

## 3D photonic crystals based poly (methyl methacrylate) for active photonic SERS substrates

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**Abstract.** Synthesis of 400 nm average size poly (methyl methacrylate) (PMMA) and fabrication onto surface-enhanced Raman scattering (SERS) active substrate were presented.

“Bottom-up” technique was employed to fabricate SERS active substrate while PMMA suspension was obtained via surfactant-free emulsion polymerization. Morphology of fabricated PMMA photonic crystals (PMMAPc) SERS substrate was observed through scanning electron microscopy (SEM) with 20 000 magnification at 10 kV power. Photonic properties measurement was carried out using ocean optic spectrometry at range of 800 nm to 900 nm. Thermal resistivity study was measured through thermogravimetric analysis (TGA) over a range of 0 °C to 500 °C. Subsequently, enhancement percentage assessment by Raman spectroscopy provided evidence that PMMAPc SERS substrate potentiality towards Raman signal by using 4-aminothiophenol (4-ATP) as probe molecule. Evidence from SEM supported that highly homogenous PMMA particles fabricated onto thin film brings wellordered arrangement in agreement with photonic crystals design. The proposed model was assessed experimentally using ocean optic spectrometry show a wide dip transmission at 899 nm and thermally stable up to 336 °C. Raman spectrum of 4-ATP using normal Raman analysis (without using PMMAPc SERS substrate) and using PMMAPc substrate support the results of the improvement of Raman signal upon 45 %. Low cost and large area fabrication would suggest PMMAPc as convenient yet affordable active SERS substrate for advance and fast detection.

### 1. Introduction

Optical properties that exist in periodic structure materials are one of excellent candidate towards technology development. This highly ordered material was so called as photonic crystals (Pc) where it has an ability to manipulate light in a very interesting way. The idea of creating these synthetic opals at first adopted from nature for example we can observe on butterflies wings, sea mice and even certain flowers [1-4]. The periodicity of Pc structures give rises to the propagation of electromagnetic (EM) in the material generally possessing photonic bandgap (PBG) where a region of range which light cannot propagate through the structure [5,6]. The potential was discovered and was divided to three types (1D, 2D and 3D) according to its ability in reflecting light. The dimensionality referred to as differing refractive index ( $n_{eff}$ ) materials within the Pc which  $n_{eff}$  varies along one, two and three direction respectively. This behavior leads to difference ability in possessing photonic PBG properties [6-8]. Thus 3dimensional (3D) Pc become major interest as it was potential to offer complete photonic band gap properties. Complete PBG is very important in development and advance new technology in telecommunication and imaging [9-11].

The unique properties of Pc attracted considerable interest in creating artificial opal to be fabricated onto thin film especially for surface-enhanced Raman scattering (SERS). There is several technique



proposed in fabricating SERS substrate for instance lithographic and dielectric layer stacking of This technique could fabricate a high quality 3D thin film however it required high cost which most company can't afford while it produced non-scalable film [12][13]. In addition, most of SERS substrate was proposed plamonic properties material for the enhanced effect and this might challenge the fabrication process thus specific instrument was used as mentioned before. Therefore it is sensible to introduced Pc as a material for SERS substrate fabricate Pc via "bottom-up" technique in which the particles were let to self-assemble onto thin film. Besides of its inexpensive choice "bottom-up" technique also can be performed in common laboratory practise which no complex procedure and expertise needed. Pc design could be constructed from many kind of material and silica is the commonly used due to its versatility however it could be a problem in etching process if using it as a template. High tendency of stacking fault is another remarkable disadvantage of using silica in construction of Pc because it will distort the sequence of lattice arrangement thus lead in distorted PBG. Yet, another great candidate in replacing is polymer. Among them, Poly (methyl methacrylate) (PMMA) is a correct option due to its short reaction period, flexible in designing, chemically stable, durable and weather resistance [14]. These characteristics of PMMA promising its ability to be incorporate in most photonic devices such as optical lenses in cameras and optical fiber [15].

