

## Electronic Supplementary Information

### **Inclusion of Guest Materials in Aqueous Coordination Network Shells Spontaneously Generated by Reacting 2,5-Dimercapto-1,3,4-thiadiazole with Nanoscale Metallic Silver**

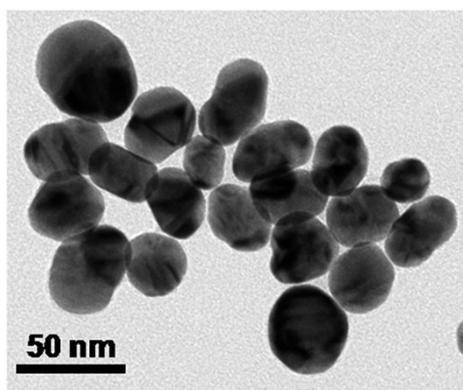
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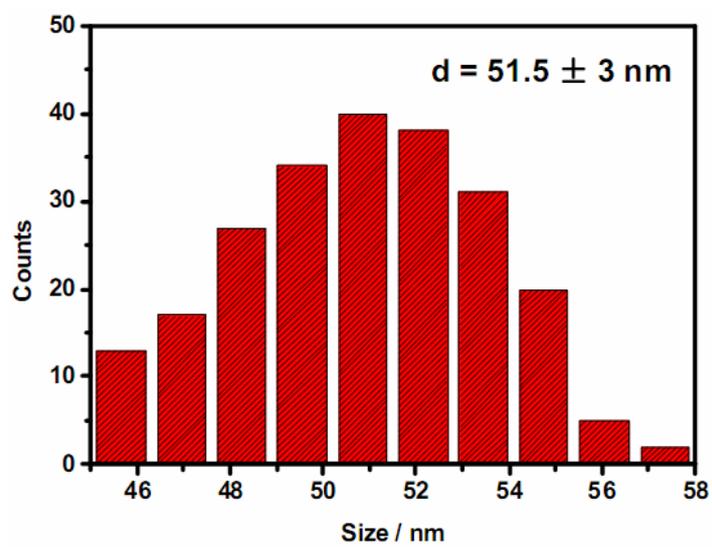
*<sup>b</sup>Anyang Institute of Technology, Anyang 455000, China*

*<sup>c</sup>Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401 (USA)*

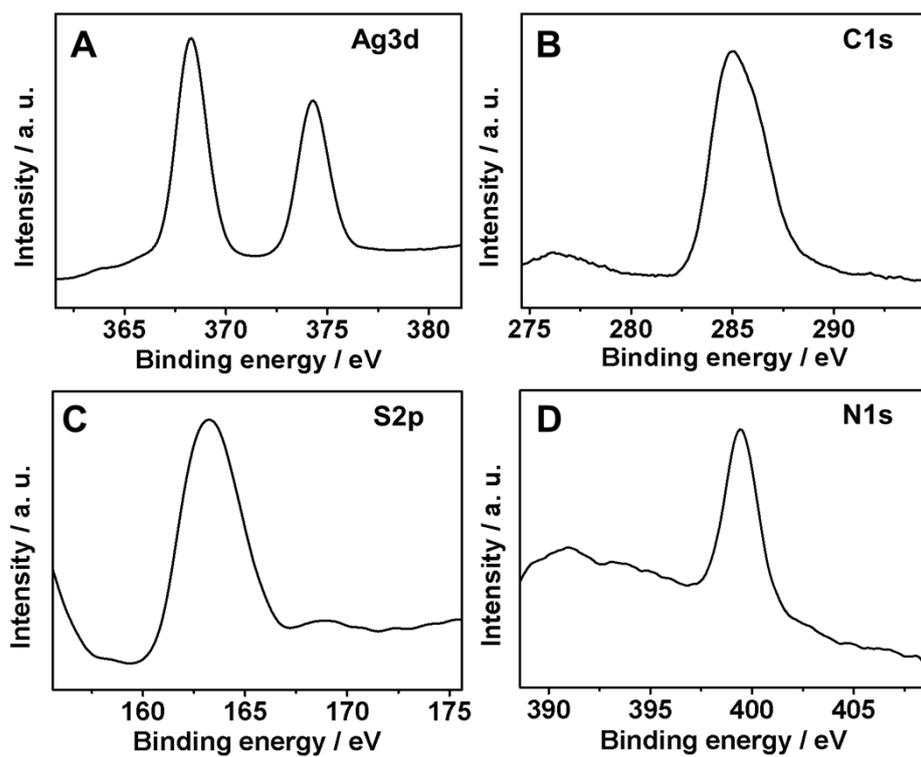
E-mail: [agshen@whu.edu.cn](mailto:agshen@whu.edu.cn); [jmhu@whu.edu.cn](mailto:jmhu@whu.edu.cn)



