellent temperature consistency is due to the creation of kinetic energy that originated from the stirring movement. Due to the movement of substance within the electrolyte solution, the kinetic energy will then be converted into thermal energy and satisfied the principle of conservation energy. The stirring process during anodization can slightly increase the local temperature of electrolyte acid and thus, further increase the rate of anodization (oxide dissolution and formation) and produce the smaller, more abundant (higher density) and homogenous nanopores array. At 300 rpm, the stirring is very much faster which causes the less hydrogen ion from electrolyte to fully attack the aluminium film. As reported elsewhere 15, 500 and 800 rpm of stirring speeds have been used in anodization process and succeeded to produce the unvarying nanopores structure. However, these speeds are applied on aluminium film thickness 0.25 mm in multi-steps anodization process with the fully complete anodization process is achieved.

Fig. 4(a-e) shows a 3-dimensional (3D) surface plot of AAO template with 5% of phosphoric acid (widening) at stirring speed of 0, 50, 100, 200 and 300 rpm, respectively. The size of analysed surface area is approximately 628 nm x 660 nm. These 3D surface plot graphs give information on their possible thicknesses, however, not on their quantitative surface roughness. Looking at these 3D graphs, confirmation on the formation of porous structure from all parameters can be deduced. The only difference shown between these surface plots is the opening porous which represents its pores size. If comparison between 0 and 300 rpm is made, identical opening porous is likely to be dominated by 50, 100 and 200 rpm of stirring speed. This observation is supported by their top-view FESEM images and plot profile. In addition, a large difference of surface plot properties between no stirring and stirring at 300 rpm is observed. With no stirring, the opening is larger than the one with being stirred at higher speed of 300 rpm. Stirring speed at 300 rpm can be considered as a saturated point for the desired pores to form. During the stirring process, perturbation on the static solution (electrolyte) is occurred with means of the dispersion of ions. Stirring rate affects the dispersion of electrolyte ions (O₂⁻ or OH⁻) to be transported to the anode surface. At 50 till 200 rpm, ions get well dispersed across the samples. However, at 300 rpm and higher, collision between ions occur vigorously which lead to the lower ions dispersion across the samples. Lower availability of ion may reduce the density of pores. In addition, at 300 rpm, the higher stirred force will be exerted to...
ions that about to start to act upon the sample. Consequently, these ions have easily been washed away before reaching the sample. In this work, AAO templates that considered to producing the high uniformity can be obtained using the extremely thin (~100 nm) layer of single anodization step. Sulka has reported the production of AAO templates with high uniformity however using the thicker aluminium foil (0.25 mm) and double steps method. Although the high uniformity template using thin aluminium layer of 200 nm has been reported, however the process implemented the four steps method. In the present work, the morphology of pore is slightly less well-ordered due to the non multi steps anodization and much shorter anodization period. In addition, the thinner aluminium can be the factor that contribute to the less well-ordered morphology.

Fig. 3: FESEM images of AAO template with 5% of phosphoric acid (widening) at stirring speed of (a) 0 rpm, (b) 50 rpm, (c) 100 rpm, (d) 200 rpm, and (e) 300 rpm. (Outset is a plot profile).

Fig. 4: 3-dimensional surface plot of AAO template with 5% of phosphoric acid (widening) at stirring speed of (a) 0 rpm, (b) 50 rpm, (c) 100 rpm, (d) 200 rpm, and (e) 300 rpm. (The analysed surface area is 628 nm x 660 nm).

Fig. 5: FESEM images of AAO template at stirring speed of 100 rpm with (a) no pore widening, (b) widening in 5 % phosphoric acid and (c) widening in 10 % phosphoric acid. (Outset is a plot profile).
Fig. 6: Surface plot of AAO template at stirring speed of 100 rpm with (a) no pore widening, (b) widening in 5 % phosphoric acid and (c) widening in 10 % phosphoric acid.