In this study, 3D photonic crystals based SERS substrate was prepared. PMMA spheres was synthesised at 400 nm average particle size and used as main material in designing Pc. These polymeric materials could be prepared by emulsion polymerization [16], batch polymerization [17] and miniemulsion [18]. However in this project we proposed of using free-surfactant emulsion polymerization due to the enormous bad effect of surfactant to environment especially in causing water pollution [19]. The "bottom-up" technique was used as the fabricating method of the SERS substrates and produced a highly ordered FCC lattice arrangement of PMMA spheres. PMMAPc SERS substrate was experimentally investigated it performance using Raman spectroscopy with probe molecule 4-aminothiophenol (4-ATP) and successfully enhanced Raman signal up to 45 %. Finally the conclusion are summarised and some finding remarks made.

## 2. Experimental

This work consists of synthesis of poly (methyl methacrylate) (PMMA) and fabrication of obtained PMMA spheres onto photonic crystals design called as PMMAPc. PMMAPc was investigated its performance as SERS substrate.

### 2.1. Materials

Methyl methacrylate monomer (MMA, 99%) was purchased from Aldrich (Milwaukee, WI, USA) while, 4-aminothiophenol (4-ATP), potassium persulphate (KPS), ammonium hydroxide (NH<sub>3</sub>OH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were purchased from R&M Marketing (U.K). Deionised water (DI H<sub>2</sub>O, resistivity 18.0 MΩ) was used as reaction medium and for the preparation of all solutions. All chemicals and solvent were used as received without further purification.

### 2.2. Synthesis of homogenous PMMA spheres

PMMA sphere was prepared via surfactant-free emulsion polymerization in line with green-chemistry approach in which toxic solvent and linking agent were also exceptionally used. 64 ml of DI H<sub>2</sub>O was heated under nitrogen gas at 90 °C in tri-neck flask by silicon oil bath. Hotplate used was equipped with stabilizer rod to highly control the temperature throughout the experimental because polymerization was highly dependence on temperature. 15 ml of monomer was added followed with initiator KPS (0.1318M, 16 ml) and the reaction were continued for 45 minutes under stirring at 250 rpm. PMMA suspension was let to cool at room temperature. The filtrates was centrifuged, redispersed and re-agitated several times before fabrication.

### 2.3. Fabrication onto 3D photonic crystals

**2.3.1. Substrate preparation.** Microscope glass slide was used as substrate for fabrication of PMMA spheres as 3D photonic crystals. The glass slide was cut and cleaned with acetone by ultrasonication for 30 minutes and further treated with a mixture of DI H<sub>2</sub>O, NH<sub>3</sub>OH and H<sub>2</sub>O<sub>2</sub> with ratio of 3:2:2 for at least an hour. This treatment is to create hydrophilic surface on the glass slide and ensure the attachment of PMMA spheres feasibly during fabrication.

**2.3.2. PMMAPc growing film.** 400 µl of PMMA suspension was dispersed in 9.6 ml of DI H<sub>2</sub>O in a glass vial. Treated glass slide was immersed in the dispersed suspension vertically at approximately 45° settlement. PMMAPc thin film was let grow in an oven at 60 °C for 2 days. Fabrication required highly control evaporation rate thus the temperature was kept constant during the process without any disturbance.

### 2.4. Characterizations

Average size of PMMA spheres was measured using particle size analyzer (PSA, Malvern, UK) in wet mode by adding several drops of PMMA suspension onto 300 ml distilled water with turbine speed of 4000 rpm upon analysis. The analysis was taken 3 times and the average was recorded. Morphology of PMMAPc was observed through scanning electron microscopy (SEM, JEOL model 6360F) at magnification of 20 000. The PMMAPc substrate was sputter coat with gold before viewing to minimize charging effects. Thermal resistivity study was performed using Mettler-Toledo thermo galvanic analysis (TGA) with a heating temperature over a range of 0 °C – 500 °C with argon gas flowrate at 10 ml per minute. Optical property was investigated using a halogen white light source. The transmitted light was collected with a detector and recorded via Ocean Optics spectrometer.

