Supporting Information

Plasmon Catalysis on Bimetallic Surface - Selective Hydrogenation of Alkynes to Alkanes or Alkenes

O. Guselnikova[a,b], A. Olshtrem[a,b], Y. Kalachyova[a,b], I. Panov[c], P. Postnikov[a,b], V. Svorcik[a], O. Lyutakov[a,b]

[a] *Department of Solid State Engineering, University of Chemistry and Technology, 16628 Prague, Czech Republic*

[b] *Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Russian Federation*

[c] *Group of Advanced Materials and Organic Synthesis, Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojová 1/135, 165 02 Prague, Czech Republic*

General experimental remarks

1H NMR spectra were recorded on Bruker Avance III™ (500 MHz) spectrometer. Chemical shifts are given in parts per million (δ/ppm), referenced to dimethylsulfoxide (2.51) as internal standards. All coupling constants are absolute values and are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet. 13C NMR spectra were recorded on Bruker Avance III™ (500 M Hz) spectrometers. Routine monitoring of reactions was performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analysed under UV-light at 254 nm and dipped into a solution of 2-naphthol (5 % naphthol in 10 % NaOH aqueous, dipping solution). Solvent mixtures are understood as volume/volume.

Synthesis of 4-ethynylbenzenediazonium tosylate (ADT-C≡CH)

To a solution of p-TsOH (1.425 g, 7.5 mmol) in acetic acid (12 mL), tert-butyl nitrite was slowly added (0.9 mL, 7.5 mmol). Next, 4-ethynylaniline (0.585 g, 5 mmol) was added in 4 steps to the reaction mixture over 1 min. The mixture was stirred for 30–40 min until TLC indicated the complete consumption of the amine (hexane/ether 1:1). After completion, the reaction mixture was precipitated by adding diethyl ether (200 mL). The precipitate was washed with diethyl ether, filtered under reduced pressure and dried under vacuum (1.176 g, 74 % yield).

Mp 88-91 °C with decomposition. IR (KBr): 2215 (N≡N) cm^{-1}. 1H NMR (500 MHz, DMSO): δ 2.29 (s, 3H), 2,5 (s, 1H), 7.12 (d, *J* = 7 Hz, 2H), 7.48 (d, *J* = 7 Hz, 2H), 8.04 (d, *J* = 9 Hz, 2H), 8.69 (d, *J* = 9.0 Hz, 2H). 13C NMR (DMSO): δ 21.36, 81.82, 91.83, 115.96, 125.97, 128.63, 133.48, 134.03, 134.46, 138.36, 145.81.

Proofs of the hydrogen production from cyclohexene under the plasmon triggering:

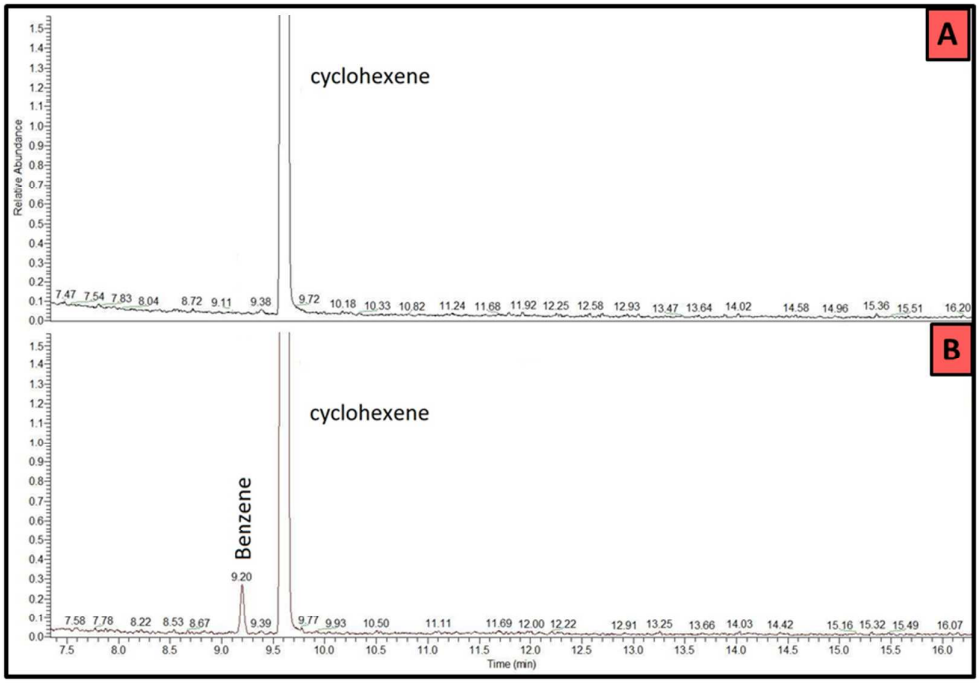

Fig. S1 Results of mass spectrometry analysis of postreaction mixture

The reaction mixture after the plasmon triggering was analyzed using the gas chromatography mass spectrometry (MS), with the aim to reveal the appearance of benzene in reaction mixture, as an evidence of active hydrogen production from cyclohexene. Results of MS indicate the presence of benzene in the postreaction mixture, which confirms the cyclohexene dehydrogenation and creation of hydrogen species under the plasmon triggering.

Table S1

Surface element concentrations (at.%) XPS measured under 90º for pristine, Au/Pt-1 (15 min of reduction of H_2PtCl_6 on Au surface), Au/Pt-2 (40 min of reduction of H_2PtCl_6), Au/Pt-1-C≡CH and Au/Pt-2-C≡CH with phenylacetylene groups on the surface.

Sample	C (1s)	O (1s)	Au (4f)	Pt (4f)
Au	52	17	31	-
Au/Pt-1	60	22	-	18
Au/Pt-2	55	18	-	27
Au/Pt-1-C≡CH	78.7	18.5	-	2.8
Au/Pt-2-C≡CH	75.9	19.3	-	4.8
Au/Pt-1-C≡CH after SPP reduction	78.5	18.6	-	2.9
Au/Pt-2-C≡CH after SPP reduction	76.0	19.2	-	4.8

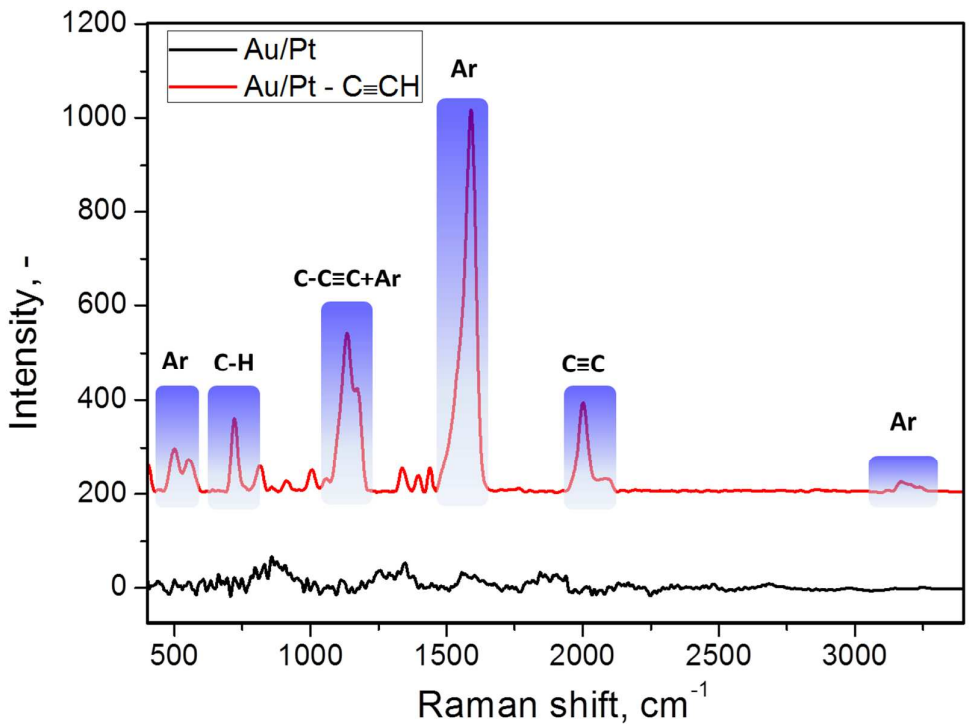

Fig. S2

Raman spectra of Au/Pt gratings and Au/Pt gratings with phenylacetylene groups.

