

# Nanoparticle-coated PDMS elastomers for enhancement of Raman scattering†‡

Gang Lu,<sup>a</sup> Hai Li<sup>a</sup> and Hua Zhang<sup>\*ab</sup>

<sup>a</sup>*School of Materials Science and Engineering,  
Nanyang Technological University, 50 Nanyang Avenue,  
Singapore 639798, Singapore. E-mail: hzhang@ntu.edu.sg, hzhang166@yahoo.com; Web:  
http://www.ntu.edu.sg/home/hzhang; Fax: +65 67909081*

<sup>b</sup>*Center for Biomimetic Sensor Science,  
Nanyang Technological University, 50 Nanyang Drive,  
Singapore 637553, Singapore*

† *This article is part of the ChemComm ‘Molecule-based surface chemistry’ web themed issue.*

‡ *Electronic supplementary information (ESI) available: Detailed experiments, characterization and Raman results. See DOI: 10.1039/c1cc12027a*

**A simple but efficient method for highly sensitive Raman detection, covering a thin polydimethylsiloxane elastomer, pre-coated with a layer of Au or Ag nanoparticles, onto the detected substrate, is proposed. Moreover, this nanoparticle-coated PDMS elastomer can be used for chemical imaging with high sensitivity.**

Since it was discovered on the electrochemically roughened Ag surface in 1970s,<sup>1</sup> as a sensitive surface characterization technique, the surface enhanced Raman scattering (SERS) has attracted much attention and has been widely employed in physics, chemistry, biology, *etc.*<sup>1–4</sup> In the past decades, various methods, such as e-beam lithography, focus ion beam lithography, colloidal lithography, nanoimprint lithography and self-assembly of nanoparticles (NPs),<sup>3,4–6</sup> have been applied to fabricate SERS-active substrates. Although lots of metallic nanostructures have been proved to be SERS active,<sup>5,7</sup> the applications of SERS is still limited due to the following reasons. First, the metallic nature of the currently used SERS substrates makes them difficult to strongly adsorb many molecules, such as aromatic molecules, DNA, protein, *etc.*<sup>3,8</sup> Second, the detected molecules are normally coated on the SERS-active substrates,<sup>9</sup> so it is difficult to get chemical images by using the conventional SERS method.

Recently, the tip-enhanced Raman spectroscopy (TERS) has been developed to overcome the aforementioned drawbacks.<sup>9–13</sup> Thanks to the local electromagnetic near-field enhancement provided by an illuminated STM or AFM tip, TERS, as a widely applicable spectroscopy and microscopy tool, has been used to detect various molecules on various substrates.<sup>9,11,12</sup> Besides these, TERS can also be used for surface chemical imaging at the nanometre scale.<sup>10,11,13</sup> However, a special setup for TERS is required, and fabrication of the tip is quite complex. Furthermore, the total Raman scattering signal from the tip area (about 20–50 nm in diameter) is rather weak.<sup>9,13</sup> Therefore, the application of TERS is limited.

In this communication, after Au or Ag NPs are adsorbed onto the 3-aminopropyltriethoxysilane (APTES)-modified polydimethylsiloxane (PDMS) elastomer, it is used as a novel tool for the enhancement of Raman scattering. This method can be used for the sensitive Raman detection of molecules adsorbed on solid substrates by simply covering the NP-coated PDMS elastomer onto the detected surface. Importantly, this method is also used for chemical imaging to distinguish the micropatterns of *p*-aminothiophenol (PATP) and methylene blue (MB) with high Raman sensitivity. Compared with TERS, the total Raman scattering volume in our method is much larger, leading to a much stronger Raman signal collected.

In this work, the Au or Ag NP-coated PDMS elastomer was fabricated and used for highly sensitive Raman detection and chemical imaging of molecules. The detailed experiments are shown in ESI.z Briefly, the thin PDMS elastomer was prepared by curing the mixture of Sylgard<sup>®</sup> 184 elastomer and curing agent (w/w = 10: 1) at 70 °C for 12 h,<sup>14</sup> followed by O<sub>2</sub> plasma treatment and then APTES modification.<sup>15</sup> Afterwards, the Au or Ag NPs were adsorbed onto the APTES-modified PDMS elastomer (Scheme 1A), thanks to the electrostatic interaction between the negatively charged NPs and the positively charged APTES self-assembled monolayers (SAMs).<sup>15,16</sup> The as-prepared NP-coated PDMS elastomer serves as a flexible, convenient and efficient tool for highly sensitive Raman detection and chemical imaging of molecules adsorbed on a solid substrate by simply covering this elastomer onto the detected surface (Scheme 1B).

