Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

In situ SERS Study of Plasmonic Nanochemistry Based on Bifunctional "Hedgehog-like" Arrays

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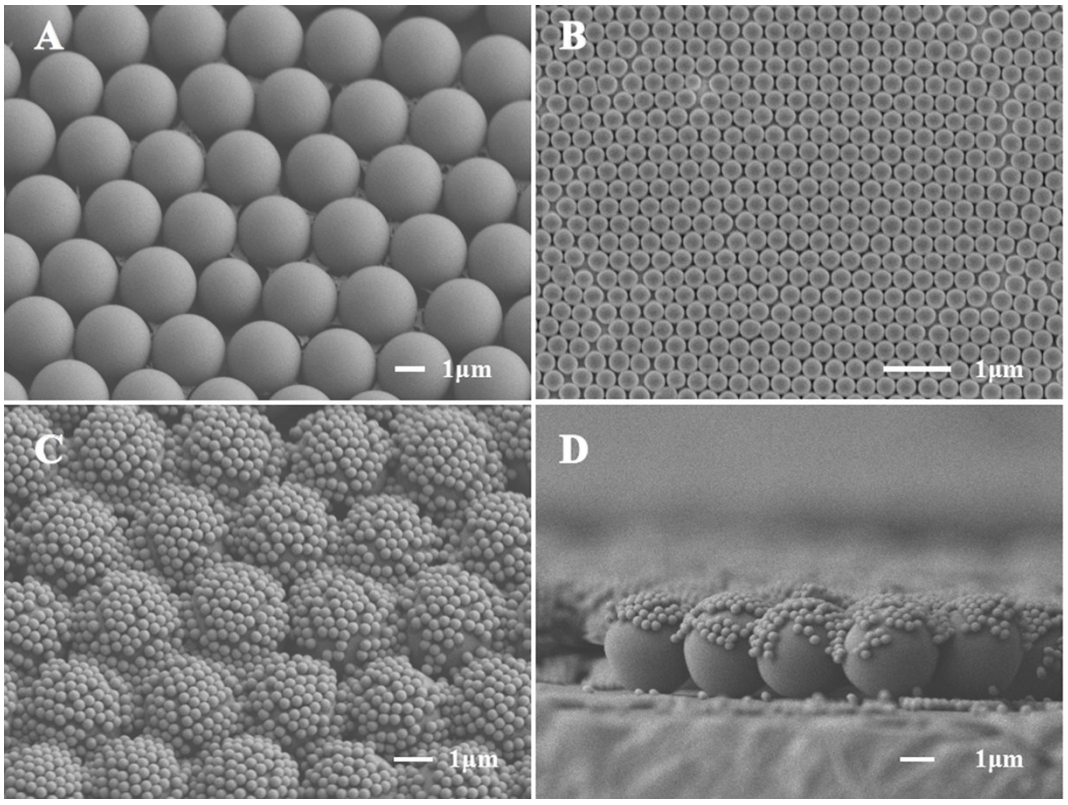

Figure S1. The SEM images of (A) PS microsphere substrate and (B) nanosphere etching masks. (C) 60° tilting view and (D) cross-sectional view of fabricated binary colloidal crystals.

The HLAs etched for 150 s is the best SERS substrate and also has the best catalytic activity (**Figure S**2). As RIE duration *t* increasing from 150 s to 240 s, the PS-3 underneath was further longitudinally etched, leading it an ellipse gradually. As the curvature of the upper surface of PS-3 decreases gradually, the light utilization rate of the HLAs in the third dimension also decreases. Therefore, when the PS-0.3 template was just completely etched, the structure had the maximum utilization rate for light, as well as the best SERS and catalytic activity.

