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SUPPLEMENTARY INFORMATION

In situ monitoring of catalytic process variations in a single nanowire by dark-field-assisted surface-enhanced Raman spectroscopy

Xin Shi[1], Haowen Li[1], Yi-Lun Ying[1], Chang Liu[2], Li Zhang[2], Yi-Tao Long[1]*

[1]Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, P. R. China

[2]College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, P. R. China

* To whom correspondence should be addressed: ytlong@ecust.edu.cn

Experimental Section

Modification procedure and catalytic reaction. Quartz glass slides were cleaned by boiling in piranha solution (H_2SO_4 and H_2O_2 in a ratio of 3:1 volume/volume) for 10 min at 60 ˚C, then rinsing the slides with acetone, ethyl alcohol and deionised water and ultrasonic cleaning for 30 min respectively. MnOOH-Ag nanowires were dispersed in alcohol and then immobilized on the quartz glass. The glass slide with nanowire adsorbed was immersed into a mixture of 10^{-2} M p-nitrothiophenol (pNTP, AR) and 10^{-2} M 2-naphthalenethiol (2-NT, AR) for 12 h. The catalytic reduction process was triggered by adding a drop of 0.1 M sodium borohydride to the slide after adjusting the position of the nanowire.

Dark- field microscopy and scattering spectroscopy. The SERS spectrum measurements were carried out with a home-built Raman spectroscopy system on an inverted microscope (Eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser ($0.8<NA<0.95$) and a 100 W halogen lamp. The Raman signal was excited by a 785 nm laser (Innovative Photonics Solutions, United States) and collected by a ×40 objective lens (NA=0.6, Nikon). A True-Colour CCD camera (DS-Fi1c, Nikon) was used for capturing dark-field images, and a spectrograph (Isoplane, Princeton Instruments, United States) with EMCCD (ProEM+1600, Princeton Instruments) was used for spectrum measurements. Samples of interest need to be moved to the position of laser spot and rotated to fit the slit of the spectrograph under the dark field. Subsequently, Raman measurements could be carried out. To follow the reaction, spectra with 700 ms exposure time and 300 ms readout time were acquired continuously. Data analysis was carried out using a home-written Matlab analysis routine.

a slit-scanning-like optical structure10 was introduced into an inverted dark-field microscope to achieve the monitoring of a catalytic process along an entire single nanowire. The optical path is presented in Fig. 1 in the main text. The 785-nm laser was focused on nanowire catalysts which were immobilized on the upper side of a quartz glass substrate. Due to the waveguide effect of the nanowire material, the entire catalyst could be illuminated by the excitation laser. Hence, the Raman signal of the molecule at each point of the wire could be excited. Subsequently, the Raman scattered photons from each site of the wire would be collected with the objective, passed through the slit, dispersed by the grating and detected by a cooled electron multiplying charge-coupled device (EMCCD) array. The dark-field image of the nanowire needs to be accurately placed into the slit of the spectrograph by moving and rotating the stage under the dark-field microscope to ensure that scattered photons from the entire nanowire could enter the spectrograph. The acquisition of the scattered Raman signal at every position of the nanowire could be achieved simultaneously by using the presented approach.

Supplementary figures

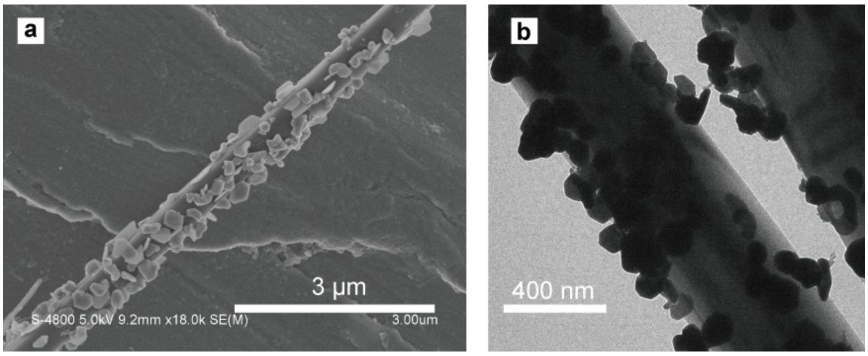

Figure S1. Magnified SEM (a) and TEM (b) images of MnOOH-Ag nanowire. Scale bar: 3 μm in (a) and 400 nm in (b).

