

**Electronic Supplementary Information for *Anal. Meth.***

***In situ* SERS Interrogation of Catalytic Reaction on Three-Dimensional  
Gold Nanowire Carpeted Polycarbonate Membranes**

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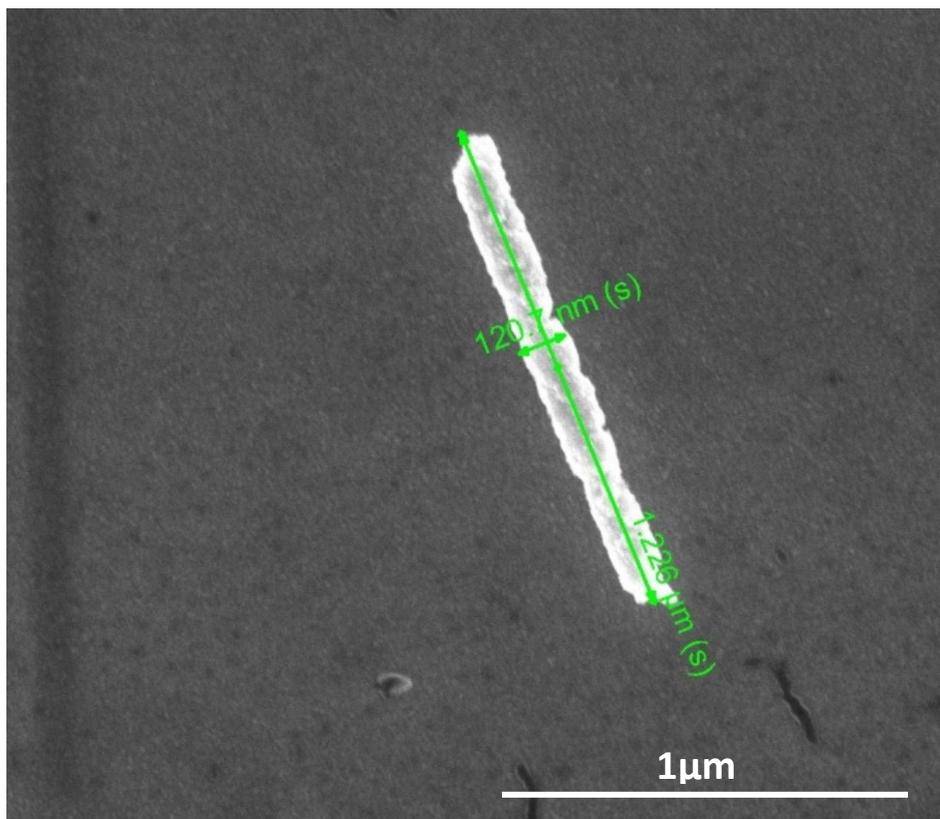
**Diameter of gold nanowire.** The size of resulting gold nanowire was roughly evaluated by SEM imaging. First, the wire-filled polycarbonate membrane was dissolved in neat chloroform until the film entirely melts out. A drop (10 $\mu$ L) of mixture was then casted on planar gold substrate, drying under the ambient conditions. The NW-bounded chip was consecutively rinsed by chloroform and methanol in order to remove organic components. Non-specific physical adsorption would partially retain these nanoscale materials on flat surface. The SEM image, in Fig. S1 shows the diameter of synthesized NW is estimated 120 nm with 1.2  $\mu$ m in length, which might be caused by fragmentation during the membrane dissolving and thoroughly rinsing procedure.

**Raman scattering on Au-coated polycarbonate membrane.** To evaluate the behavior of porous polycarbonate film corresponding to metal evaporation, the 300nm-thick gold layer was deliberately coated on one-side of film, resulting in laminar structure. On the identical conditions, Raman spectra were acquired on two terminals, polymer and metal layer, respectively. The results, shown in Fig. S2, as expected, reveal quite a distinct outline. No appreciable signal can be observed on gold side, while the decent Raman spectrum is acquired with ease from polymer side, indicating the full coverage by metal would totally eliminate the scattering light from polymer itself.