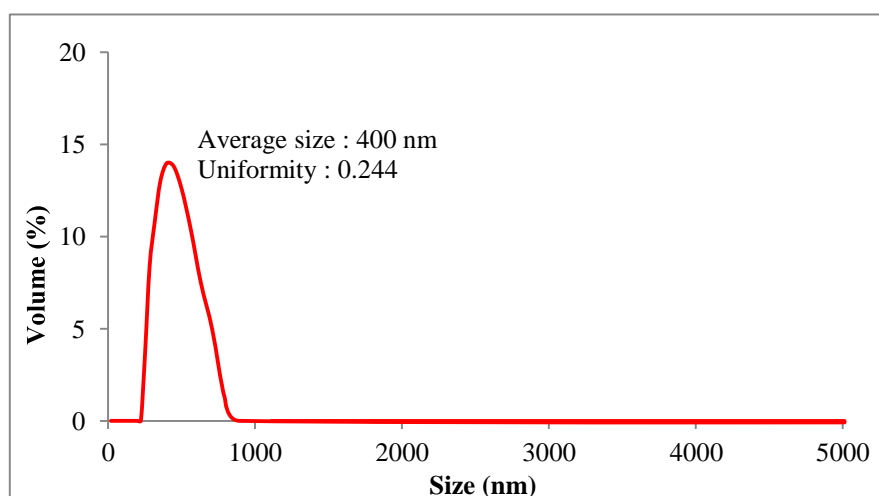
### 2.5. PMMAPc as SERS substrate

4-aminothiophenol (4-ATP) was used as SERS probe molecule and was prepared at concentration of  $1.0 \times 10^{-7}$  M. 50 µl of prepared 4-ATP was drip onto fabricated PMMAPc and let dried in ambient condition for several minutes. The analysis was performed using microconfocal Raman spectroscopy (InVia Renishaw) at 514 nm with laser power of 200 mW, 20x lenses magnification and 2 s accumulation time. The analysis was taken 7 times to ensure the stability of PMMAPc as SERS substrate.

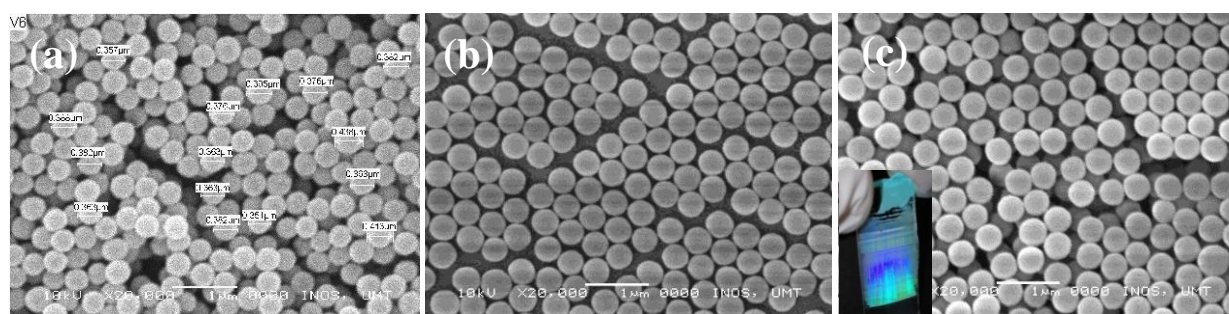
## 3. Results and discussion

### 3.1. Physical characterizations

A size distribution plot of PMMA measured by PSA is shown in figure 1. In view of the results obtained narrow distribution was observed from the analysis graph and the average size was obtained at 400 nm. Accordingly, the uniformity index was recorded at 0.244 showing narrow distribution properties. These statistics provide information of highly homogenous PMMA spheres was successfully synthesised even with exceptionally used of surfactant. In this work the homogeneity of PMMA sphere was an important parameter in construction to photonic crystals. This was advance checked by SEM as shown in figure 2 (a) and the average size with uniformity was found to be no significant different with those measured using PSA.

