Supplementary Information

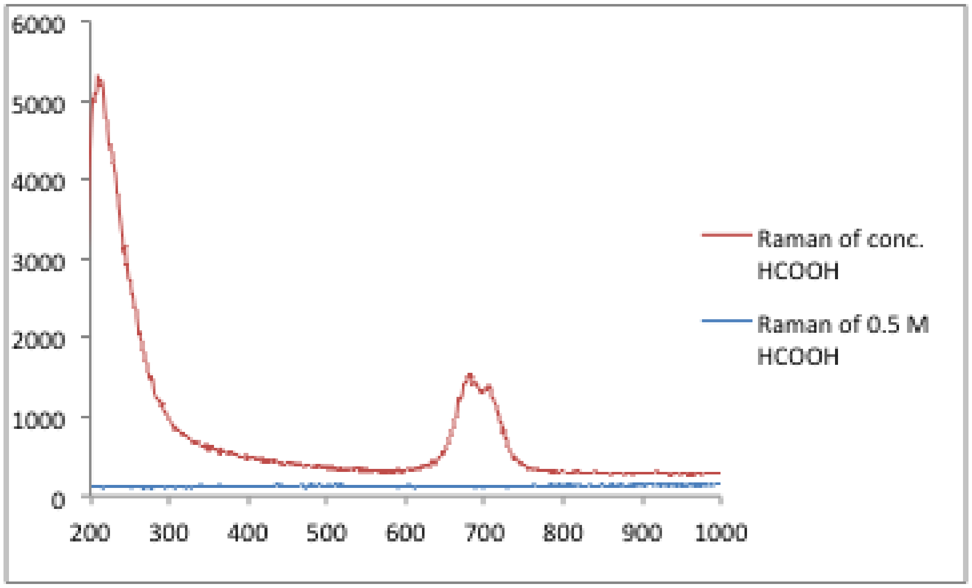

Figure S.1 Normal Raman spectra of 0.5 M and concentrated formic acid. Excitation wavelength at 647 nm from an Argon and Krypton laser (Coherent, Innova 70C series) with 35 mW of power, 5 s of exposure time and 1 accumulation.

Figure S.1 shows the normal Raman spectra of 0.5 M formic acid and concentrated solution of formic acid. Peak at about 205 cm^{-1} is due to OH…H out of plane bend and peak at belong to OCO bend.[1] No clear peak was observed in the range of 250 - 300 cm^{-1} which indicates that there is no interference from the formic acid in aqueous solution during the SERS measurements.

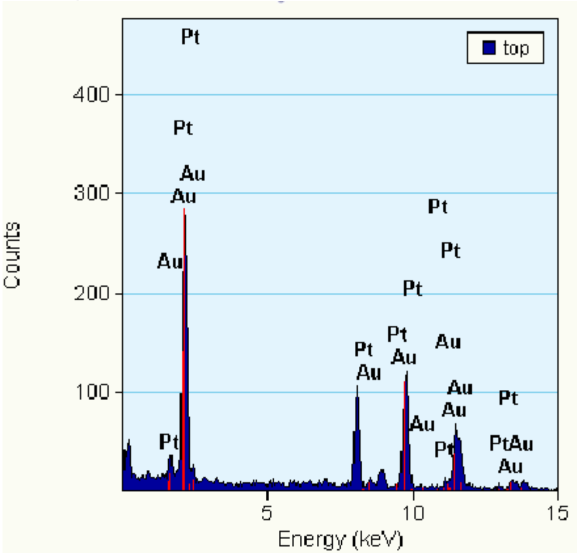

Figure S.2. Energy dispersive X ray (EDX) spectrum of Pt-modified Au (10 minutes) surface.

Figure 2 shows the EDX spectrum of the Pt@Au surface with a deposition time of 10 minutes. The presence of both the gold and platinum peaks was confirmed.