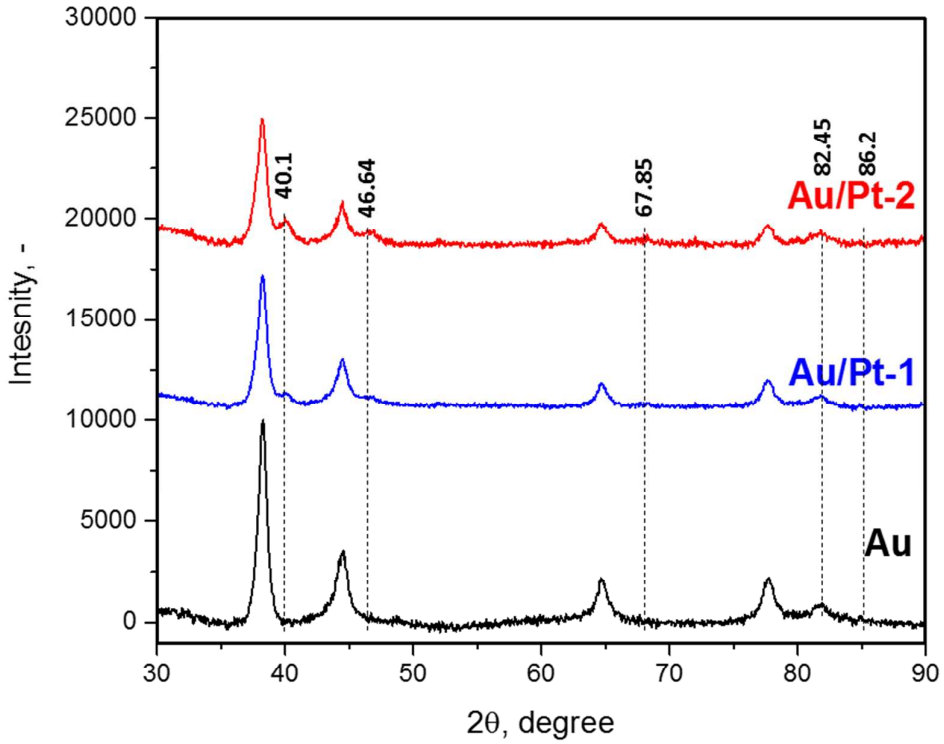

Fig. S3 X-ray diffraction spectra of Au, Au/Pt-1, and Au/Pt-2 gratings.

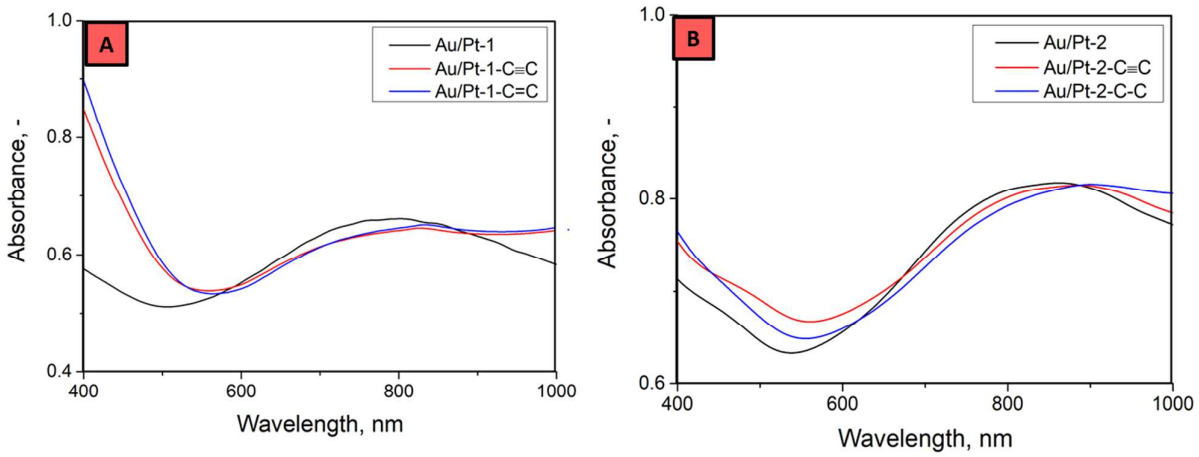

Fig. S4 UV-Vis spectra of A – Au/Pt-1 grating, modified by ADT- C≡CH and after illumination with 785 nm wavelength in the cyclohexene (laser density 9.6 μW/μm^2) and A – Au/Pt-2 grating, modified by ADT- C≡CH and after illumination with 785 nm wavelength in the cyclohexene (laser density 9.6 μW/μm^2)

