Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Charge Transfer Progress in Ag/MPH/TiO_2 Interface by SERS: Alignment of Fermi Level

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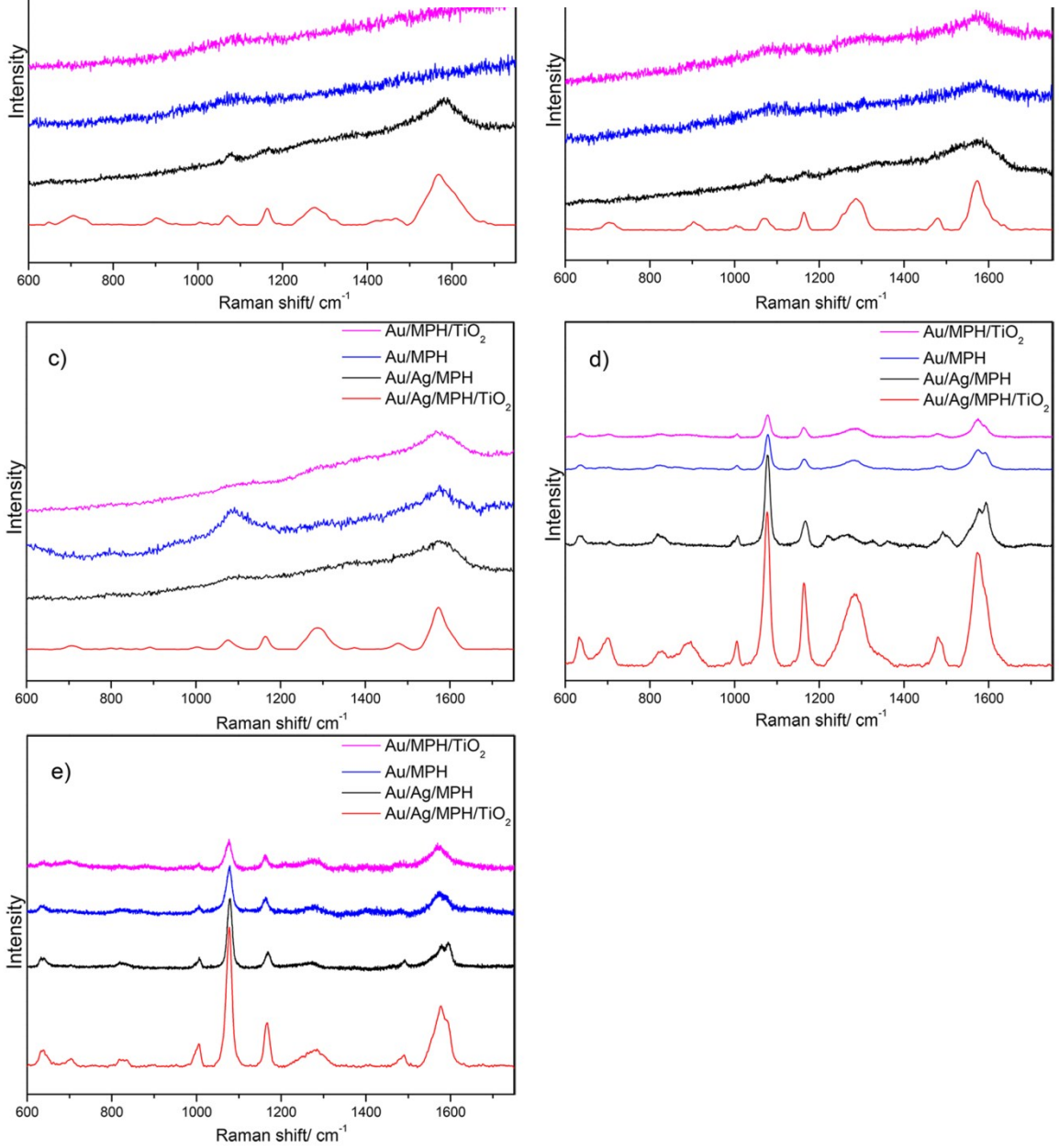
Figure S1 The SERS spectra of Au/MPH/TiO_2, Au/MPH, Au/Ag/MPH and Au/Ag/MPH/TiO_2 assemblies at a) 477 nm, b) 514 nm, c) 532 nm, d) 633 nm, and e) 785 nm excitation.