It has been reported that Au NPs can enhance the Raman signal of molecules, which adsorbed on or were close to the Au NPs.<sup>17,18</sup> On the surface of as-fabricated Au NP-coated PDMS elastomer, lots of Au NPs are coated, which serve as the hot spots in Raman detection. When the Au NP-coated PDMS elastomer covers the detected substrate, the Au NPs contact with or are close to the molecules on the solid substrate, resulting in Raman signal enhancement of the molecules. As shown in Fig. 1A, the highly sensitive Raman intensity of the MB monolayer on the Ag surface was measured with the aid of the 38 ± 3 nm Au NP-coated PDMS elastomer. The enhancement factor (EF) can be calculated using the equation  $EF = (I_{surf}/I_{bulk})(N_{bulk}/N_{surf})$ .<sup>19</sup> Before covering with the 38 ± 3 nm Au NP-coated PDMS elastomer, the EF of MB on the Ag surface is  $3.2 \times 10^4$  (based on the band at 1625 cm<sup>-1</sup>), while it increases to  $3.8 \times 10^6$  after covering with the 38 ± 3 nm Au NP-coated PDMS elastomer, resulting in a 120 times increase (Fig. 1A). We believe that the Raman enhancement arises from the formed Ag–MB–Au NPs sandwich structures between the Ag surface and Au NPs on the PDMS elastomer.

In a typical TERS, the EF around the tip is about 10<sup>4</sup>.<sup>10</sup> However, due to the limited tip area (*ca.* 20–50 nm in diameter)<sup>9,13</sup> and the only one tip serving as the Raman hot spot, the total Raman scattering signal is quite weak. In our experiment, there are about 200 Au NPs (size of 38 ± 3 nm) in 1 μm<sup>2</sup> area (Fig. 2C) serving as Raman hot spots, resulting in the dramatic enhancement of the Raman signal in our experiment since the size of a typical laser beam in a confocal Raman spectrometer is *ca.* 1 μm<sup>2</sup>.

As shown in Fig. 1B, the detected Raman intensity of MB on the Ag surface after covering with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer is quite uniform, indicating the uniform Raman enhancement of our method. Although the adsorption of 38 Au NPs on the PDMS elastomer is not uniform in the nanometre scale (Fig. 2C), it is relatively uniform in the micrometre scale. Since the diameter of the laser beam is in the micrometre range, the Raman mapping of MB shows quite uniform Raman intensity after covering with the Au NP-coated PDMS elastomer. All the aforementioned experimental results demonstrate that the Au NP-coated PDMS elastomer can serve as a simple, efficient and convenient tool to uniformly enhance the Raman signal of molecules on solid substrates at the micrometre scale. In addition, the Au NP-coated PDMS elastomer can be reused, since the MB molecules are not adsorbed on the elastomer, which only exist on the underneath Ag substrate.

In our experiments, the PDMS elastomer was chosen to adsorb Au NPs and then used for enhancement of the Raman signal of molecules adsorbed on solid substrates, because the PDMS elastomer is transparent, soft and easy to be attached onto the solid substrates, leading to the uniform contact with the underneath detected surface. As a comparison, glass, much more rigid than PDMS, is not suitably used in this method, since the Au NP-coated glass cannot contact very well with the underneath detected surface, leading to much larger distance between Au NPs and the molecules on the solid substrate. Therefore, the Raman intensity does not show the obvious enhancement (data not shown here).

