

SERS ENHANCEMENT OF RHODAMINE 6G BY A MIXTURE APPROACH WITH GRAPHENE QUANTUM DOTS ON HYBRID CORE-SHELL Pd@Ag NPs

Rutuja Mandavkar, Rakesh Kulkarni, Shusen Lin, Sanchaya Pandit, Sundar Kunwar and Jihoon Lee

Department of Electronic Engineering, College of Electronics and Information, Kwangwoon University, Nowon-gu Seoul 01897, South Korea.

Abstract

The bimetallic or core-shell nanoparticles (NPs) can find applications as a surface-enhanced Raman spectroscopy (SERS) substrate due to their large surface area and strong localized surface plasmon resonance (LSPR) [1]. Among the various plasmonic metallic NPs, the palladium (Pd) and silver (Ag) have been widely proposed for the SERS substrates due to better stability and biocompatibility. The solid-state dewetting (SSD) [2] can offer a promising route to fabricate the dynamic morphology of bimetallic NPs like the hybrid core-shell Pd@Ag NPs with the secondary background Ag NPs as showed in Fig. 1(b). The hybrid core-shell Pd@Ag NPs exhibit the improved LSPR properties as compared to the pure Ag or Pd NPs such as a narrowing of LSPR peaks with the blue-shift as shown in Fig. 1(b-1). This is due to the unique configuration of core-shell Pd@Ag NPs and a log of background Ag NPs.

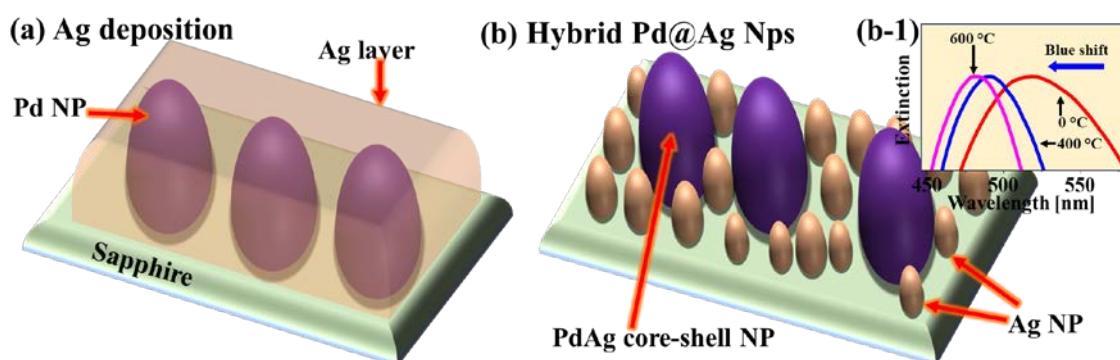


Figure 1. Fabrication Pd@Ag hybrid core-shell NP by the solid-state dewetting method [3].

Further, the SERS signal enhancement with the incorporation of graphene quantum dots (GQDs) on the hybrid core-shell Pd@Ag NPs has been investigated in this work for the ultrasensitive surface-enhanced Raman scattering (SERS) substrate [3] as shown in Fig. 2(a). The hybrid nano-construction of NPs along with the GQD provides a greater number of hotspots in between the highly-dense background NPs and in small spacing between particles [4]. The dangling bonds on the edge of the GQDs [5] effectively adsorb the probe molecules R6G and demonstrated a strong enhancement with lower molarity of R6G. The enhanced SERS signal is attributed to the synergistic effect of chemical enhancement from the GQDs and electromagnetic enhancement from the hybrid core-shell Pd@Ag NPs as displayed in Fig. 2(b).