Because Au NPs film cannot be fully covered by Ag NPs (Figure 2 SEM images), there also exist some interferences (Au/MPH/TiO_2, Au/MPH and Au/Ag/MPH) in Au/Ag/MPH/TiO_2 assembly. To eliminate these interferences and verify the interaction between Au NPs and Ag NPs, we performed controlled trials. As the Figure S1 shows, there exist apparent fluorescence effects when Au/MPH/TiO_2, Au/MPH and Au/Ag/MPH assemblies are at 477, 514, 532 nm excitation. Meanwhile, at 633 nm and 785 nm excitation, the SERS spectra of Au/MPH/TiO_2, Au/MPH and Au/Ag/MPH assemblies is much weaker than that of Au/Ag/MPH/TiO_2 assembly. Thus, it can be concluded that the enhancement of b2 mode in SERS spectra comes from Au/Ag/MPH/TiO_2 assembly, where a new charge transfer state forms due to the interaction between Au NPs and Ag NPs.

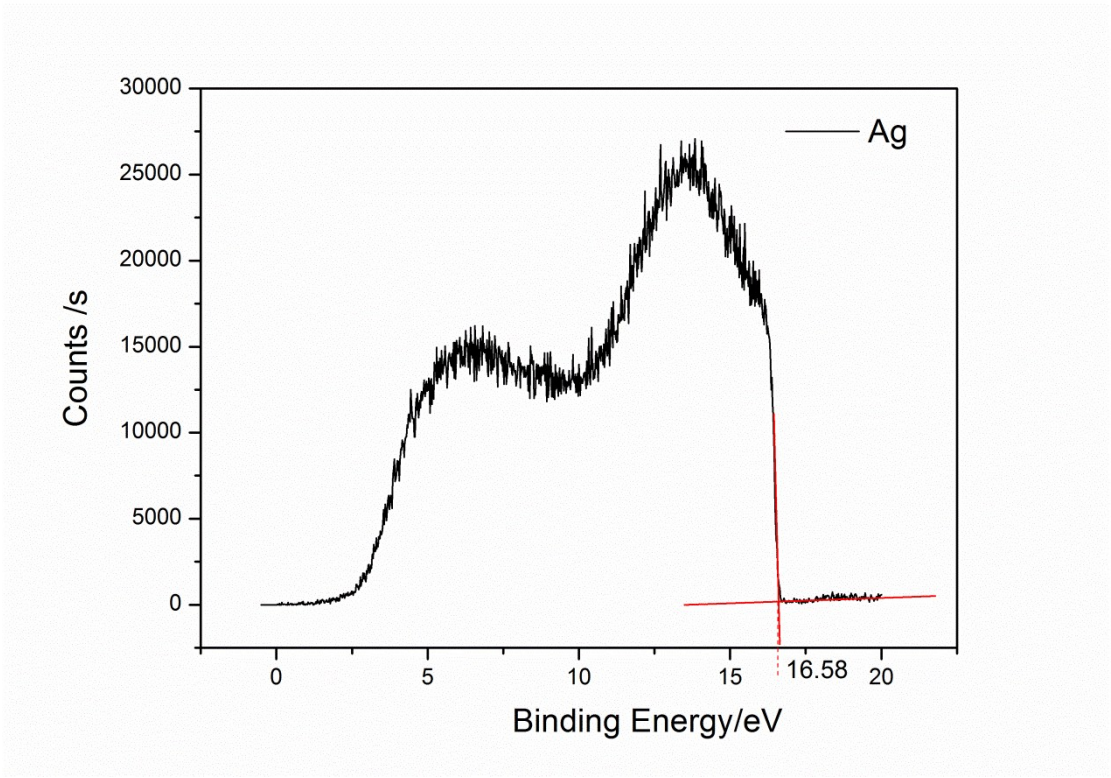


Figure S2 The UPS of Ag NPs.

In Figure S2, the location of Fermi level of Ag can be calculated out through the formula: WF=hν-ΔE. Thus, the Fermi level of Ag is at 4.64 eV from the vacuum level.