As shown in Fig. 2, the size of adsorbed Au NPs plays an important role in enhancement of the Raman signal. The  $13 \pm 1$  nm Au NP-coated PDMS elastomer (Fig. 2A) gives poor Raman enhancement, which is only a 13 times increase for MB (band at  $1625\text{ cm}^{-1}$ ) after covering it on the MB-coated Ag surface (curve a in Fig. 2D). However, the Raman enhancement is much larger for larger Au NPs. Fig. 2D shows the results for the  $16 \pm 8$  and  $38 \pm 3$  nm Au NP-coated PDMS thin elastomers, and the Raman intensity of MB increased 32 and 120 times (band at  $1625\text{ cm}^{-1}$ ), respectively. The better performance of larger Au NPs is due to the stronger coupling between the larger Au NPs.<sup>17</sup> For PATP, the Raman signal can hardly be observed before covering with the Au NP-coated PDMS thin elastomer. However, after covered with the Au NP-coated PDMS thin elastomer, the Raman intensity of PATP increased dramatically and was easily observed (Fig. 2E). Similarly, the  $38 \pm 3$  nm Au NP-coated PDMS elastomer gives largest enhancement of PATP coated on the Ag substrate, resulting in EF values of  $4.6 \times 10^6$  and  $7.9 \times 10^7$  for bands at  $1072$  and  $1141\text{ cm}^{-1}$ , respectively. In addition, an Ag NP-coated PDMS thin elastomer can also serve as an efficient, convenient and flexible tool for highly sensitive Raman detection of molecules (Fig. S1, ESI†).

Our experimental results mentioned above indicate that the Au or Ag NP-coated PDMS elastomer can be used for highly sensitive Raman detection of molecules on Ag substrates. More importantly, by using this method, the highly sensitive chemical imaging can be easily achieved. Fig. 3 demonstrates the detection of PATP and MB micropatterns on Ag surface. The patterns were fabricated *via* microcontact printing ( $\mu\text{CP}$ ) of PATP dots, followed by passivation with MB

(Fig. 3A). In normal conditions, the as-fabricated PATP-MB micropatterns cannot be imaged with confocal Raman microscopy even with a long integration time of 0.5 s (Fig. 3B). However, after covered with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer, the patterns can be easily imaged even with a short integration time of 0.01 s. Fig. 3C and D show the Raman imaging of MB (bands: 1600–1645  $\text{cm}^{-1}$ ) and PATP (bands: 1550–1580  $\text{cm}^{-1}$ ), respectively. The Raman signals of PATP and MB micropatterns are easily detected (Fig. 3E). It is noted that, in PATP dot patterns, the Raman signal of MB is also detected, and its intensity (band at 1625  $\text{cm}^{-1}$ ) is  $\sim 1.6\%$  of that in the pure MB region. This indicates the defects existed in the formed PATP SAMs generated by mCP, which were then partially covered by MB, resulting in the weak Raman signal of MB observed in PATP patterns.

As discussed above, the Au NP-coated PDMS elastomer can be used for chemical imaging of molecules with high sensitivity, which is the major advantage of our method. Using the conventional SERS method, the detected molecules must be adsorbed onto the SERS-active substrates, so it is difficult to be used for chemical imaging (see Fig. 3B). Unlike the conventional SERS, TERS can be used for chemical imaging, but the total Raman scattering signal from the tip area (about 20–50 nm in diameter) is rather weak,<sup>9,13</sup> resulting in the quite low sensitivity. Compared with the conventional SERS and TERS methods, our method can be used for highly sensitive chemical imaging by simply covering the Au NP-coated PDMS elastomer onto the detected substrate. Thanks to the high-density Au NPs coated on PDMS serving as Raman hot spots, the collected Raman signal can be dramatically enhanced, which is much higher than that obtained in the typical TERS. Even though the lateral resolution is sacrificed compared with TERS, our method is simple and convenient in contrast to the special setup and complex operation of TERS. Therefore, our method can be used as an efficient and convenient tool for chemical imaging of molecules with high sensitivity.

In conclusion, a simple and convenient method has been developed to successfully enhance the Raman signals of molecules adsorbed on a solid substrate by covering the Au or Ag NP-coated PDMS elastomer onto the detected surface. By using this method, the chemical imaging is also achieved, which is difficultly obtained with the conventional SERS and low sensitive TERS methods. As a proof of concept, the micropatterns of PATP and MB are imaged. These promising results demonstrate that the NP-coated PDMS elastomer can be employed as a simple, efficient and flexible tool for highly sensitive Raman detection and chemical imaging of molecules on solid substrates.

This work was supported by AcRF Tier 2 (ARC 10/10, No. MOE2010-T2-1-060) from MOE, CRP (NRF-CRP2-2007-01) from NRF, CREATE program (Nanomaterials for Energy and Water Management) from NRF, and New Initiative Fund FY 2010 (M58120031) from NTU in Singapore.