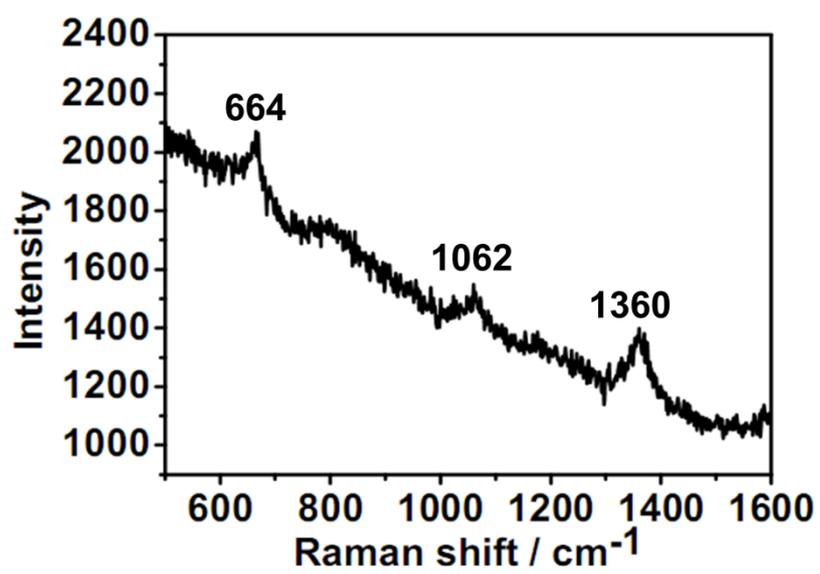
**Figure S1.** The TEM image of Au NPs after being incubated with 100  $\mu$ L DMcT aqueous solution for about 3 h at room temperature.



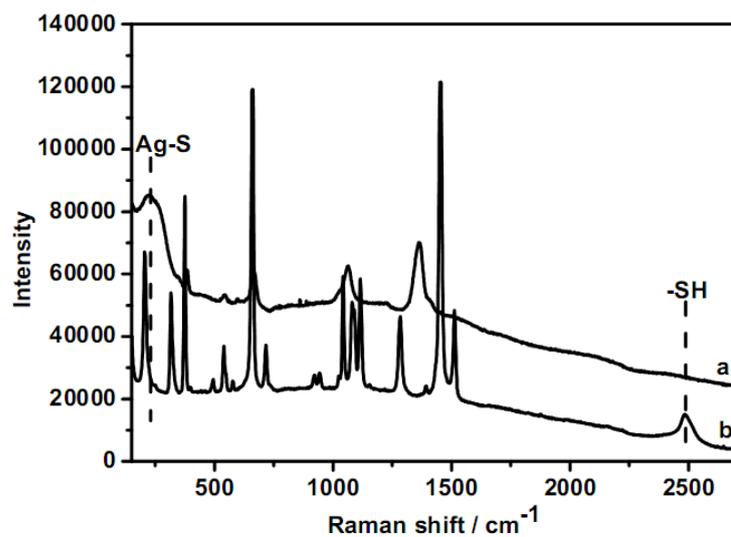
**Figure S2.** Statistic data of the size of more than 200 Au@Ag@void@ICPs 1 NPs.