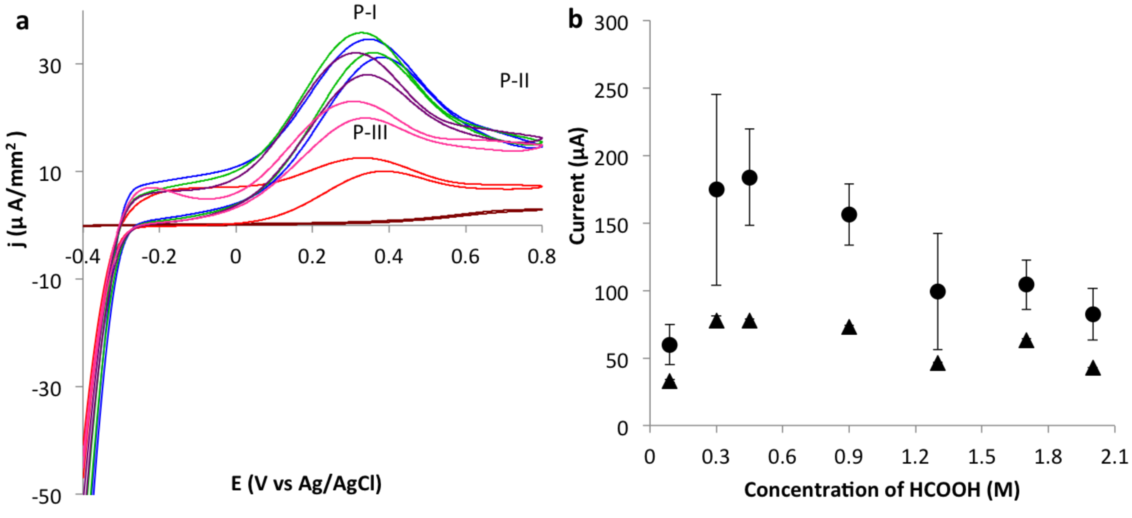

Figure S.3 a) Electrooxidation of formic acid on Pt-modified Au (10 minutes) and Au surface (in blue) in a solution containing 0.09 M (red), 0.3 M (blue), 0.45 M (green), 0.90 M (purple) and 1.7 M (pink) HCOOH respectively, and on Au in solution containing 0.1 M HCOOH (brown) The voltammograms were collected with a scan rate of 50 mV/s. b) Plot of the oxidation current of HCOOH vs. the concentration, peak I (circles) and CO peak II (triangles). The standard error is obtained from minimum of 3 experiments.

Figure S.3 (a) shows the CVs for the electrooxidation of formic acid at concentrations of 0.09 M, 0.30 M, 0.45 M, 0.90 M, 1.7 M and 2.0 M in 0.125 M perchloric acid on the Pt@Au electrode. The characteristic oxidation peaks/processes P-I, II, III can be clearly seen in all voltammograms. However, the peak shapes observed at lower concentrations are different from that obtained at higher concentrations. At 0.09 M, though it is evident that formic acid is oxidized, there is no distinguishable peak (P-II) for CO. At concentrations of 0.30 M and higher, a distinctive peak for CO oxidation is observed between 0.6 - 0.8V. This can be explained by the increase in overall poison present in the system.[2] Therefore, at lower concentrations, formic acid is mostly oxidized by the dehydrogenation pathway. As the concentration increases, more formic acid molecules take the dehydration pathway. Figure S.3 (b) shows the relationship between peak current and formic acid concentration. As the formic acid concentration increases, peak current of P-I (circles) for the direct oxidation of formic acid increases and reaches a maximum of 180 µA at 0.45 M, then drops to about 100 µA at 1.7 M. On the other hand, as the concentration of formic acid increases, the peak current of P-II for the CO oxidation (triangles) increases initially. However when the concentration of formic acid is above 0.3 M, the P-II current hovers around 60 µA. Interestingly, the oxidation current of both peaks decreases as the concentration of formic acid is further increased above 1.7 M. These phenomena suggest that the dehydrogenation pathway is more predominant on Pt@Au surface when the formic acid concentration is below 0.45 M.

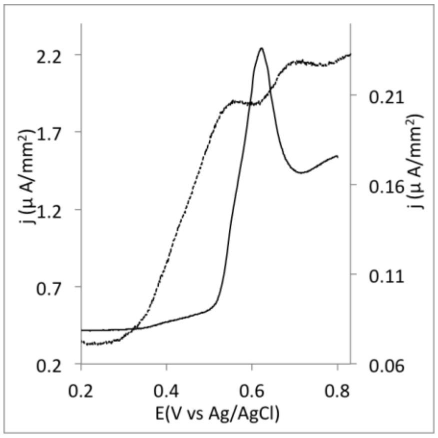

Figure S.4. CO stripping curves of Pt-modified Au (10 minutes; dashed line, right Y-axis) and poly Pt surface (solid line, left Y-axis) in 0.125 M $HClO_4$ at a scan rate of 50 mV/s.

CO stripping measurements were done following previous procedure.[3] Briefly, CO was bubbled in to the electrochemical cell for 15 minutes followed by holding at 0.05 V for 15 minutes. Then, nitrogen was purged in for 30 minutes to remove any CO in the solution before taking the measurements. As reported previously, plain Au does not absorb any CO.[3] Therefore, the voltammogram is not shown here. Figure S.4 shows the CO stripping curves obtained on polycrystalline Pt and Pt-modified Au surface. On bare Pt surface, CO is oxidized at 0.60 V which agrees well with previous reports.[4,5] Interestingly, there are two peak potentials for CO adlayer oxidation on the Pt spontaneously deposited Au surface ca. 0.53 V and 0.67 V. This phenomenon was also observed before on Pt spontaneously deposited Au (111) surface.[5] The peak at 0.53 V is attributed to CO oxidation on Pt islands larger than 10 nm while the one at 0.67 V is ascribed to CO oxidation on Pt islands less than 10 nm.[3,6,7] Clearly, Pt-modified Au surface is active for CO oxidation and its activity highly depends on the structure of the Pt deposits.

References

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