## Notes and references

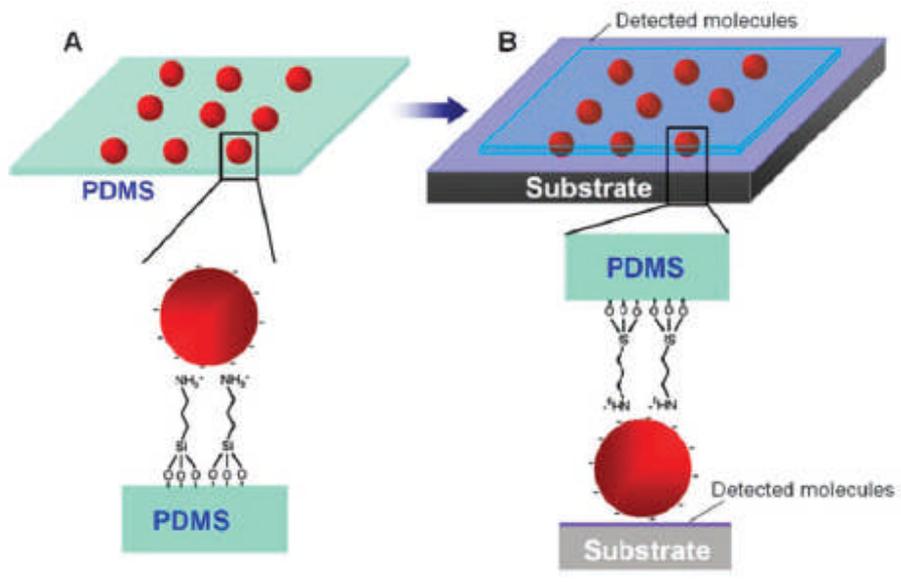
- 1 M. Fleischm, P. J. Hendra and A. J. McQuilla, *Chem. Phys. Lett.*, 1974, **26**, 163–166.
- 2 M. Moskovits, *J. Raman Spectrosc.*, 2005, **36**, 485–496; J. A. Dieringer, A. D. McFarland, N. C. Shah, D. A. Stuart, A. V. Whitney, C. R. Yonzon, M. A. Young, X. Y. Zhang and R. P. Van Duyne, *Faraday Discuss.*, 2006, **132**, 9–26; J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nat. Mater.*, 2008, **7**, 442–453; J. Kneipp, H. Kneipp and K. Kneipp, *Chem. Soc. Rev.*, 2008, **37**, 1052–1060.
- 3 K. Hering, D. Cialla, K. Ackermann, T. Dorfer, R. Moller, H. Schneidewind, R. Mattheis, W. Fritzsche, P. Rosch and J. Popp, *Anal. Bioanal. Chem.*, 2008, **390**, 113–124; M. D. Porter, R. J. Lipert, L. M. Siperko, G. Wang and R. Narayananana, *Chem. Soc. Rev.*, 2008, **37**, 1001–1011.
- 4 P. L. Stiles, J. A. Dieringer, N. C. Shah and R. R. Van Duyne, *Annu. Rev. Anal. Chem.*, 2008, **1**, 601–626.
- 5 L. D. Qin, S. L. Zou, C. Xue, A. Atkinson, G. C. Schatz and C. A. Mirkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 13300–13303.
- 6 H. Ko, S. Singamaneni and V. V. Tsukruk, *Small*, 2008, **4**, 1576–1599.
- 7 T. Qiu, Y. J. Zhou, J. Q. Li, W. J. Zhang, X. Z. Lang, T. J. Cui and P. K. Chu, *J. Phys. D: Appl. Phys.*, 2009, **42**, 175403; G. Braun, Pavel, A. R. Morrill, D. S. Seferos, G. C. Bazan, N. O. Reich and M. Moskovits, *J. Am. Chem. Soc.*, 2007, **129**, 7760–7761; J. P. Camden, J. A. Dieringer, Y. M. Wang, D. J. Masiello, L. D. Marks, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2008, **130**, 12616–12617; S. J. Lee, A. R. Morrill and M. Moskovits, *J. Am. Chem. Soc.*, 2006, **128**, 2200–2201.
- 8 K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari and M. S. Feld, *J. Phys.: Condens. Matter*, 2002, **14**, R597–R624.
- 9 E. Bailo and V. Deckert, *Chem. Soc. Rev.*, 2008, **37**, 921–930.
- 10 R. M. Stockle, Y. D. Suh, V. Deckert and R. Zenobi, *Chem. Phys. Lett.*, 2000, **318**, 131–136.
- 11 B. Pettinger, B. Ren, G. Picardi, R. Schuster and G. Ertl, *Phys. Rev. Lett.*, 2004, **92**, 096101.
- 12 V. Deckert, *J. Raman Spectrosc.*, 2009, **40**, 1336–1337.
- 13 B. S. Yeo, J. Stadler, T. Schmid, R. Zenobi and W. H. Zhang, *Chem. Phys. Lett.*, 2009, **472**, 1–13; K. F. Domke and B. Pettinger, *ChemPhysChem*, 2010, **11**, 1365–1373.
- 14 A. Kumar, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1994, **10**, 1498–1511.
- 15 H. Li, J. Zhang, X. Z. Zhou, G. Lu, Z. Y. Yin, G. P. Li, T. Wu, F. Boey, S. S. Venkatraman and H. Zhang, *Langmuir*, 2010, **26**, 5603–5609.
- 16 B. Li, G. Lu, X. Z. Zhou, X. H. Cao, F. Boey and H. Zhang, *Langmuir*, 2009, **25**, 10455–10458.
- 17 Z. H. Zhu, T. Zhu and Z. F. Liu, *Nanotechnology*, 2004, **15**, 357364.
- 18 C. E. Talley, J. B. Jackson, C. Oubre, N. K. Grady, C. W. Hollars, S. M. Lane, T. R. Huser, P. Nordlander and N. J. Halas, *Nano Lett.*, 2005, **5**, 1569–1574.
- 19 Z. Q. Tian, B. Ren and D. Y. Wu, *J. Phys. Chem. B*, 2002, **106**, 94639483.