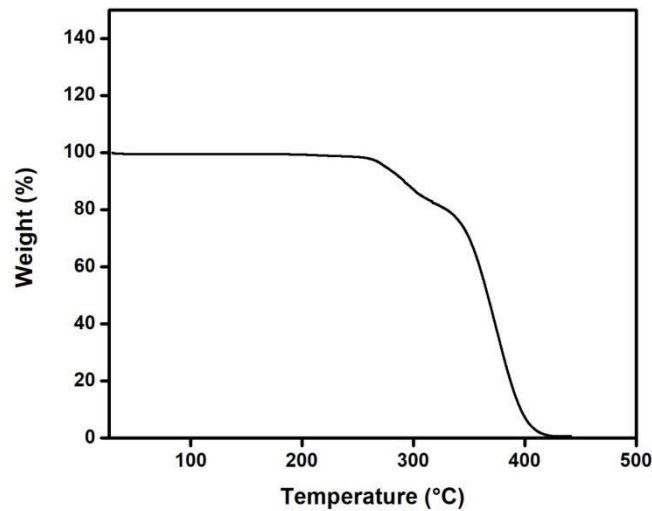


**Figure 1.** PSA analysis of PMMA suspension



**Figure 2.** SEM image of PMMA spheres (a) in dispersion (b) monolayer PMMA film and (c) double layer PMMA film

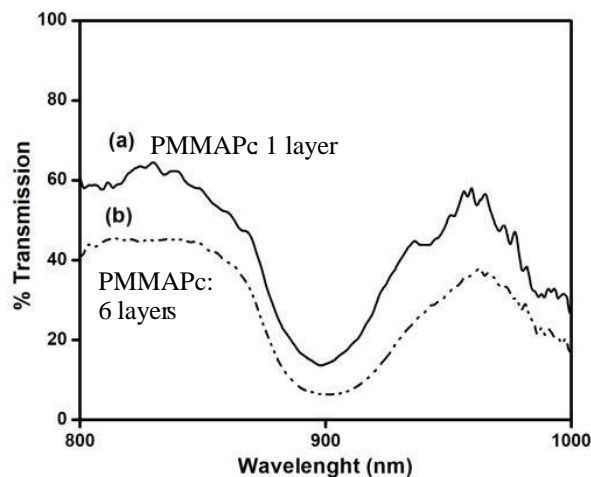
Figure 2 shows SEM images of PMMA sphere in dispersion and after the fabrication. As earlier mentioned the average size of PMMA obtained have nearly similar as measured using PSA, however slight shrinkage might be observed from SEM compared to PSA might due to the shrinkage of PMMA spheres from heating process during sample preparation for SEM viewing. In figure 2 (b), the image of fabricated PMMA or PMMAPc was display a highly homogenous and well-ordered in face-centred cubic (FCC) lattice structure. From the image, the self-arrangement of PMMA colloidal sphere onto FCC lattice structure would give rise to photonic band gap (PBG) properties hence beneficial in manipulating Raman signal [20, 21]. Accordingly, homogenous spheres play an important role in successfully creating FCC lattice structure thus exhibit PBG properties. Figure 2 (c) shows SEM image of PMMAPc film that consist of two layer of particles. The size and parameter is equal however the volume of PMMA suspension was double during the fabrication process. It can be observed clearly the existence of second layer beneath. This indicate that layer of PMMAPc was tunable by changing the volume of uspension during preparation as mentioned in section 2.3.2. The supplementary insert photograph image displays the fabricated PMMA thin film that appear opalescence on naked eyes when interact with light. Simple and cost-effective SERS substrate could be developed by highlighting the unique yet powerful photonic crystals properties in manipulating Raman signal. Furthermore, “bottom-up” technique could be practised upon fabrication of photonic crystals film which promising high quality large area substrate. The overall performance of PMMAPc substrate will be discussed in the next section.