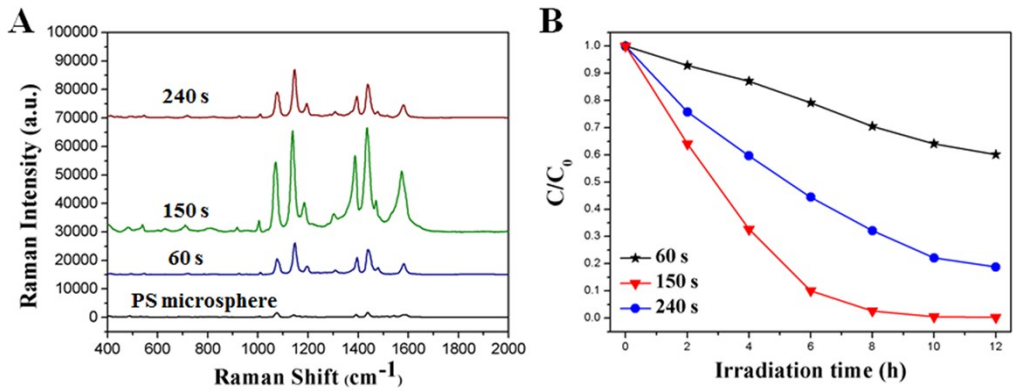

Figure S2. (A) SERS spectra of 1 × 10^{-5} M p-aminothiophenol (PATP) collected on HLAs etched for different times. (B) Time dependent concentration of the MB solution with HLAs etched for different times.

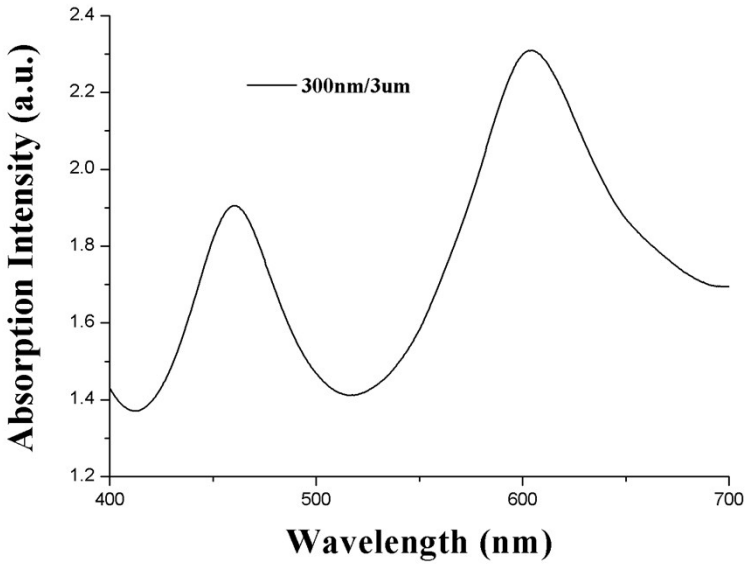

Figure S3. UV-Vis absorption spectrum of the HLAs.