Stirring speed of 100 rpm is chosen for the further synthesis of porous alumina of different pore widening parameters due to its capability in producing uniform structured porous. Fig. 5(a-c) shows the FESEM images and plot profiles of AAO template at stirring speed of 100 rpm with no pore widening, widening in 5 % phosphoric acid and widening in 10 % phosphoric acid, respectively. As expected, the porous alumina with no pore widening treatment, presents the irregular pores size with elongated-like porous. This formation is comparable with the porous alumina that synthesized at 300 rpm of 5 % phosphoric acid pore widening treatment. Both stirring speed and pore widening treatment play the essential roles in producing the porous alumina template. Rounded-sphere pores will unlikely to be formed if the highest stirring speed or lowest molarity of phosphoric acid is applied. No pore widening treatment has led to an occurrence of non-expansion nucleated pore. Fig. 6 (a-c) shows the 3D surface plots of porous alumina template with no pore widening, widening in 5 % phosphoric acid and widening in 10 % phosphoric acid, respectively. The 3D surface plots support the formation of porous structure displayed in top view of FESEM images.

Fig. 7(a) shows the top-view FESEM image of alumina: VOPcPhO nanocomposite with the inset is its plot profile. Infiltration of VOPcPhO is done onto the porous alumina that synthesized from the parameter of 100 rpm stirring speed and 5 % of phosphoric acid. As expected, the top surface (morphology) of nanocomposite is different from the top surface of porous alumina. This is due to the success infiltration of VOPcPhO into the porous alumina arrays. No rounded-sphere pores are detected from the top surface of nanocomposite apart from its undulating top surface. Undulating surface is most probably originated from the formation of VOPcPhO layer on top of porous alumina surface. Infiltration and thin layer formation of VOPcPhO are supported by the cross-section view of FESEM image shown in Fig. 7(b). The FESEM image shows the infiltrated VOPcPhO between the pores with a thin layer of VOPcPhO on top of it. This brings to the fabrication of alumina: VOPcPhO nanocomposite with the thickness of porous alumina and VOPcPhO layer on top of it, is approximately 85 and 95 nm, respectively. It is clearly seen that two different regions of brighter and darker which corresponds to alumina and VOPcPhO, respectively, are successfully created. As reported elsewhere 24, 25, VOPcPhO solution is capable to infiltrate into nanoporous with pores size between 20 and 200 nm. There is no doubt for the VOPcPhO infiltration to occur into the porous alumina with pores size between 10 and 60 nm as synthesized in the present study. However, due to the lengthy immersion time of 6 hours, excess layer of VOPcPhO is created which makes total thicknesses of VOPcPhO inside the porous arrays (85 nm) and its top layer (95 nm) is approximately 180 nm. Fig. 7(c) shows the 3D surface plot of alumina: VOPcPhO nanocomposite which its dissimilarity with porous alumina template’s morphological properties is observed. This observation has confirmed the postulation on having VOPcPhO as a capable guest material to wetting the pores’ wall of higher surface tension. VOPcPhO solution with concentration of 5 mg/ml has undergone a flow into a channel of closed-end. A particular phenomenon considered in understanding fluid transport on nanoscale is capillary filling (CF) of nanochannel. This process has been studied for open capillaries which are in contact with a liquid bath at one channel end. Under this condition, CF happens with action of capillary force of viscous drag. In the sufficient length channel, CF was first done by a fast density increase due to the accommodation of molecules on the inner pore surface with unbinding of meniscus. After that, the meniscus will be accelerated towards the pore opening 26. It can be predicted that similar mechanism of fluid mechanics has occurred during the infiltration of VOPcPhO into the pores.