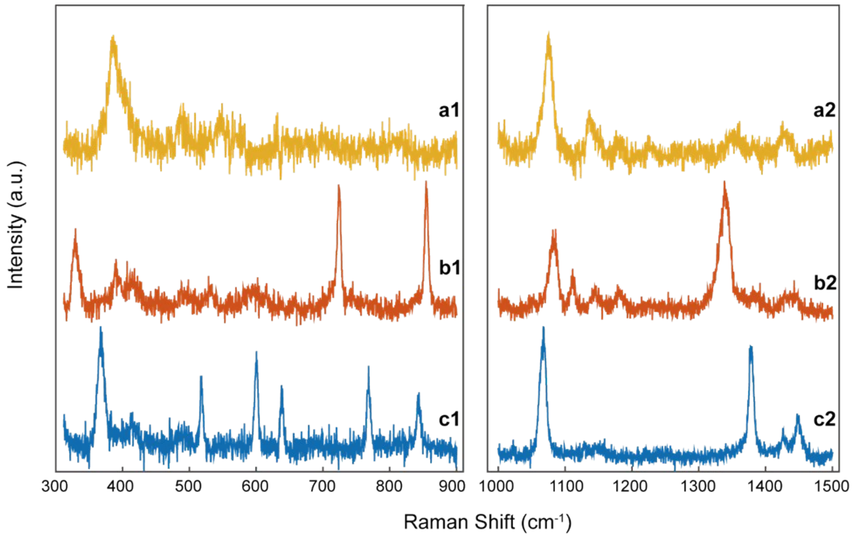

Figure S2. SERS spectra collected from p-aminothiophenol (pATP, a1, a2), p-nitrothiophenol (pNTP, b1, b2) and 2-naphthalenethiol (2-NT, c1, c2) on single MnOOH-Ag composite nanowires. λ_{laser}= 785 nm, intensity: 20 mW, acquisition time: 1 s. SERS spectra from single nanowire were obtained by summing up intensity value of each row of pixels in the spectral image of single nanowire.

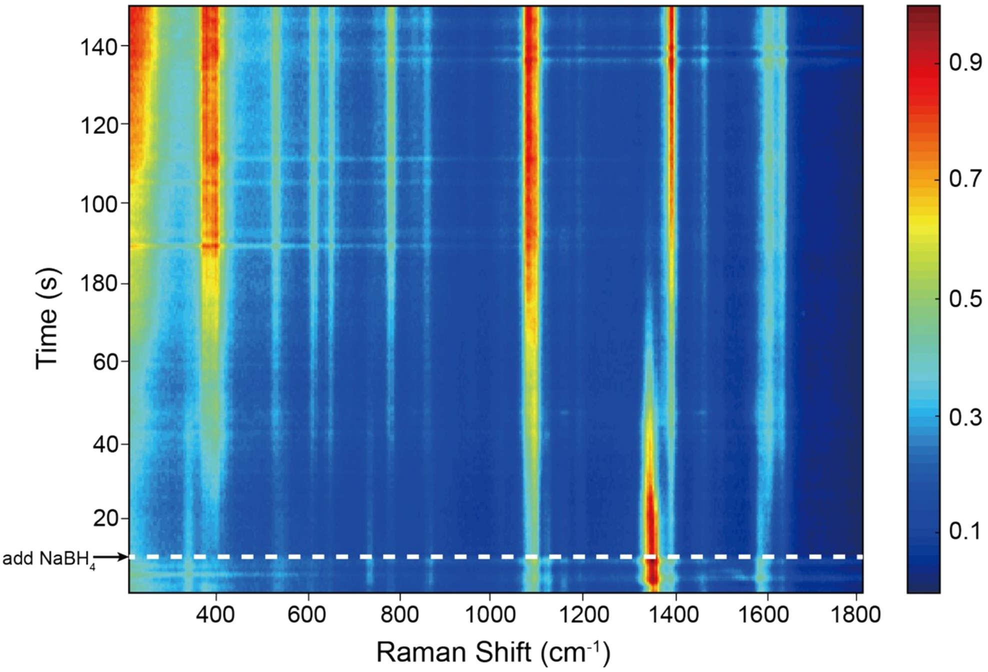

Figure S3. Colour-coded intensity map of time-resolved SERS spectra of the reduction of pNTP (bottom) to pATP (top, spectrum mixed with that of pNTP) with range of 300~1800 cm^{-1}. λ_{laser}= 785 nm, intensity: 20 mW, acquisition time: 1 s