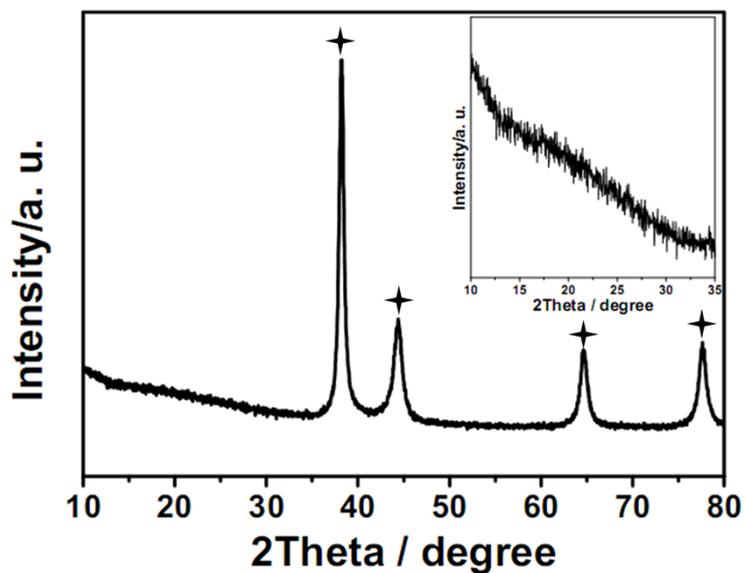
**Figure S3.** XPS spectra of the as-synthesized Au@Ag@void@ICPs 1: (A) high resolution of Ag spectrum; (B) high resolution of C spectrum; (C) high resolution of S spectrum and (D) high resolution of N spectrum.



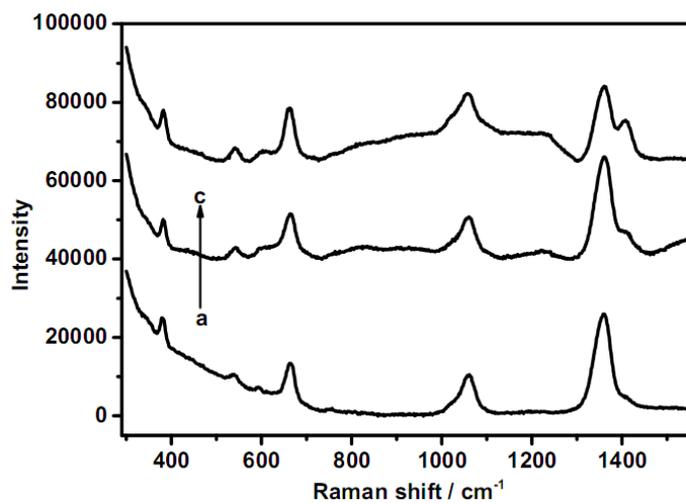
**Figure S4.** SERS spectra of the as-synthesized Au@Ag@void@ICPs 1.



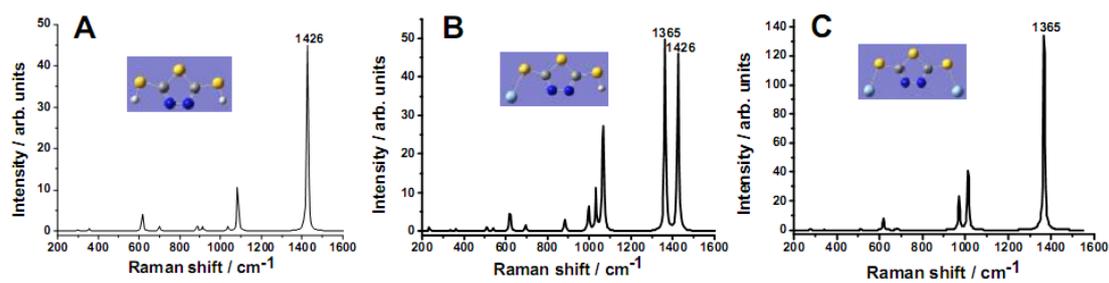
**Figure S5.** SERS spectra of the reaction products of DMcT with Au@Ag NPs (a) and DMcT in solid state (b).