Fig. 8(a) presents the bar chart of pores size of porous alumina template that not undergoes a stirring process with the mode and counts is 30 nm and 164 counts per area, respectively. The total counts of pores are 560 with the mean of its diameter size recorded to be 50.34 ± 17.63 nm. Porous alumina template that obtained from the stirring speed of 50 rpm (Fig. 8(b)) shows a higher homogeneity of structured pores if compared with the one without stirring. As the stirring speed is increase to 100 rpm (Fig. 8(c)), the pores size is almost similar, however, it is highly dense
with more counts per area. Mode of pore size is 20.0 ± 9.56 nm with its counts per area is 608 and the total pores available are 1540 counts. Porous alumina template that synthesized by stirring at 200 rpm almost has the similar pores size with the former, however, recorded a slightly lower homogeneity of pores (Fig. 8(d)). Porous alumina template with no stirring can produce a larger pores size despite of having non-homogenous pores size. In contrary to the pores size, template that produced higher pore counts per unit area has resulted to the decrease in size. Fig. 8(e) presents the similar pores size and pores counts per unit area as Fig. 8(c) since they undergone the similar anodization parameter process. Fig. 8(f) depicts the pore distribution of template with 10% of phosphoric acid of pore widening treatment. With the higher concentration of acid, the largest pores size of 40 nm can be formed with the counts per unit area are 292. The reason to the largest formation of the pore size is the occurrence of individual pores’ merging with their neighbouring pores. A higher molarity of phosphoric acid can contribute to a higher availability of hydrogen ions and molecules. Therefore, the reaction rate to form the pore is increased, with more area is being attack by hydrogen ions and molecules to construct a bigger pore. Except for 300 rpm and no stirring, diameter and pattern of pores obtained are comparable to pores obtained by H. Zhou et al. However, smaller pores available in the present work due to employment of sulphuric acid instead of oxalic acid.

Optical characteristics of porous alumina and alumina:VOPcPhO nanocomposite

Fig. 9(a) demonstrates the transmission spectra of glass and porous alumina template of different stirring speeds deposited onto glass. As demonstrated in the spectra, glass with no deposition of alumina, depicts 100% of transmittance which is used as reference. W. Zaghoudi et. al reported that glass substrate has 100% transmittance value while shape of graphs obtained are comparable with H. Zhou et. al. Porous alumina templates that obtained by stirring the speed between 50 and 200 rpm record transmittance between 45 and 85% with 200 rpm of stirring speed produced a higher transparency template. Meanwhile, porous alumina template that fabricated with no application of stirring recorded the lowest transmittance percentage of 28%. Highest transparency presented by template without stirring has much connected to its morphological properties. As mentioned earlier, template without stirring has a wider pore size distribution between 10 and 90 nm than the template with stirring. The range of pore size distribution of template with stirring is between 10 and 60 nm. Due to the variations of pore size, light interference order and light absorption will be higher. The less transparent porous alumina template of larger pore size variations can cause to the higher absorption by the available acid radical and aluminium remains since template is not undergoes the annealing treatment. Refractive index of glass, $n_{\text{g}}$, are calculated using the equation given in (1) while other samples’ refractive index are calculated using manifacier method. Porous alumina template of no stirring, 50, 100 and 200 rpm has recorded a refractive index of 3.86, 3.76, 3.38 and 2.94, respectively, while a refractive index of glass substrate used in this study is 1.15. Since the sample of 0 rpm has low homogeneity of porous structures, it possesses fewer pores compared to stirred samples. Therefore, it has the lowest transmittance. In perfect transmittance situation, the vibrations of the electrons will be passed on to neighbouring atoms through the bulk of the material and reemitted on the opposite side of the object. However, in our work, the light wavelength is undergone Rayleigh scattering due to the presence of nanochannel structures. Sample of 0 rpm possessed the highest Rayleigh scattering. This is due to the variation of pore size between 10 to 90 nm. Furthermore, low homogeneity of porous will further reduce the scattering all over sample’s structure. The stirred samples have lower Rayleigh scattering since their pores’ structures are more homogenous in diameter. These are the reasons for the stirred sample to have a higher value of transmittance compared to the no stirred one.

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2}$$

Where $T_s$ = transmittance of glass and $n_s$ = refractive index of glass.