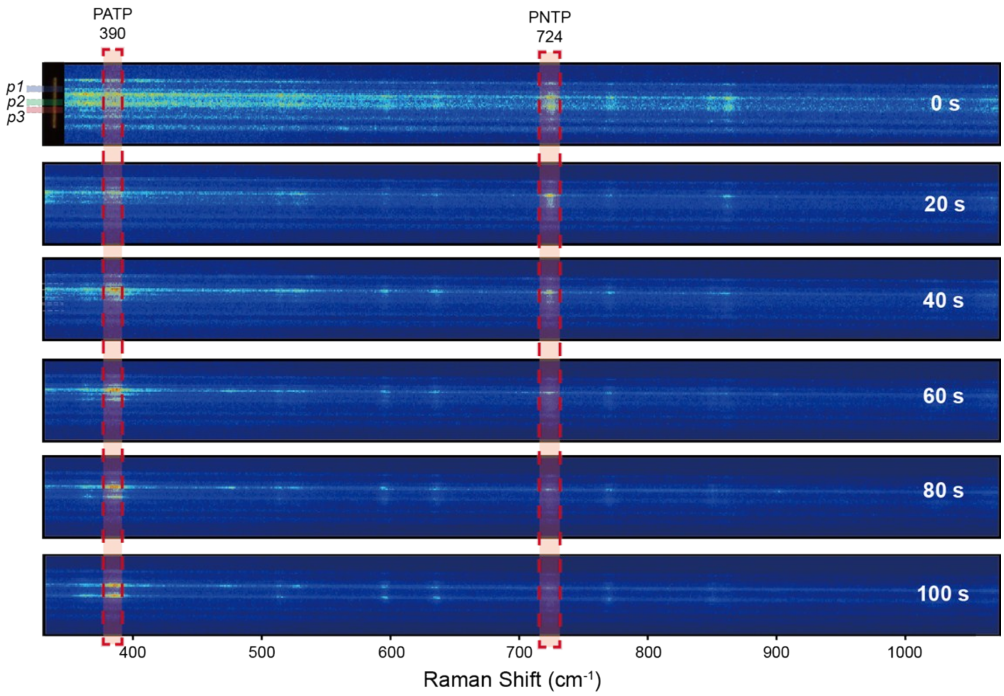

Figure S4. SERS Spectral-image variation of a single nanowire, taken every 20 s after the addition of sodium borohydride, Corresponding to the figure 4 in the main text. In each image, the space-resolved intensity of compounds could be obtained. The image was obtained by 25.6 mm wide CCD sensor and a 1200 grooves/mm grating.

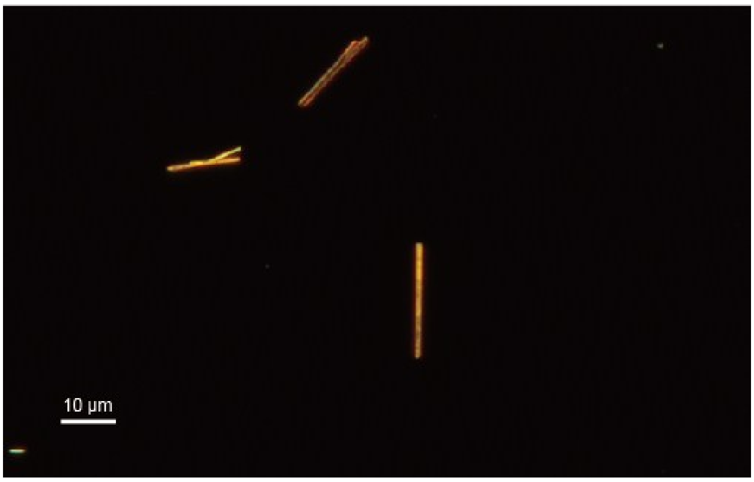

Figure S5. Dark-field micrograph of MnOOH-Ag Composite nanowire.