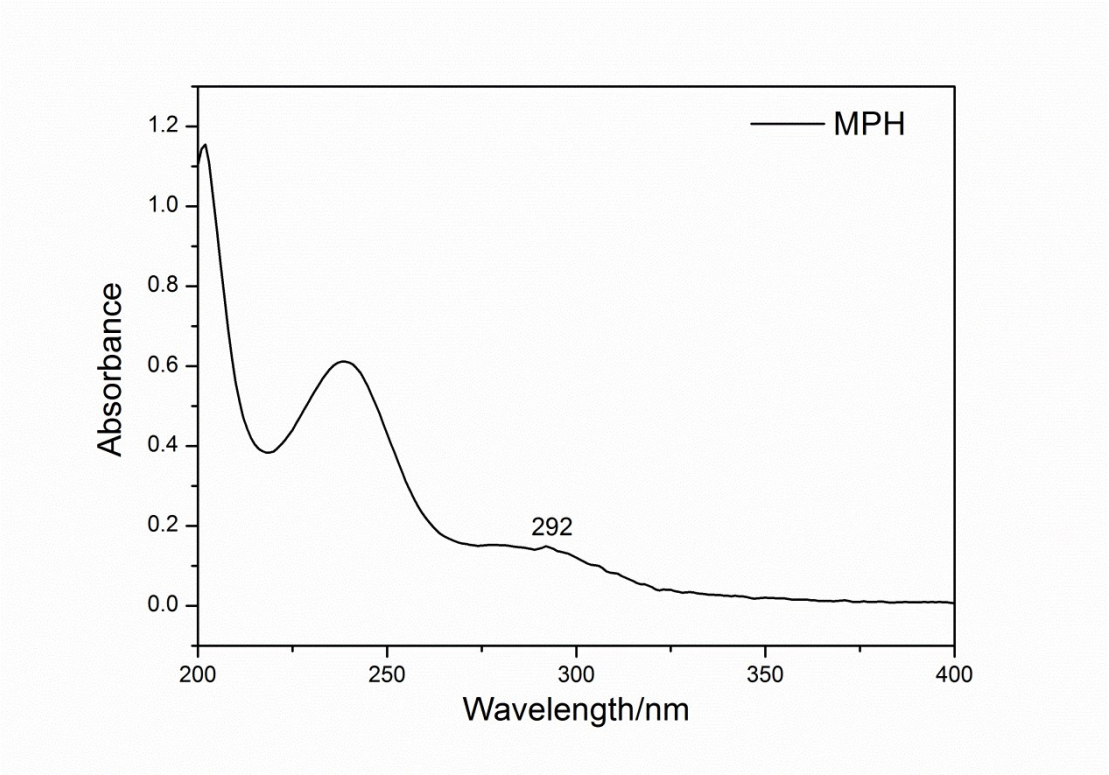
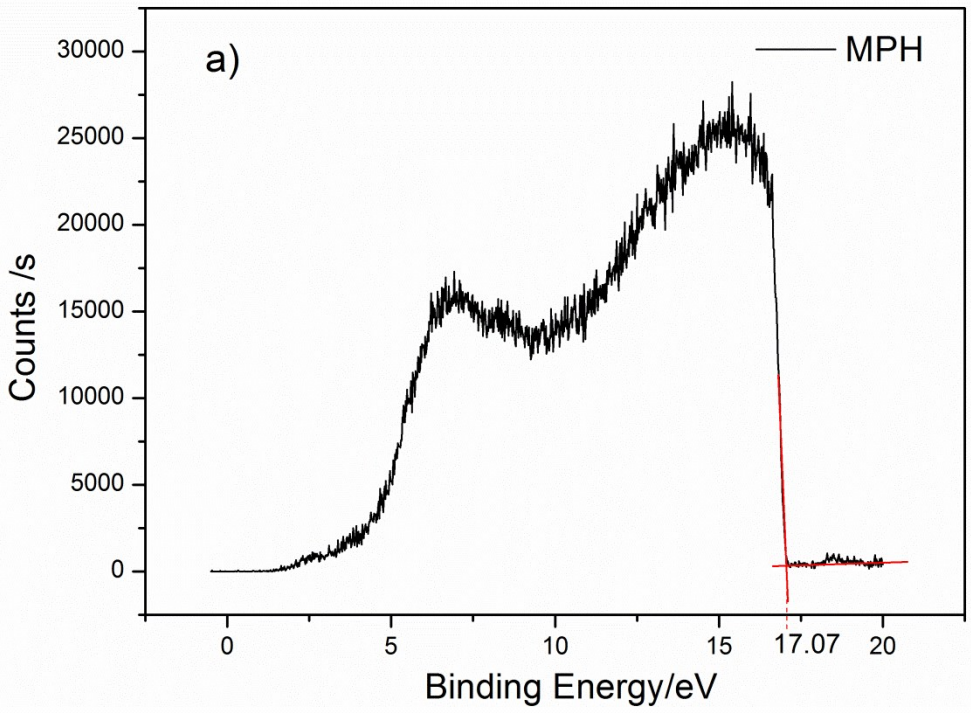
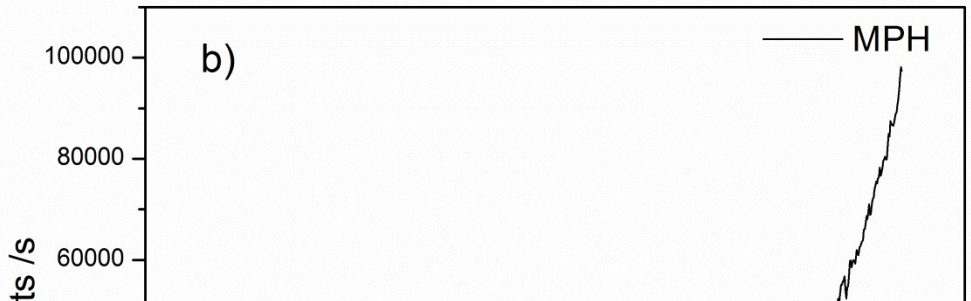