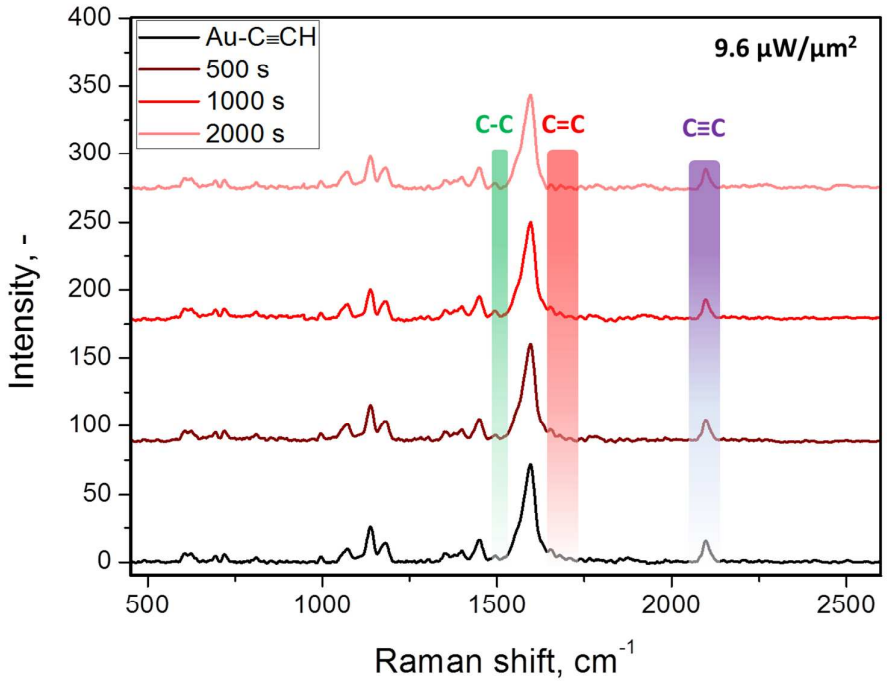

Fig. S5 Time-dependent SERS spectra Au grating modified by ADT-C≡CH after illumination with 785 nm wavelength in the cyclohexene (laser density 9.6 μW/μm^2).

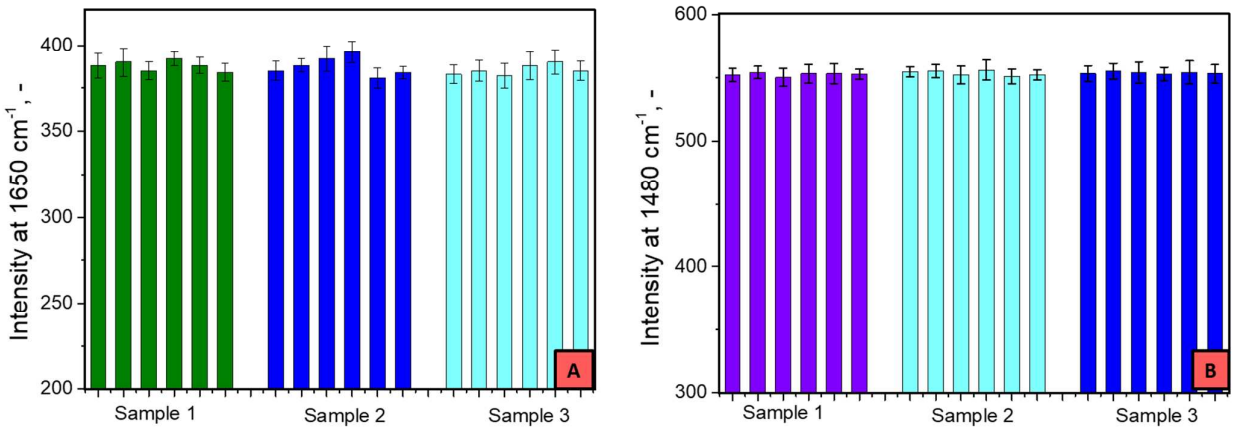

Fig. S6 Reproducibility SERS measurement of hydrogenation of phenylacetylene groups on: (A) - Au/Pt-1 using characteristic peak at 1650 cm^{-1} (C=C stretching vibrations); (B) - Au/Pt-2 gratings using characteristic peak at 1480 cm^{-1} (C-H bending under continuous exposure to laser illumination (wavelength - 785 nm, intensity – 9.6 μW/μm2).