## List of Schemes

Scheme 1 (A) Au or Ag NPs were adsorbed on an APTES-modified PDMS elastomer. (B) Raman detection by covering the as-fabricated NP-coated PDMS elastomer (A) onto the detected substrate.

## List of Figures

- Fig. 1 (A) Raman signals of MB on Ag surface before (a,  $\times 50$ ) and after (b) it was covered with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer. (B) Raman mapping of MB on the Ag surface which was covered with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer. Inset: the cross section analysis of the white line in (B).
- Fig. 2 SEM images of Au NPs with size of (A)  $13 \pm 1$ , (B)  $16 \pm 8$  and (C)  $38 \pm 3$  nm adsorbed on PDMS elastomers which were coated with a 10 nm Pt film. Raman detection of MB (D) and PATP (E) on Ag substrates which were covered by the Au NP-coated PDMS elastomer. Curves (a–c) were obtained with different sized Au NP (A–C) coated PDMS elastomers.
- Fig. 3 (A) Schematic illustration of micropatterns of PATP and MB formed on the Ag substrate. (B, C) Raman mapping of MB (bands:  $1600\text{--}1645\text{ cm}^{-1}$ ) before and after covering with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer. (D) Raman mapping of PATP (bands:  $1550\text{--}1580\text{ cm}^{-1}$ ) after covering with the  $38 \pm 3$  nm Au NP-coated PDMS elastomer. (E) Raman signals in MB and PATP patterned regions.