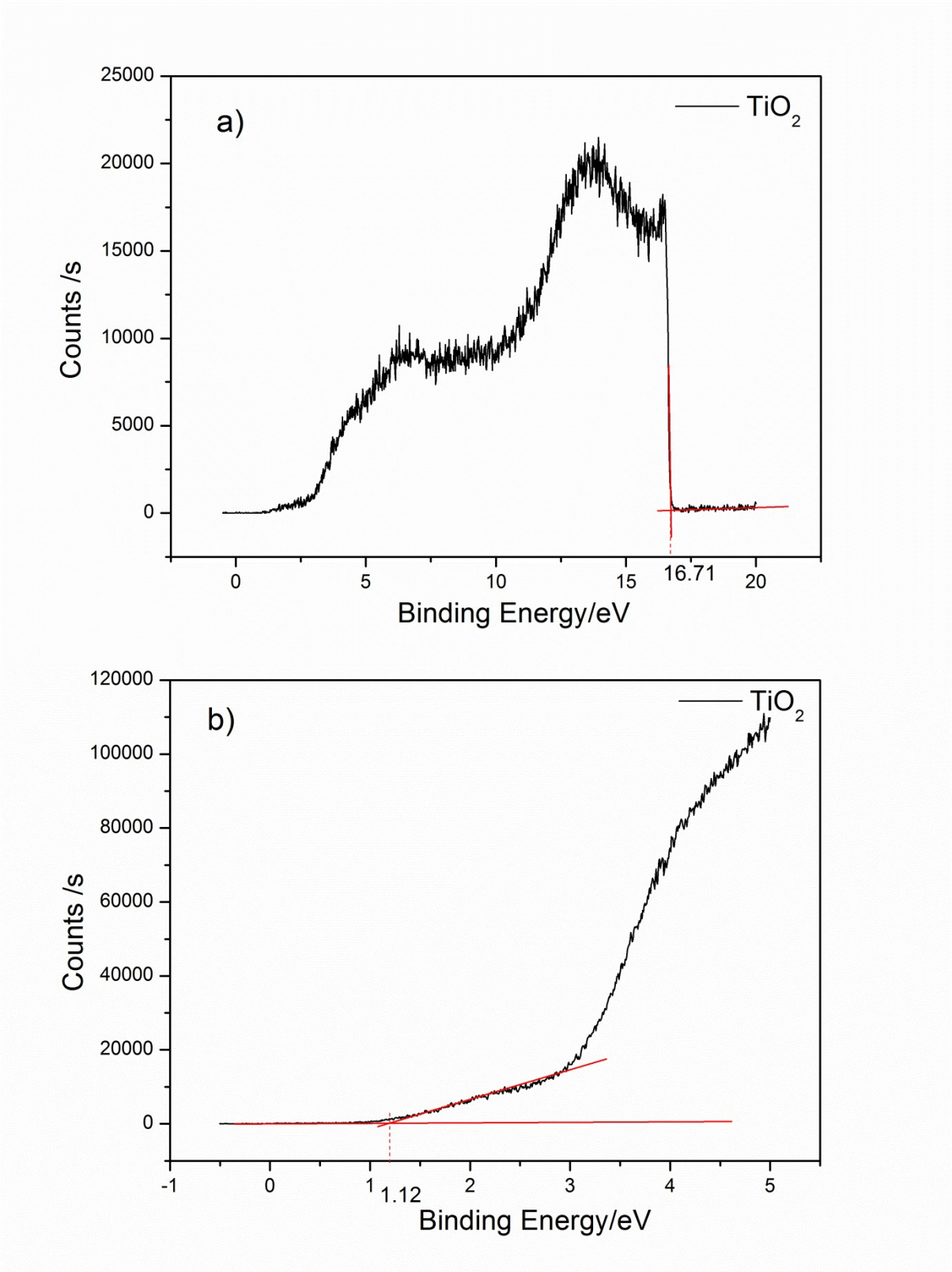
Figure S3 The UV-vis spectrum of MPH.