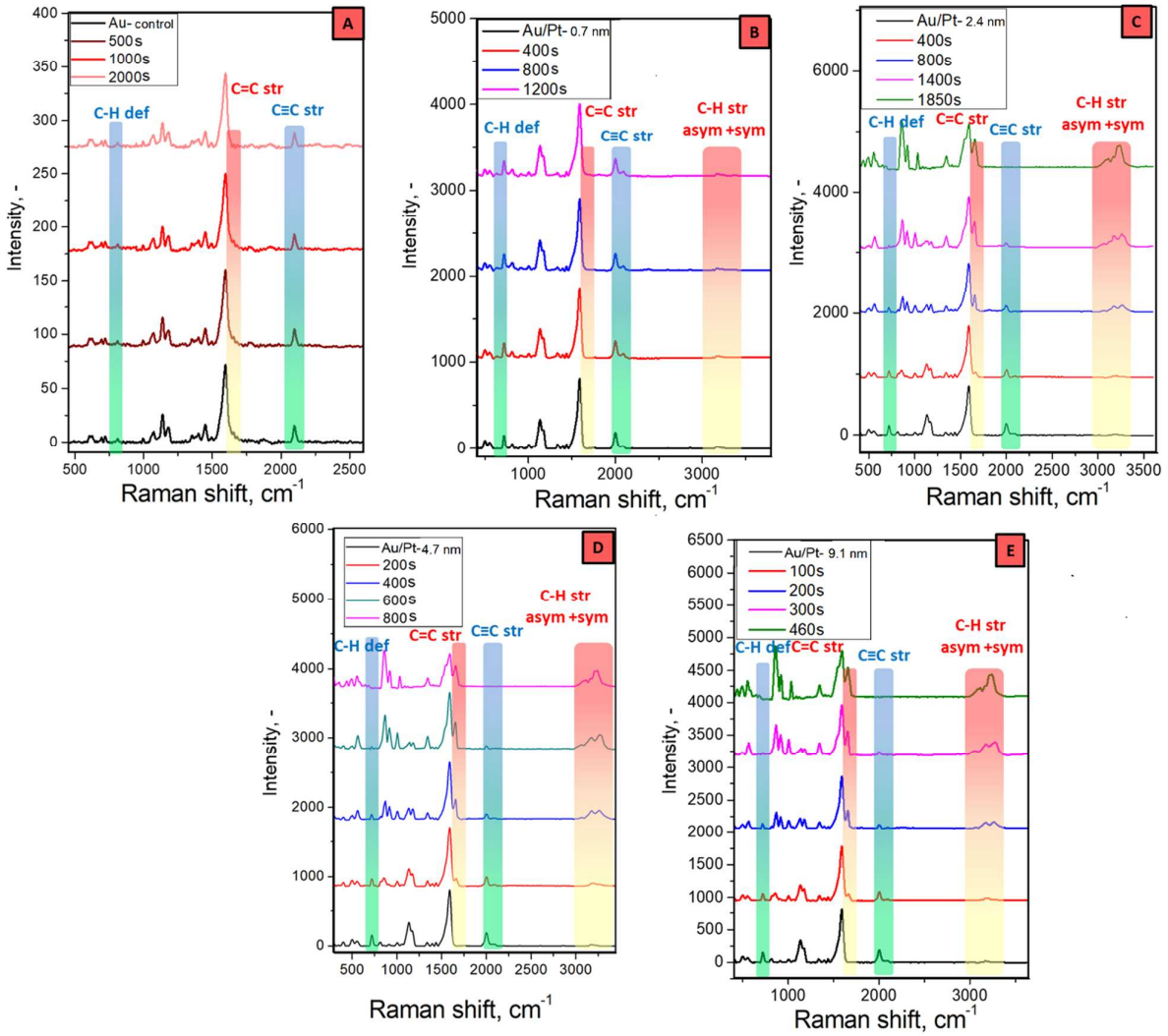

Fig. S7 Pristine and time-dependent (time in s) SERS spectra of plasmon-assisted hydrogenation of phenylacetylene groups on: (A) – Au grating, (B)- Au grating coated 1.5 nm Pt layer, (C)- Au grating coated 5 nm Pt layer, (D)- Au grating coated 10 nm Pt layer, (E)- Au grating coated 18 nm Pt layer under continuous exposure to laser illumination (wavelength - 785 nm, intensity - 7.2 $\mu W/\mu m^2$).