**Figure 3.** TGA curve of PMMA spheres

Figure 3 shows percentage loss of PMMA under thermal stress over a range of 0 to 500 °C using TGA at 10 °C/minute in argon atmosphere with a purge rate of 10 ml/minute. In view of the result obtained, a little weight loss (8.06 %) occurred up to a temperature of 297 °C. However, immediately beyond this temperature, a major decrease in weight was observed, and at 441 °C, almost complete weight loss was observed. This major weight loss is recorded to 68.05 % corresponding to degradation of random chain scission process of PMMA polymer [22][23].

### 3.2 Optical properties



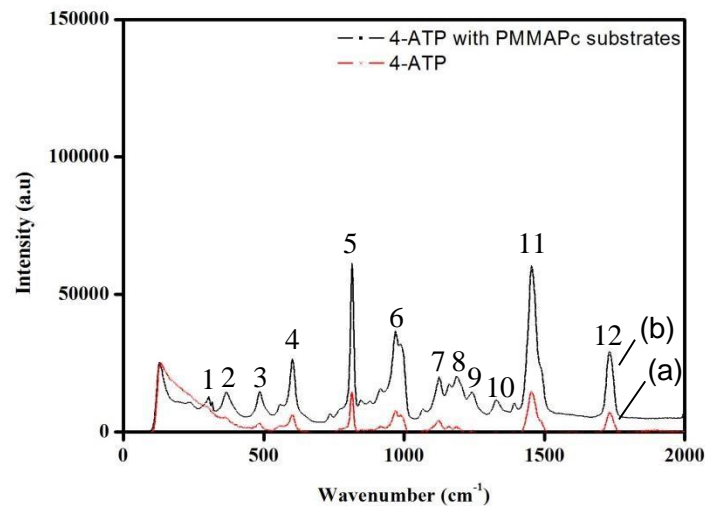
**Figure 4.** Transmission spectra of PMMAPc film in correlation to layer of the film (a) 1 layer and (b) 6 layers.

Figure 4 shows transmission spectra obtained from ocean optic spectrometer for a layer and 6 layers of PMMAPc according to curve (a) and (b) respectively. White light was strikes at 0° and the spectra were collected from the detector. As can be seen wavelength dependence for transmission which their periodicity and amplitude decrease when increasing the number of layers. Wide dip in the transmission spectra at 899 nm corresponding to the Bragg reflection peak, when propagation through the opal is nearly forbidden.