a)
MPH
30000
25000
20000
15000
10000
5000
0
Counts /s
0
5
10
15
17.07
20
Binding Energy/eV


b)
MPH
100000
80000
60000

As the Figure S3 shows, one of the UV-vis absorption bands is located at 292 nm. Thus, the band gap of MPH between HOMO and LUMO is 4.25 eV. According to Figure S4, the work function of MPH is 4.15 eV and the HOMO of MPH is situated at 5.82 eV. The LUMO of MPH is situated at 1.57 eV.

Figure S5 The UPS of TiO_2 layer.



According to Figure S5, the work function of TiO_2 is 4.41 eV and the VB of TiO_2 is situated at 5.63 eV. The band gap of TiO_2 between VB and CB is 3.2 eV. Thus, the CB of TiO_2 is situated at 2.43 eV.

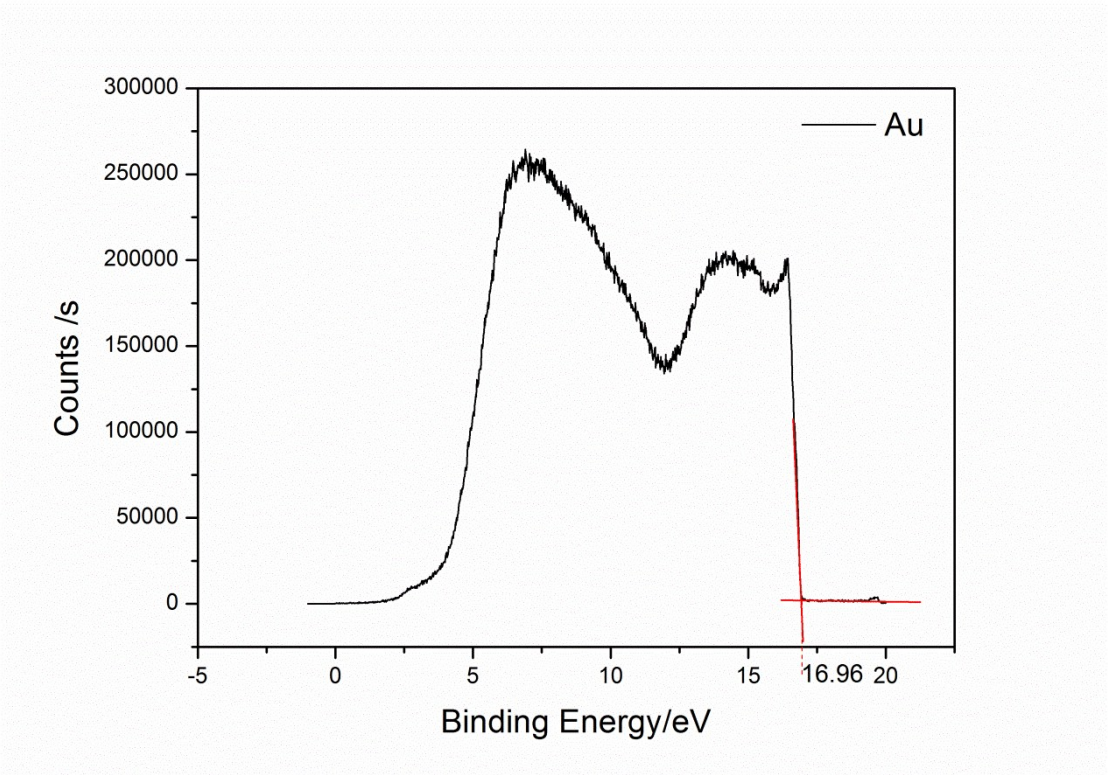
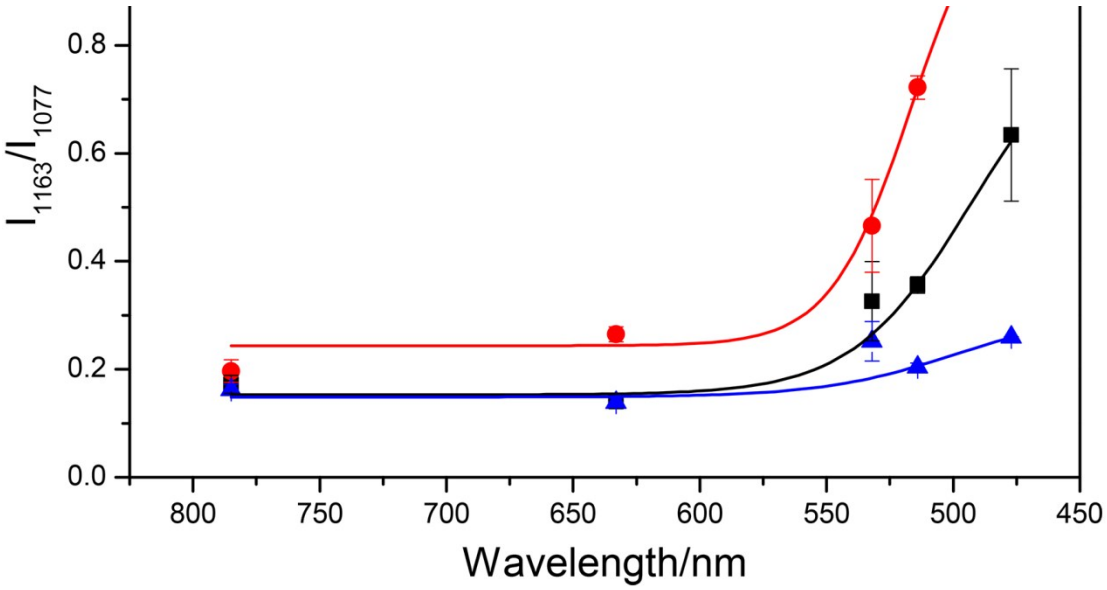


Figure S6 The UPS of Au NPs.

In Figure S6, the location of Fermi level of Au can be calculated out through the formula: WF=hν-ΔE. Thus, the Fermi level of Au is at 4.26 eV from the vacuum level.

Figure S7 Display of the SERS intensity ratio between the modes at 1163 and 1077 cm^{-1} in Pt/Ag/MPH/TiO_2, Pt/Ag/MPH and Ag/MPH assemblies as a function of excitation wavelengths. The data show an average of 5–7 independent measurements at different locations and the error bar indicates the standard deviation.