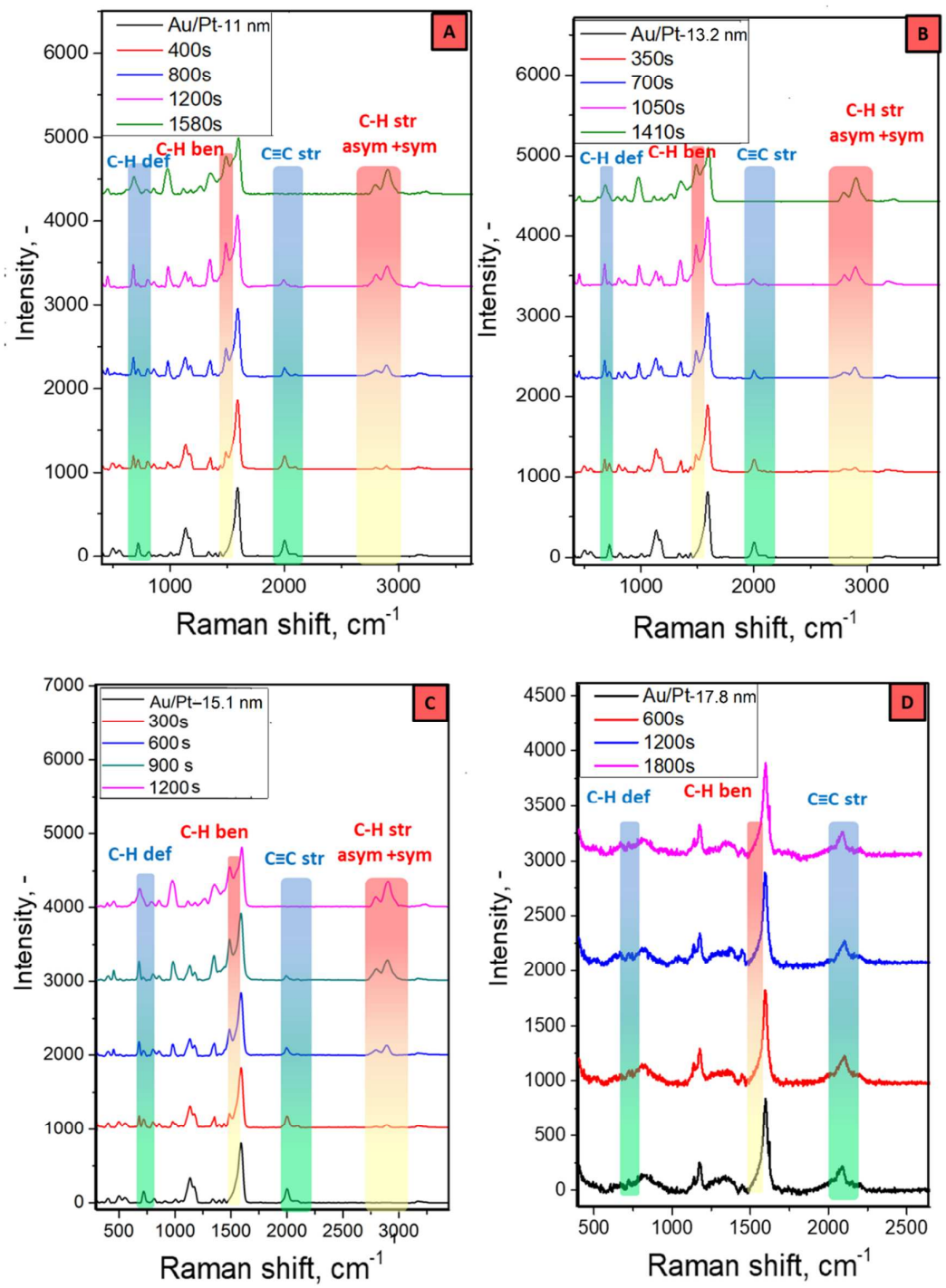

Fig. S8 Pristine and time-dependent (time in s) SERS spectra of plasmon-assisted hydrogenation of phenylacetylene groups on: (A)- Au grating coated 22 nm Pt layer, (B)- Au grating coated 25 nm Pt layer, (C)- Au grating coated 30 nm Pt layer, (D)- Au grating coated 35 nm Pt layer, under