![Fig. 8: Chart distribution of template with pores diameter of (a) 0 rpm, (b) 50 rpm, (c) 100 rpm, (d) 200 rpm, (e) widening in 5 % phosphoric acid and (f) widening in 10 % phosphoric acid.](image-url)
Table 1. Peaks absorption of alumina: VOPcPhO nanocomposites.

<table>
<thead>
<tr>
<th>Bands / Stirring speeds</th>
<th>0 rpm</th>
<th>50 rpm</th>
<th>100 rpm</th>
<th>200 rpm</th>
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</thead>
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<tr>
<td>B-band</td>
<td>354 nm</td>
<td>354 nm</td>
<td>355 nm</td>
<td>354 nm</td>
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<tr>
<td>1st Q-band</td>
<td>677 nm</td>
<td>678 nm</td>
<td>679 nm</td>
<td>683 nm</td>
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<tr>
<td>2nd Q-band</td>
<td>715 nm</td>
<td>718 nm</td>
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Fig. 9: (a) Effects of stirring speed on transmittance of porous alumina and (b) UV-vis absorption spectra of alumina: VOPcPhO nanocomposites.

Fig. 10: (a) Photoluminescence (PL) spectra and (b) Raman spectra of alumina: VOPcPhO nanocomposites.

Table 2. Photoluminescence (PL) peaks of all parameters that obviously corresponded to their UV-vis absorption spectra.

<table>
<thead>
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<th>Bands</th>
<th>Stirring speeds</th>
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<td>B-band</td>
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<td>2nd Q-band</td>
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Postulation on the dependency between photon absorption, π-π* transition and architecture of template can be rather acceptable. VOPcPhO that have been infiltrated into the various pores size (10 - 100 nm) will halt the π-π* transition. Quenching effect is observed by the nanocomposites that fabricated from the porous alumina template synthesized at stirring speeds of 100 and 200 rpm which exhibited a better photo-induced charge transfer.
In addition, the red-shifted shown at B-band and 2nd Q-band by the 100 rpm and red-shifted at 1st Q-band shown by 200 rpm of UV-vis absorption spectra are correlated with the red-shifted shown in their PL spectra. This characteristic is highly significant for the sensor fabrication and production. Fig. 10(b) shows the Raman spectra of alumina: VOPcPhO nanocomposites of all parameters. Nanocomposites have exhibited the similar Raman shifts however with different in their intensities. Assignments and changes of wavenumbers are presented in Table 3. Alumina:VOPcPhO nanocomposite that fabricated from the template of 100 rpm has shown similarity in its Raman shifts at 687, 1003, 1193, 1236, 1341, 1464, 1528, 1591 and 1616 cm\(^{-1}\) with VOPcPhO nanotubes that have been reported elsewhere. The other Raman shifts at 838 and 1113 cm\(^{-1}\) have similarity with the Raman shift of VOPcPhO thin film. These Raman shifts could be due to the presence of VOPcPhO thin film layer on top of the infiltrated VOPcPhO. There are two Raman shifts at 1395 and 1479 cm\(^{-1}\) that have not been reported for VOPcPhO which could be from the contribution of alumina.

Table 2: Photoluminescence peaks of alumina: VOPcPhO nanocomposites.

<table>
<thead>
<tr>
<th>PL peaks (nm)</th>
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<th>100 rpm</th>
<th>200 rpm</th>
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<tr>
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<td>883</td>
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<td>885</td>
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Table 3: Raman shift and assignments of alumina: VOPcPhO nanocomposites.

<table>
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<th>Raman shift (cm(^{-1}))</th>
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<tr>
<td>686</td>
<td>Macrocycle breathing</td>
</tr>
<tr>
<td>838</td>
<td>Macrocycle stretching</td>
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<td>1002</td>
<td>Benzene ring breathing</td>
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<td>C-H bending</td>
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<td>Pyrrole stretching</td>
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<tr>
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<td>1615</td>
<td>C=C stretching</td>
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