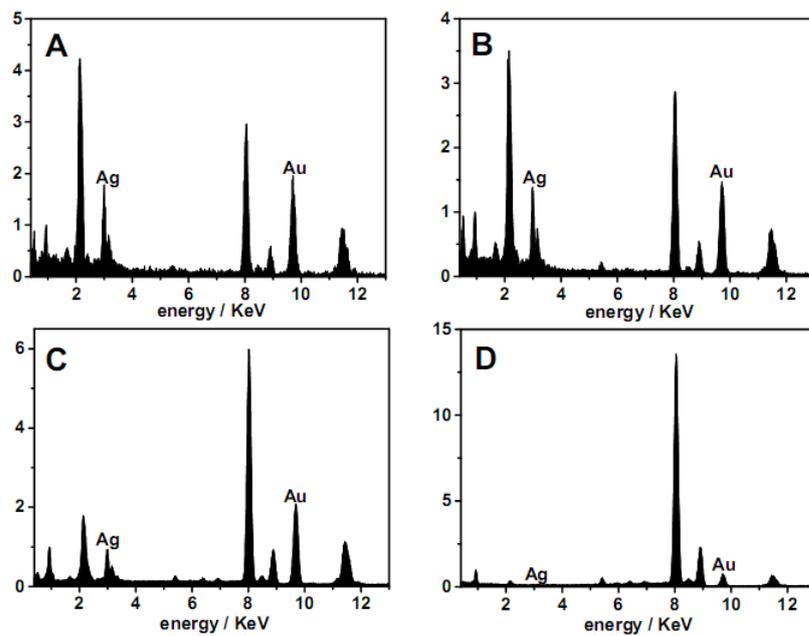
**Figure S6.** Power XRD patterns of the hollow core-shell Au@Ag@void@ICPs **1**. The inset shows the lower-angle diffraction peaks contributed by the Ag-DMcT ICPs shell and the marked peaks are assigned to the Au@Ag core.



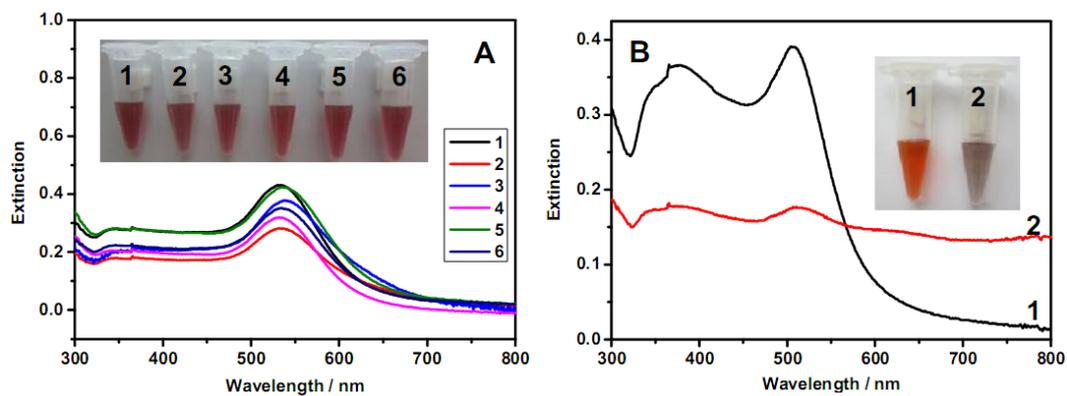
**Figure S7.** Evolution of normalized SERS spectra of Au@Ag NPs after being incubated with 50  $\mu$ L DMcT solution for different times: (a) 1, (b) 20, and (c) 180 min.