To prove the presence of TiO_2 layer in Au/Ag/MPH/TiO_2 system, XPS measurements were carried out (Figure S8). Figure S8 shows that Au, Ag, Ti, S, O elements exist on the surface of the charge-transfer systems. The peaks at 84.2 eV and 87.9eV are assigned to Au, which become weak as other layers are introduced (Figure S8b). The peaks at 368.5 eV and 374.4 eV are assigned to Ag (Figure S8c), while appears after the introducing of Ag NPs layer (Figure S8c). Compared with Au and Au/Ag in Figure S8d, peaks attributed to S in 162.7 eV appears in Au/Ag/MPH and Au/Ag/MPH/TiO_2, which is because -SH of MPH molecule is introduced subsequently. The Ti2p photoelectron (Figure S8e) shows a Ti2p3/2 peak at 459.4 eV and a Ti2p1/2 peak at 465.1 eV in Au/Ag/MPH/TiO_2 system. The observed peak position, the doublet separation between the 2p1/2 and 2p3/2 peaks of ~5.7eV is characteristic of Ti^{4+}. In Figure S8f, the peak at 530.7 eV is assigned to O1s which indicates the oxygen is bound to tetravalent Ti ions and the small shoulder at 532.6 eV implies that the surface is partially covered with hydroxide -OH groups.