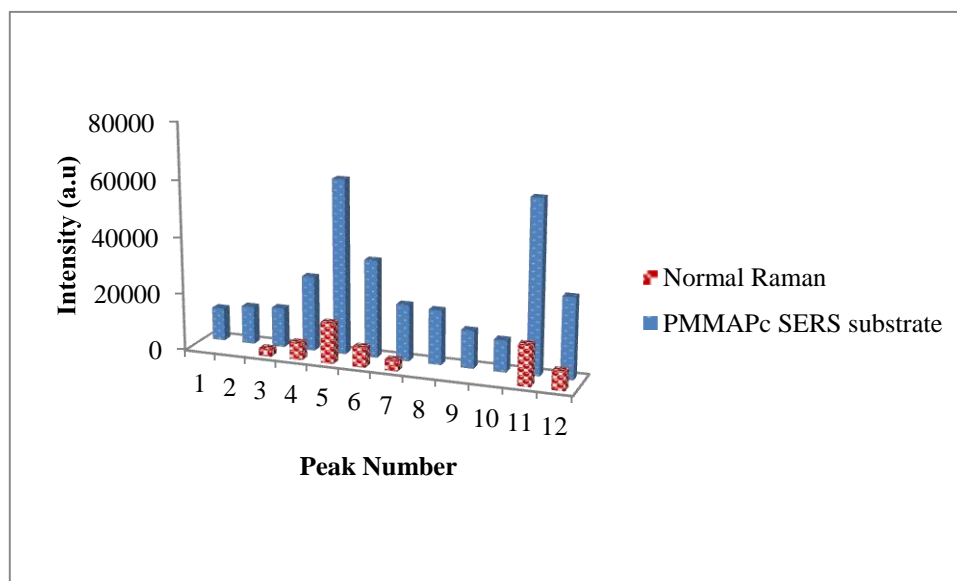
### 3.3 PMMAPc as SERS substrate

Final investigation towards PMMAPc ability in enhancing Raman signal was performed using Raman spectroscopy with 4-ATP as SERS probe molecule. 4-ATP was analysed without using PMMAPc SERS substrate and by using the substrate and the obtained spectrum was summarized in figure 5.



**Figure 5.** Raman spectra of 4-ATP (a) without PMMAPc substrate and (b) with PMMAPc substrate

Figure 5 shows graph obtained from Raman spectroscopy analysis of 4-ATP by normal Raman and by using PMMAPc substrate. From the graph the red line (line (a)) indicating the curve of 4-ATP from normal Raman while black line (line (b)) is corresponding to the curve of 4-ATP using PMMAPc substrate. It can be seen clearly that the obtained curve of 4-ATP using PMMAPc substrate was found to be higher than the one who does not use the substrate. Several absent peaks of 4-ATP were also remarked from line (a) compared to line (b), indicating that the sensitivity of detection was increased by using PMMAPc SERS substrate. Graph of enhancement for each peak was summarized in figure 6 to visually show a clearer enhancement for each peak accordingly.



**Figure 6.** Enhancement of intensity for each corresponding peak in figure 5

Figure 6 shows intensity for the enhancement of each peak accordingly (refer figure 5). Peak 1, 2, 8, 9 and 10 does not show up in normal Raman analysis however enhancement up to 11595, 13320, 1194, 1250 and 1333 a.u was obtained from SERS analysis. To be noted, the analysis was performed on a very low concentration of 4-ATP which is  $1.0 \times 10^{-7}$  M. This reveals the sensitivity of PMMAPc SERS substrate that would be beneficial in detection of limited sample for example in forensic and cancer studies. The other major enhancement were also spotted from peak 3, 4, 5, 6, 7, 11 and 12 up from 20 to 45 % in average. An excellent performance of PMMAPc SERS substrate was successfully proved from the analysis thus the proposed design of using Pc as one of developed materials in SERS substrate was reasonable.

#### 4. Conclusion

This work was devoted to assess the ability of PMMAPc to enhanced Raman analysis. This was performed by investigating the enhancement peak for normal Raman of 4-ATP with a 4ATP/PMMApC SERS substrate. The results of PSA shows a homogenous PMMA sphere was successfully obtained from surfactant-free emulsion polymerization. From SEM observation PMMAPc substrate have well-ordered FCC lattice structure that would exhibit PBG properties as explained by ocean optic analysis. TGA analysis shows PMMAPc have experienced polymer degradation at temperature 336 °C this properties supported the uses of PMMAPc as SERS substrate as it could stand at high temperature during sample preparation or analysis process. An experiment was carried out to assess the proposed SERS substrate and comparison to normal Raman analysis using 4-ATP probe molecule. Sensitive PMMAPc SERS substrate able to reveals several peak that was absence during normal Raman analysis and also increase the enhancement of Raman spectra up to 45 %. It is considered that the PMMAPc SERS substrate can provide a low cost, robust, large area and sensitive detection over Raman analysis. All the obtained results suggest that photonic crystals have a bright potentiality in enhanced Raman analysis thus the combination of this material with metallic nanoparticles into such metalodielectric photonic crystals (MDPCs). The MDPCs structure was expected to enhance Raman signal thus serve as ultrasensitive SERS substrate.

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