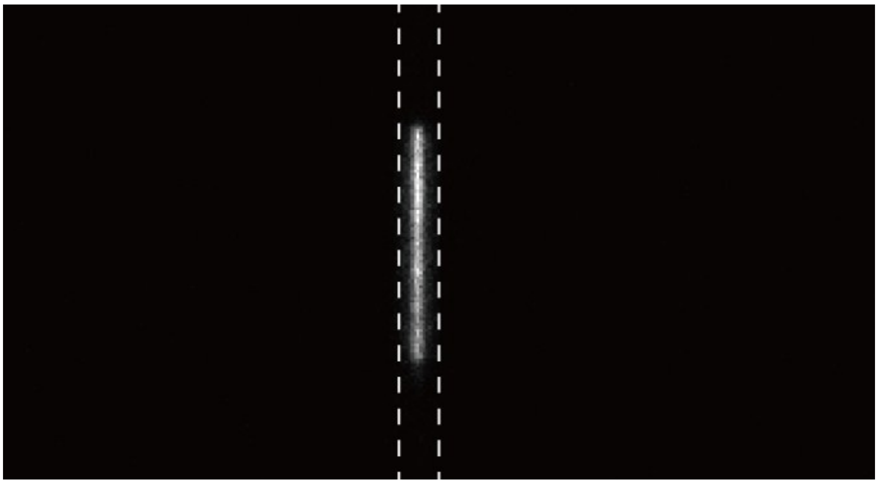

Figure S6. Zero order spectral image of single nanowire in the slit of spectrometer. Dash line indicated the edge of slit of spectrograph, placing on the image plane of microscope. By moving and rotating the stage under the dark field, the image of the nanowire needs to be accurately placed into the slit of the spectrograph.

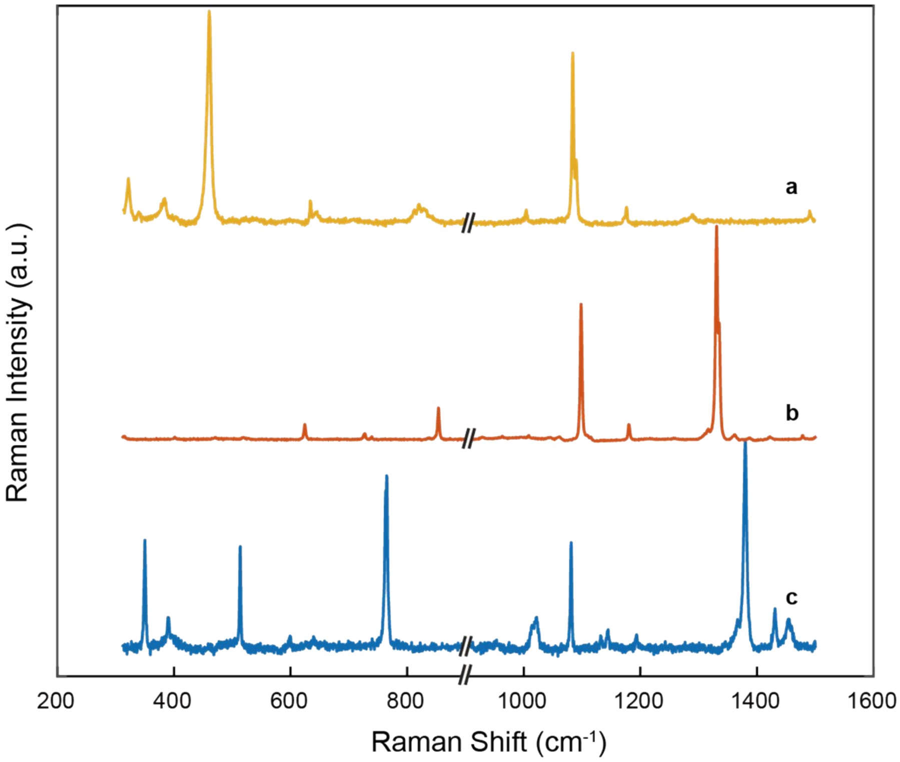

Figure S7. Raman Spectra of p-aminothiophenol (pATP, a), p-nitrothiophenol (pNTP, b) and 2-naphthalenethiol (2-NT, c). Raman Spectra were obtained from the Solid powder of these compounds

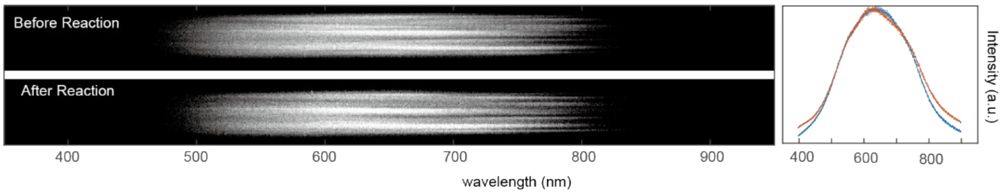

Figure S8. Rayleigh scattering spectra of single MnOOH-Ag nanowire. Left: Rayleigh scattering spectral image of single MnOOH-Ag nanowire before and after the catalytic reaction. Right: averaged Rayleigh scattering spectra of entire single MnOOH-Ag nanowire before and after the catalytic reaction.