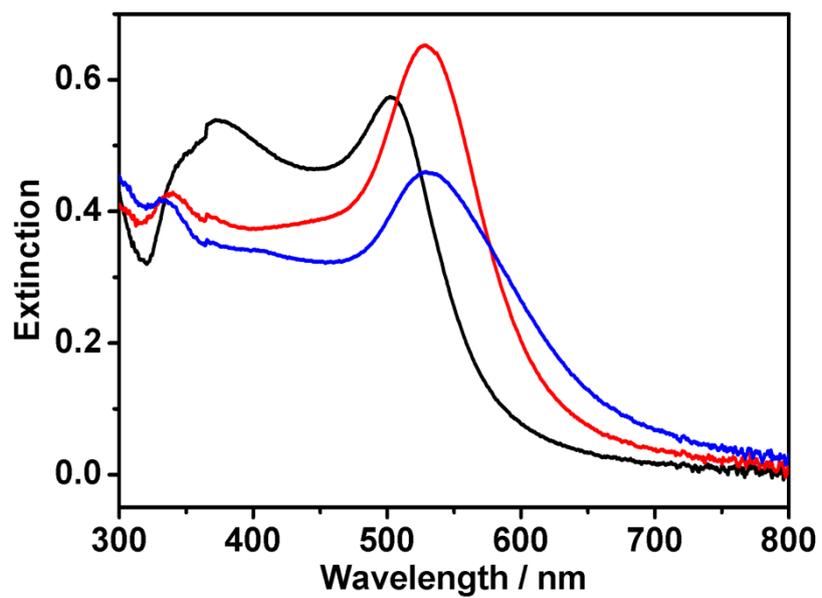
**Figure S8.** DFT calculated Raman spectra of free DMcT (A), one S-H of DMcT molecules interaction with one Ag atom (B) and two S-H of DMcT molecules interaction with two Ag atoms (C). Insert: the corresponding optimized structures based on DFT.



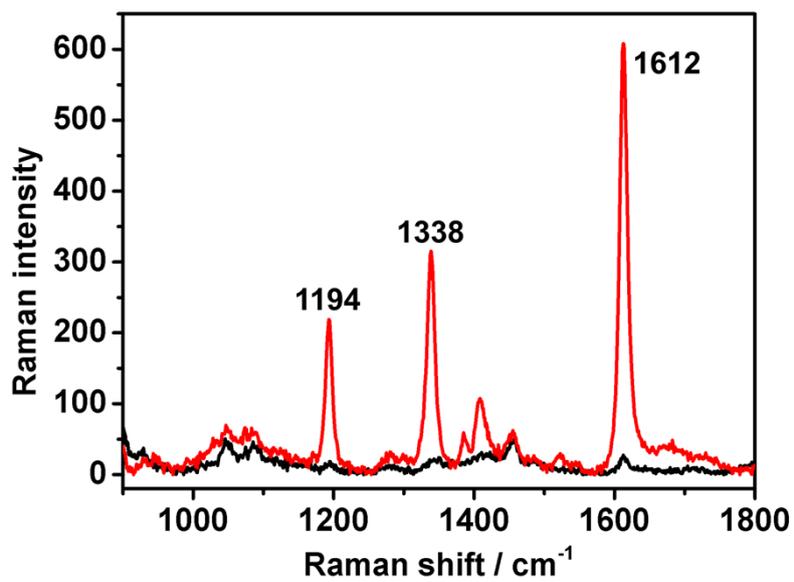
**Figure S9.** Normalized EDX spectra of Au@Ag NPs after being incubated with (A) 0, (B) 10, (C) 100 and (D) 500  $\mu$ L DMcT solution for 3 h.



**Figure S10.** (A) The UV-*vis* absorption spectra of the as-synthesized Au@Ag@void@ICPs **1** redispersed in (1) pure water, (2) 50 mM NaCl aqueous solution, (3) pH 4.0 aqueous solution, (4) pH 12.0 aqueous solution, (5) ethanol and (6) methanol. (B) The UV-*vis* absorption spectra of Au@Ag NPs redispersed in (1) pure water, (2) 50 mM NaCl aqueous solution.



**Figure S11.** UV-*vis* spectra of Au@Ag NPs (black line), Au@Ag@void@ICPs 2 (red line) and the corresponding Au@Ag@void@ICPs/HRP (blue line).



**Figure S12.** Raman spectra of TMB and Au@Ag@void@ICPs/HRP in the absence (black line) and presence (red line) of 30 μM H<sub>2</sub>O<sub>2</sub>.