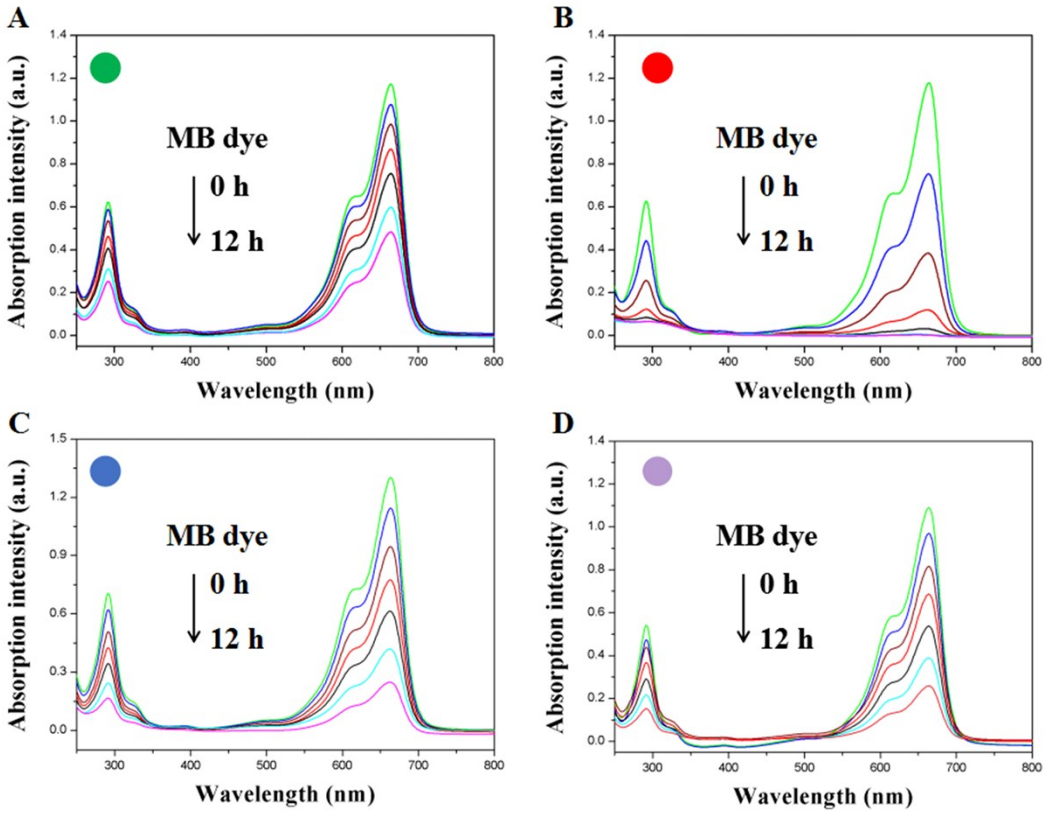

Figure S4. UV-Vis absorption spectra of MB under different irradiation times with the HLAs exposed to different wavelengths of light: (A) green light, (B) red light, (C) blue light and (D) UV light.

We have proved the existence of $^{\bullet}O_2$ and $^{\bullet}OH$ in the process of reactions under the illumination. First, we investigated the $^{\bullet}OH$ generation from the HLAs by using sodium terephthalate as a probe. As shown in **Figure S**5A, after the exposure to illumination for 10 min, the fluorescence intensity of the solution contained HLAs was obviously increased compared to the control group. It proved that $^{\bullet}OH$ is generated in the solution with HLAs under illumination.[1] Then, the $^{\bullet}O_2$ was measured with the Superoxide Assay Kit (S0060, Beyotime, China) in the solution with HLAs after the exposure to illumination for 10 min. Compared with the control groups, the UV-Vis absorption spectrum of the solution with HLAs is significantly enhanced at the wavelength of 450 nm (**Figure S**5B), which proves the existence of $^{\bullet}O_2$ in the solution with HLAs under illumination.[2]

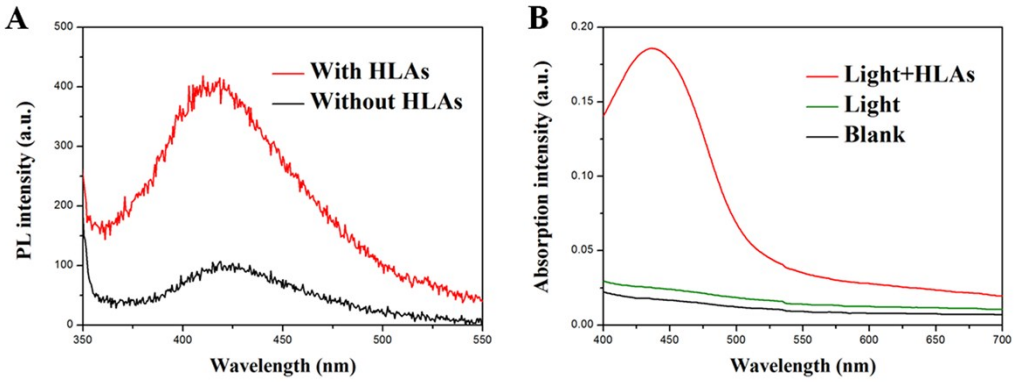

Figure S5. (A) Fluorescence spectrum of $^{\bullet}OH$ detection by sodium terephthalate. (B) UV-Vis absorption spectra of $^{\bullet}O_2$ detection by Superoxide Assay Kit.

Notes and references

1. Z. Guo, S. Zhu, Y. Yong, X. Zhang, X. Dong, J. Du, J. Xie, Q. Wang, Z. Gu, Y. Zhao, *Adv. Mater.* 2017, **29**, 1704136.

2. G. Wang, W. Jin, A. M. Qasim, A. Gao, X. Peng, W. Li, H. Feng, P. K. Chu, *Biomaterials* 2017, **124**, 25-34.