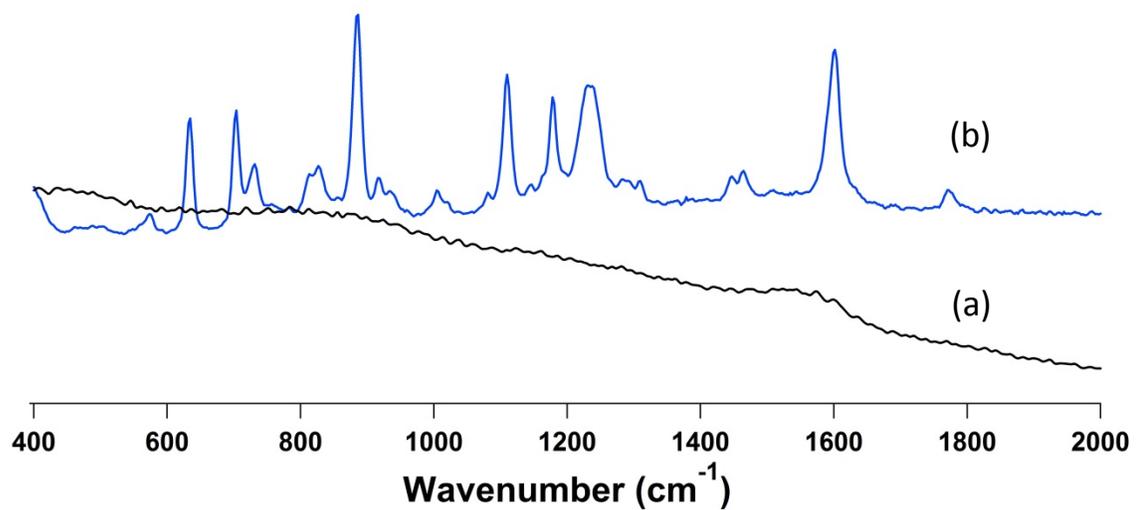
**Quantitation of catalytic reaction on GNW.** Due to nonlinear property of SERS measurement, enhanced signal intensity is not proportional to actual molecule density on surfaces, but following the same trend. Here, uv-vis extinction spectrum is spatially and temporally correlated with Raman microscope in a way that the concentration of the resulting product is determined from solution. Fig. S3 shows the uv-vis extinction spectra during the catalytic reaction, where sample concentration is calculated according to its absorbance coefficient and inset exhibits the kinetic curve of catalytic reaction. At wavelength 400nm, starter, 4-NP exhibits maximal absorption, while resulting product, 4-AP has negligible contribution to uv-spectrum. Thus, spatially correlated uv-vis extinction is employed to quantitatively characterize the chemical process, which, from what we observed is a typical first-order-reaction. In SERS monitoring, the prominent peak intensity exhibits same kinetic curve aligning with real time uv-vis spectrum, though absolute quantitative SERS measurement is questionable, since many factors are responsible for optical enhancement, not plainly from molecule density. Roughly,

gradually increase SERS intensity of 4-AP exhibits the similar tendency as uv-vis response in solution phase (Fig. 6 in manuscript).