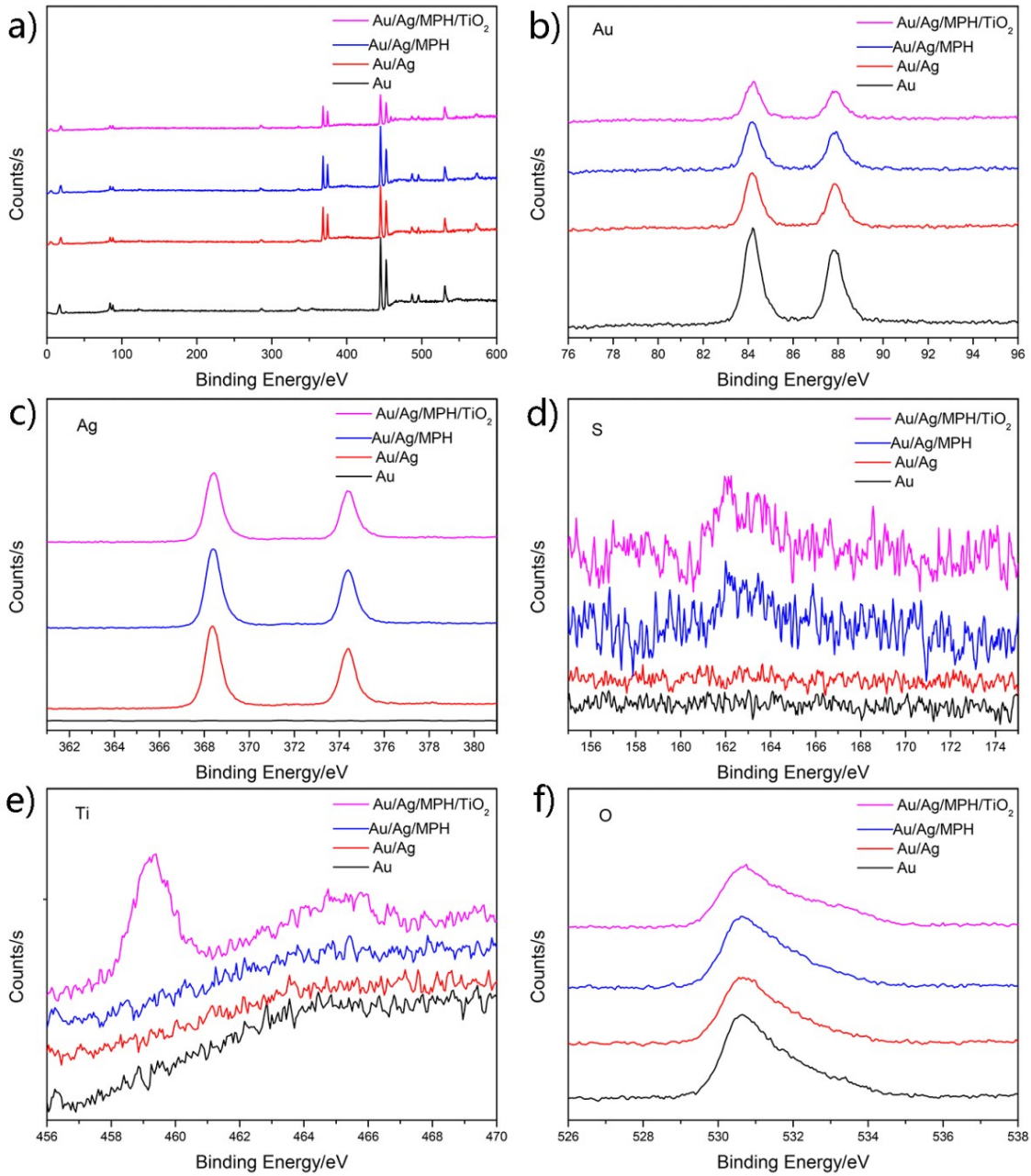


Figure S8 The X-ray photoelectron spectroscopy (XPS) of the charge-transfer systems, a) full spectrum, b) Au, c) Ag, d) S, e) Ti, f) O.