Scheme 1

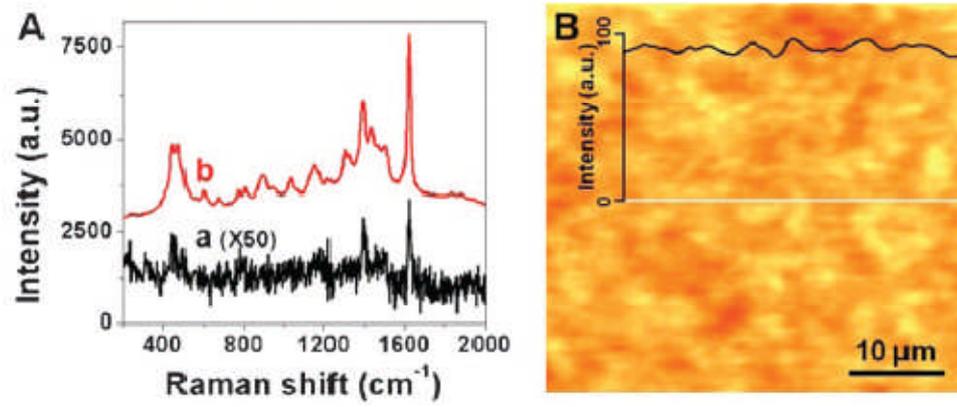


Fig. 1

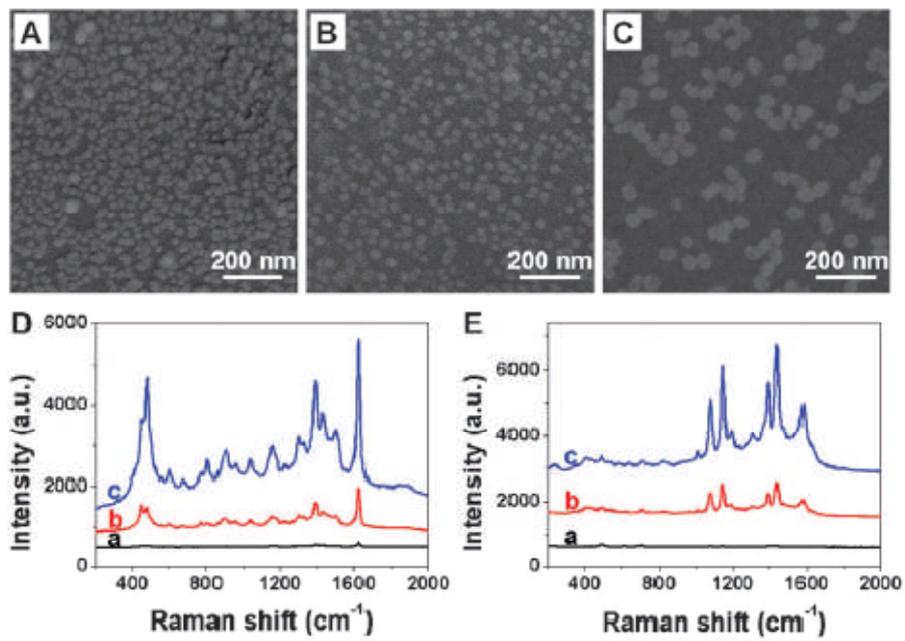


Fig. 2

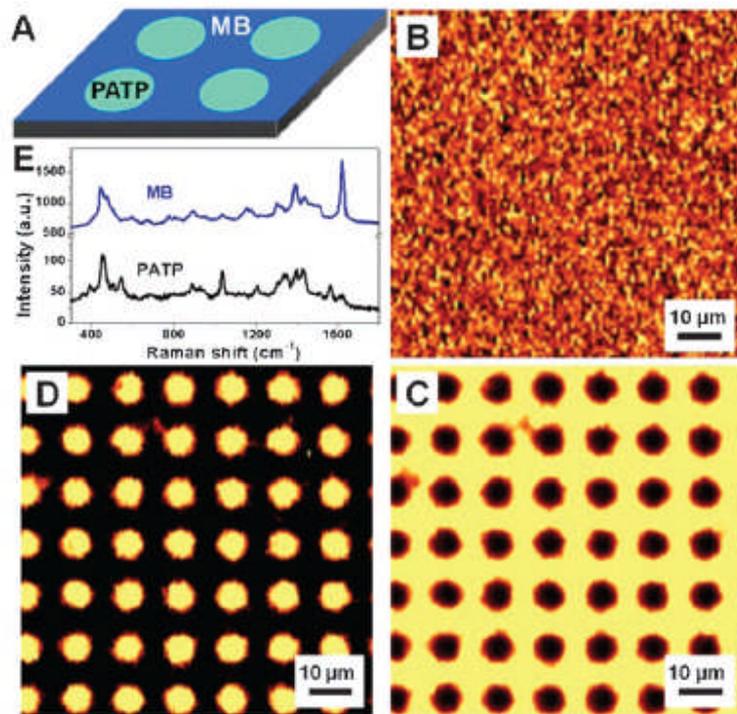


Fig. 3