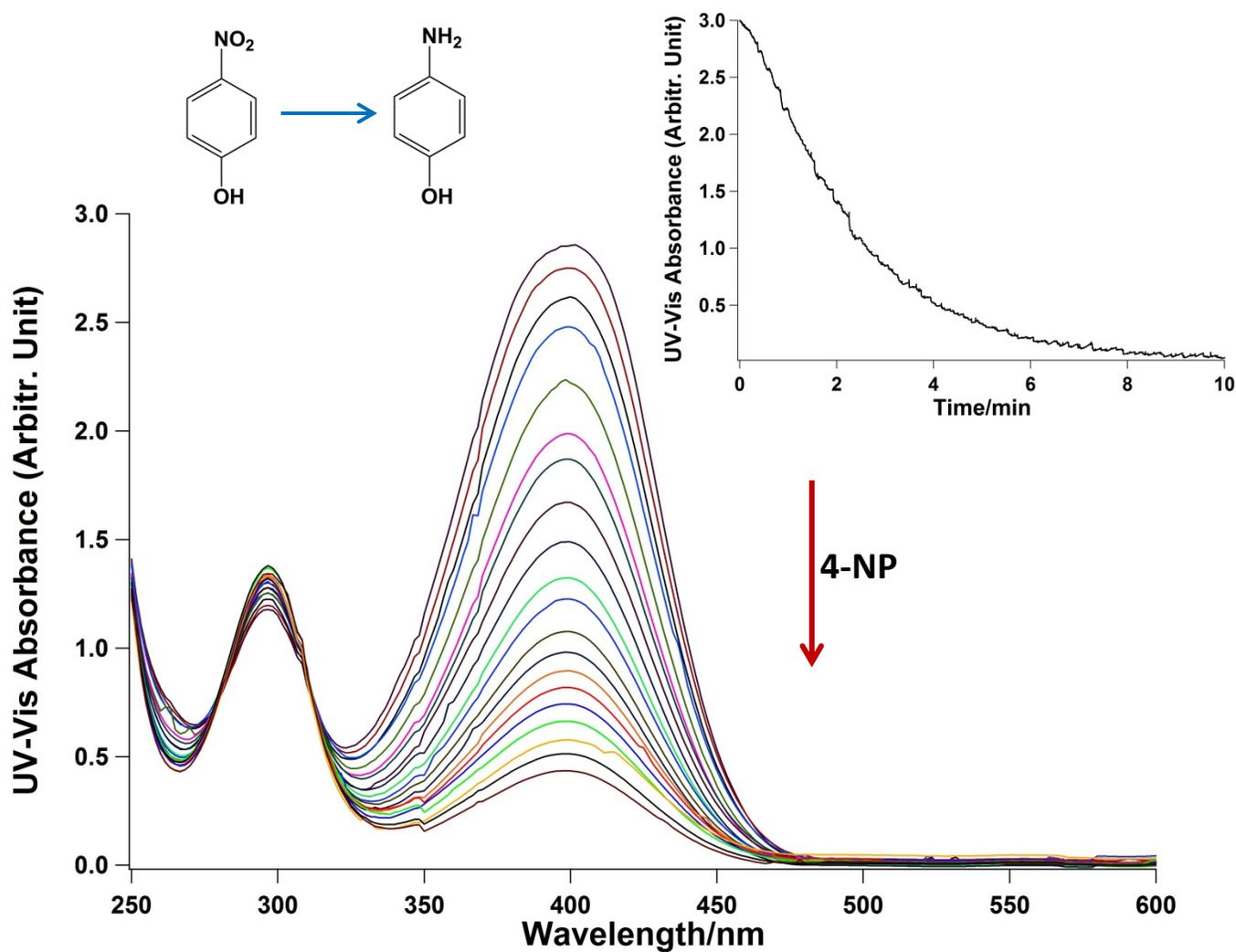
**Spatially correlated SEM and SERS image.** In order to study the uniformity of optical enhancement on gold nanowire, a special marker is registered to generate spatial correlation of SEM, light micrograph and SERS image in same scale, as indicated in Figure S4. In the same sample spot, SEM micrograph delineates the surface morphology, while, correlated SERS image defines contour of optical enhancement, implying that the surface morphology of gold nanowire impinges decisive effect on Raman detection.



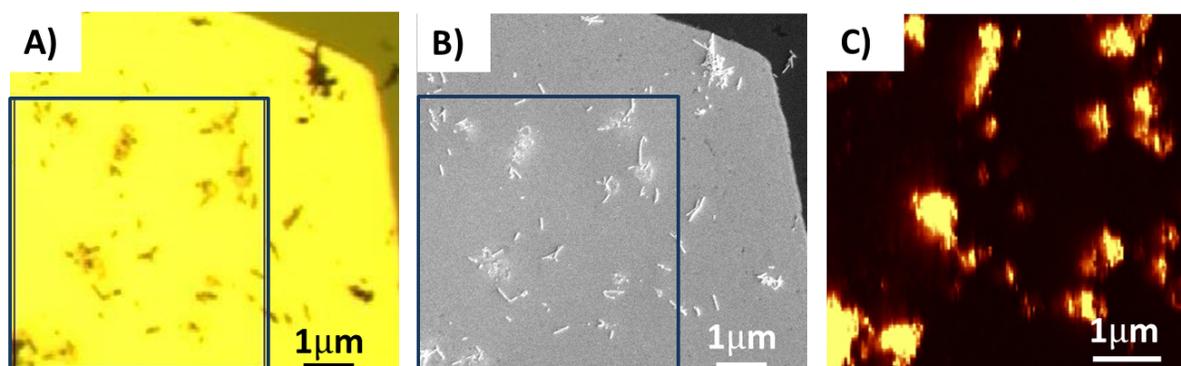
**Figure S1.** SEM micrograph of a single gold nanowire on planar substrate. The length of Au NW measured in image is estimated 1.2  $\mu\text{m}$  with 120 nm in diameter.



**Figure S2.** The Raman spectra acquired from 300nm-thick gold-deposited NCAM. (a) Raman scattering from gold side, (b) corresponding Raman spectrum on polycarbonate layer. No any appreciable signal is observed on gold layer. Spectra were subject to offset for clarity.



**Figure S3.** Uv-visible absorbance spectra of 4-NP over distinct reaction times. Inset: kinetic study of molecular conversion catalyzed by gold nanowire ensembles at the excitation of 400nm, which is characteristic peak of 4-NP aqueous solution, while the catalytic product 4-AP gives rise to the unique extinction peak near 317nm.



**Figure S4.** Spatially correlated light microscope, SEM and SERS images of ATP-terminated gold nanowires deposited on gold (200 μm in depth) coated silicon wafer.