

**Scanned Chemical Enhancement of Surface-Enhanced Raman  
Scattering Using a Charge-Transfer Complex**

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## EXPERIMENTAL DETAILS

**Materials.** Poly (diallyldimethylammonium chloride) (PDDA):  $M_w = 200\ 000 - 350\ 000$ , 20wt% aqueous solution) and 4-mercaptophenols (4-MPH) were obtained from Sigma. All other chemicals were analytic grade from Beijing Chemical Reagent Factory and used without further purification.

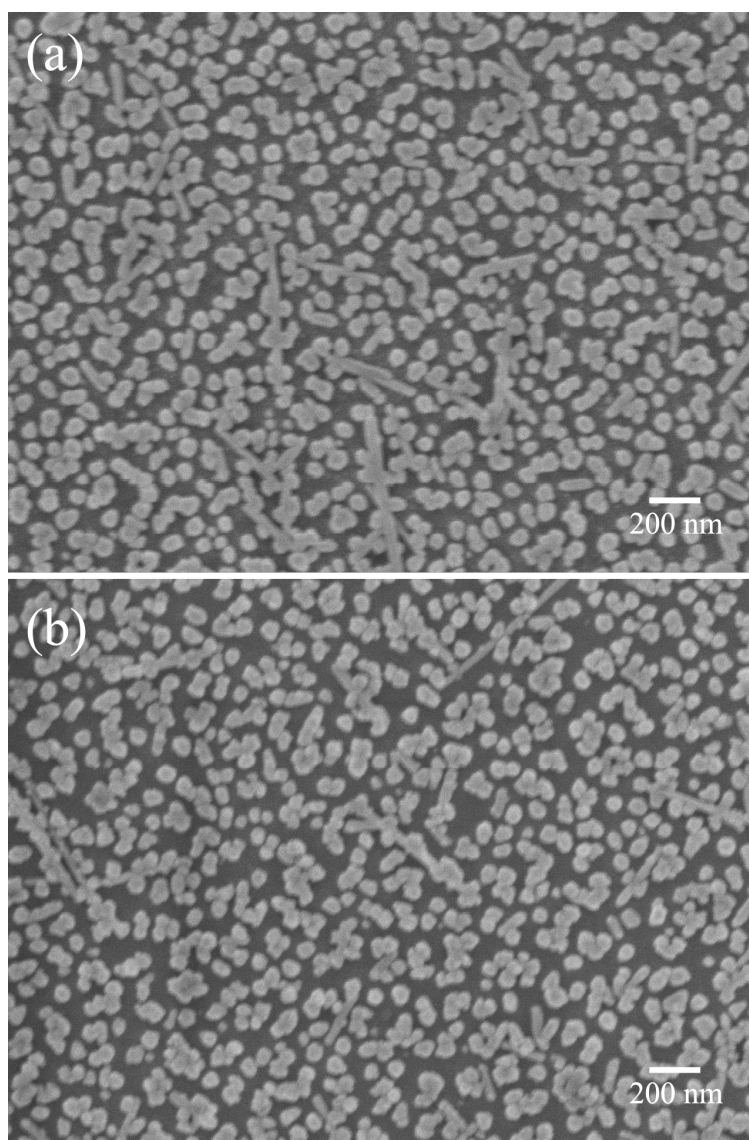
**Sample Preparation.** The silver colloid was prepared using the conventional synthetic route reported elsewhere.<sup>[1]</sup> The glass with hydroxyl surface was immerse in a 0.5% PDDA solution for 1 h. After exhaustive rinsing by water and drying by nitrogen, the PDDA coated slides were soaked in silver colloid for 6 h and then rinsed with water. Assembled silver nanoparticles were coated with  $TiO_2$  layer by surface sol-gel (SSG) process that originally developed by Kunitake.<sup>[2]</sup> The SSG procedure is schematically shown in Figure 1. Briefly, the glass slides covered with a layer of silver nanoparticles were immersed in 4-MPH solution ( $10^{-3}$  M) for 1 h. After modified with 4-MPH molecules, the slides were transferred into titanium(IV) butoxide (100 mM in a 1:1 (v/v) mixture of toluene/methanol) for 8 min and then washed with methanol. Finally, the slides were submerged in water for 1 min, dried with nitrogen gas.