continuous exposure to laser illumination (wavelength - 785 nm, intensity - 7.2 μW/μm^2).

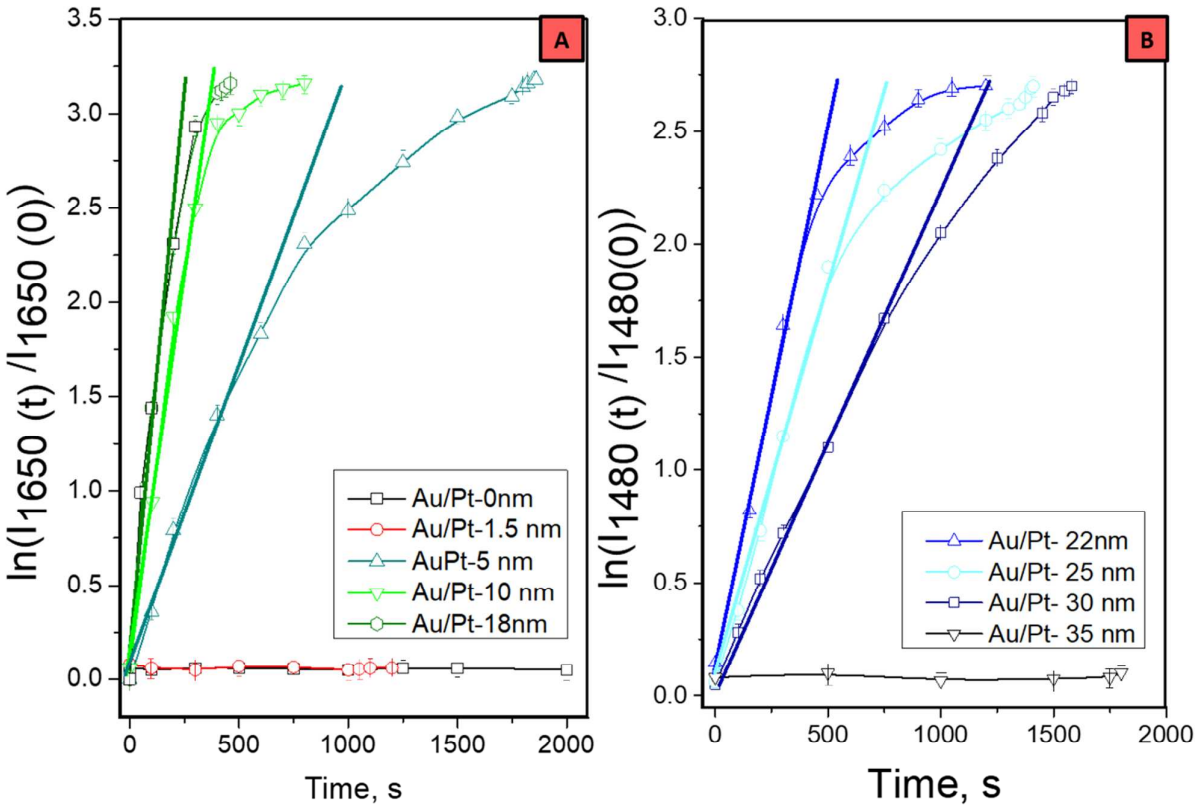

Fig. S9 First order reaction kinetic curves of plasmon-induced hydrogenation of phenylacetylene groups on gold gratings with Pt layer (A) 0-18 nm, (B) – 22-35 nm at laser power 7.2 μW/μm^2