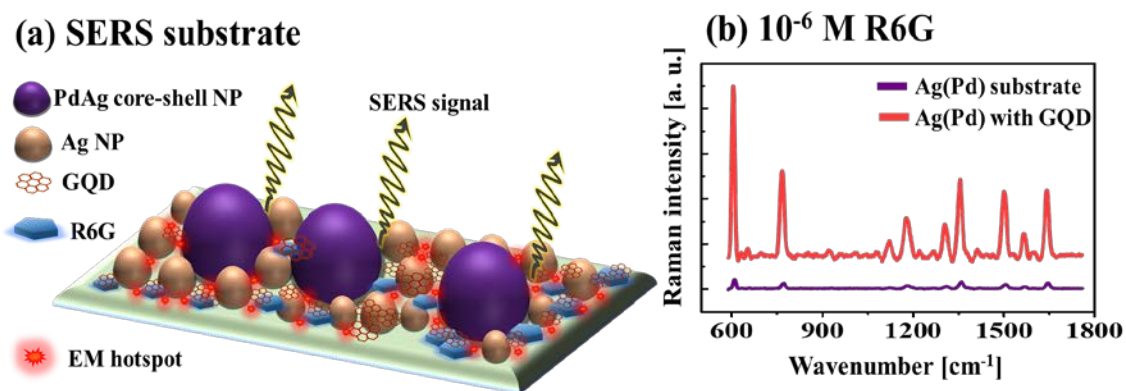


Figure 2. (a) Schematic of surface-enhanced Raman spectroscopy (SERS) substrate constructed on the Pd@Ag core-shell NPs and GQDs. (b) SERS signal enhancement for R6G with the incorporation of GQD and Pd@Ag core-shell NPs [3].

Acknowledgments

Financial support from the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (MSIP) (No. NRF-2019R1A2C4069438 and NRF-2018R1A6A1A03025242) and in part by the research grant of Kwangwoon University in 2021 is gratefully acknowledged. Special appreciation to Ms. So Hee Kim from the Korea Institute of Science and Technology (KIST) for the SEM-EDX characterizations.

Author Contributions

Sanchaya Pandit: Conceptualization, Methodology, Writing - review & editing. Sundar Kunwar: Methodology, Writing - review & editing. Rakesh Kulkarni: Data curation. Rutuja Mandavka: Data curation. Shusen Lin: Data curation. Jihoon Lee: Conceptualization, Methodology, Writing - review & editing.

References

1. J. C. Fraire, S. Stremersch, D. Bouckaert, T. Monteyne, T. De Beer, P. Wuytens, R. De Rycke, A. G. Skirtach, K. Raemdonck, and S. De Smedt, Improved label-free identification of individual exosome-like vesicles with Au@ Ag nanoparticles as SERS substrate, *ACS applied materials & interfaces* 11(43), 39424–39435 (2019).
2. N. Gazit, G. Richter, A. Sharma, L. Klinger, and E. Rabkin, Engineering of hollow AlAu₂ nanoparticles on sapphire by solid state dewetting and oxidation of Al, *Materials & Design* 165, 107557 (2019).
3. S. Pandit, S. Kunwar, R. Kulkarni, R. Mandavka, S. Lin, and J. Lee, Applied Surface Science Fabrication of hybrid Pd @ Ag core-shell and fully alloyed bi-metallic AgPd NPs and SERS enhancement of Rhodamine 6G by a unique mixture approach with graphene quantum dots, *Applied Surface Science* 548(October 2020), 149252 (2021).



4. D. Liu, X. Chen, Y. Hu, T. Sun, Z. Song, Y. Zheng, Y. Cao, Z. Cai, M. Cao, L. Peng, Y. Huang, L. Du, W. Yang, G. Chen, D. Wei, A. T. S. Wee, and D. Wei, Raman enhancement on ultra-clean graphene quantum dots produced by quasi-equilibrium plasma-enhanced chemical vapor deposition, *Nature Communications* 9(1), 193 (2018).
5. X. Liang, N. Li, R. Zhang, P. Yin, C. Zhang, N. Yang, K. Liang, and B. Kong, Carbon-based SERS biosensor: from substrate design to sensing and bioapplication, *NPG Asia Materials* 13(1), 8 (2021).