**General Characterization.** The UV–vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The surface morphology of the samples was measured on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operating at 3.0 kV. Analysis of X-ray photoelectron spectroscopy (XPS) was performed on ESCLAB MKII using Al as the excitation source. Surface-enhanced

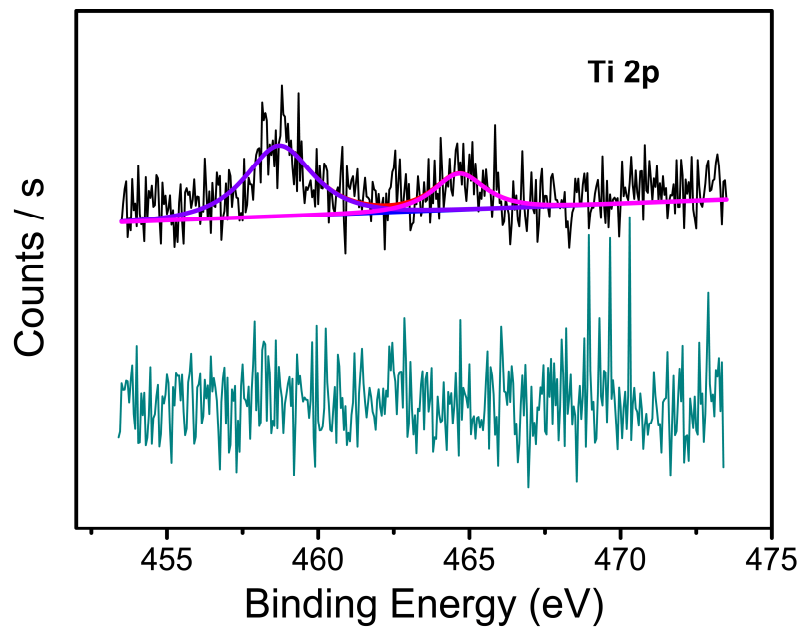
Raman (SERS) spectra were measured on a Horiba Jobin Yvon T64000 system with 514.5 and 488 nm radiations. The 488 and 514.5 nm lines from a 20 mW Ar<sup>+</sup> laser (Spectra Physics Model 2017) were used as the excitation source. The other SERS spectra were measured on a Horiba Jobin Yvon LabRam ARAMIS system. The 632.8 nm line from a 20 mW He/Ne laser (Melles Griot) or the 532 nm line from a 20 mW Laser (MPC Ventus) or the 785 nm excitation line was from the BRM-785 laser were used as the excitation source. The laser beam was focused onto a spot approximately 1  $\mu\text{m}$  in diameter with an objective microscope with magnification of the order of 50 $\times$ . The data acquisition time was usually 30 s.

**Complete Ref 7:**

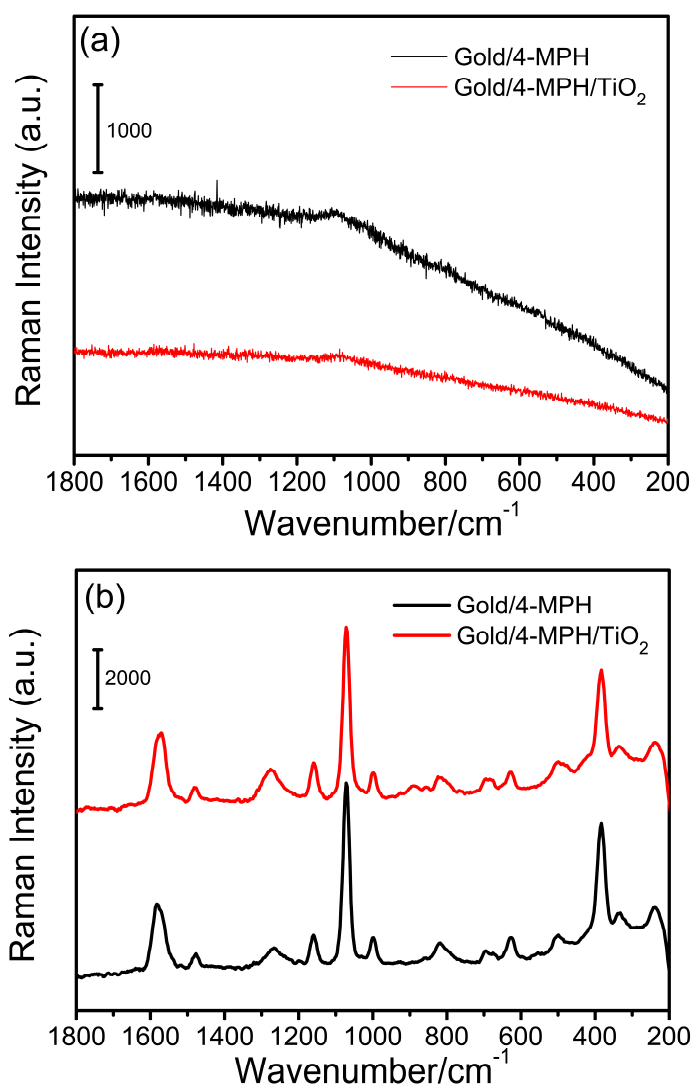
(7) D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley, X. Y. Zhu, *J. Phys. Chem. B* **2003**, *107*, 6668-6697.



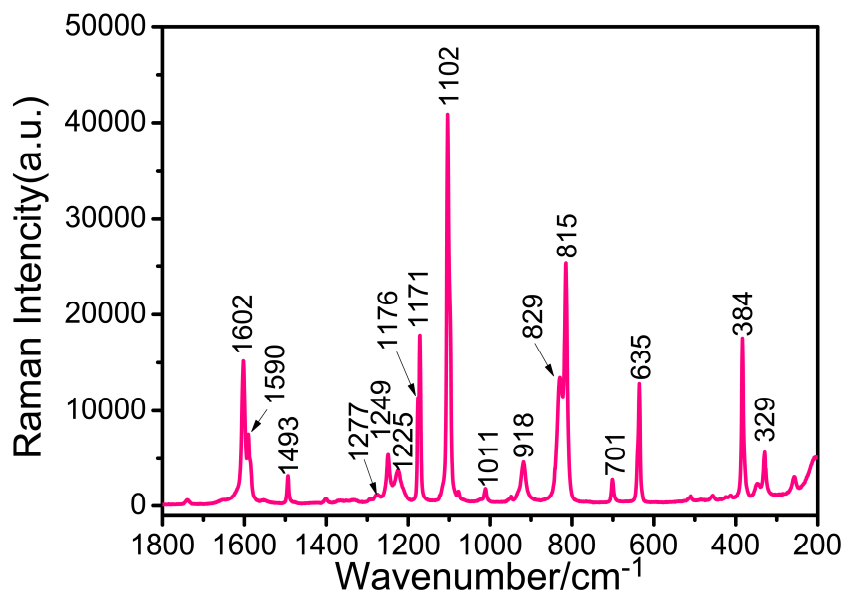
**Fig. S1.** SEM image of (a) the silver nanoparticles and (b) silver/4-MPH/TiO<sub>2</sub> nanosystem.



**Fig. S2.** Titanium 2p XPS of the Silver\MPH\TiO<sub>2</sub> system (on the top) and the Sliver-MPH system (on the bottom).



**Fig. S3.** SERS spectra of 4-MPH molecules in the gold/4-MPH nanosystem and gold/4-MPH/TiO<sub>2</sub> nanosystem at the excitation wavelength of (a) 514.5 nm and (b) 785 nm. The Au/4-MPH/TiO<sub>2</sub> system does not show the b<sub>2</sub> mode enhancement like the Ag/4-MPH/TiO<sub>2</sub> system (Fig. 3). This suggests that TiO<sub>2</sub> would be a necessary condition for CT phenomenon, but not a sufficient condition. With the 785 nm excitation, we do not observe the selective enhancement of b<sub>2</sub> modes after forming the CT complex. This result also suggests that the 785 nm laser does not have enough energy to excite CT, which is similar to that observed in Ag/4-MPH/TiO<sub>2</sub> system.



**Fig. S4.** Raman spectrum of MPH solid powders.

**TABLE S1: Raman Frequencies and Assignments of 4-mercaptophenol in 600-1800  $\text{cm}^{-1}$  Region**

Raman <sup>a,b</sup>	SERS				assignment <sup>a,c</sup>
	514.5 nm		785 nm		
	adsorbed on Ag particles	in Ag/MPH/TiO <sub>2</sub> assembly	adsorbed on Ag particles	in Ag/MPH/TiO <sub>2</sub> assembly	
1600	1597		1595	1599	v CC, 8a (a <sub>1</sub> )
1585	1583	1572	1579	1584	v CC, 8b (b <sub>2</sub> )
1492	1488	1479	1488	1492	v CC+ $\delta$ CH,19b (b <sub>2</sub> )
1277	1279	1291	1273	1273	$\delta$ CH+v CC,3 (b <sub>2</sub> )
1256					13
1220					$\beta$ OH
1171	1169	1163	1169	1173	$\delta$ CH,9b(b <sub>2</sub> )
1098	1075	1072	1073	1077	v CH+v CS+v CC,1(a <sub>1</sub> )
1007	1003	1003	1004	1008	$\gamma$ CC+ $\gamma$ CCC,18a (a <sub>1</sub> )
910					$\delta$ SH
829	823	827	821	825	$\pi$ CH, 17b(b <sub>1</sub> )
818					$\pi$ CH, 11(b <sub>1</sub> )
695	696	701	697	701	$\pi$ CH+ $\pi$ CS+ $\pi$ CC, 4(b <sub>2</sub> )
637	636		629	627	$\gamma$ CCC, 12(a <sub>1</sub> )
389	389		386	387	$\tau$ 7a(a <sub>1</sub> )

<sup>a</sup> Data and assignments obtained from ref. <sup>[3]</sup> <sup>b</sup> Note that 1492 and 1171  $\text{cm}^{-1}$  bands assignment was afresh made by using that for p-aminothiophenol<sup>[4]</sup> and thiophenol.<sup>[5]</sup> <sup>c</sup> Approximate description of the modes (v, stretch;  $\gamma$  and  $\delta$ , bend;  $\pi$ , wagging).

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