Supporting Information

Photocatalytic Surface Restructuring in Individual Silver Nanoparticles

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S1 | Scanning electron microscopy imaging of Ag NDs on silicon

In our optical studies, we use Ag NDs fabricated on a glass substrate. However, due to the insulating nature of these substrates, it is not possible to perform electron microscopy measurements to visualize the particle-to-particle heterogeneity. As such, we also fabricate Ag NDs on a silicon substrate to perform SEM imaging.

Silver nanodisks with the same dimensions (~95 nm diameter and 40 nm height) but with an interparticle spacing of 500 nm are fabricated on a silicon wafer (Fig S1A and B). From the zoomed-in images of Ag NDs, we clearly observe local structural heterogeneities on these particles.

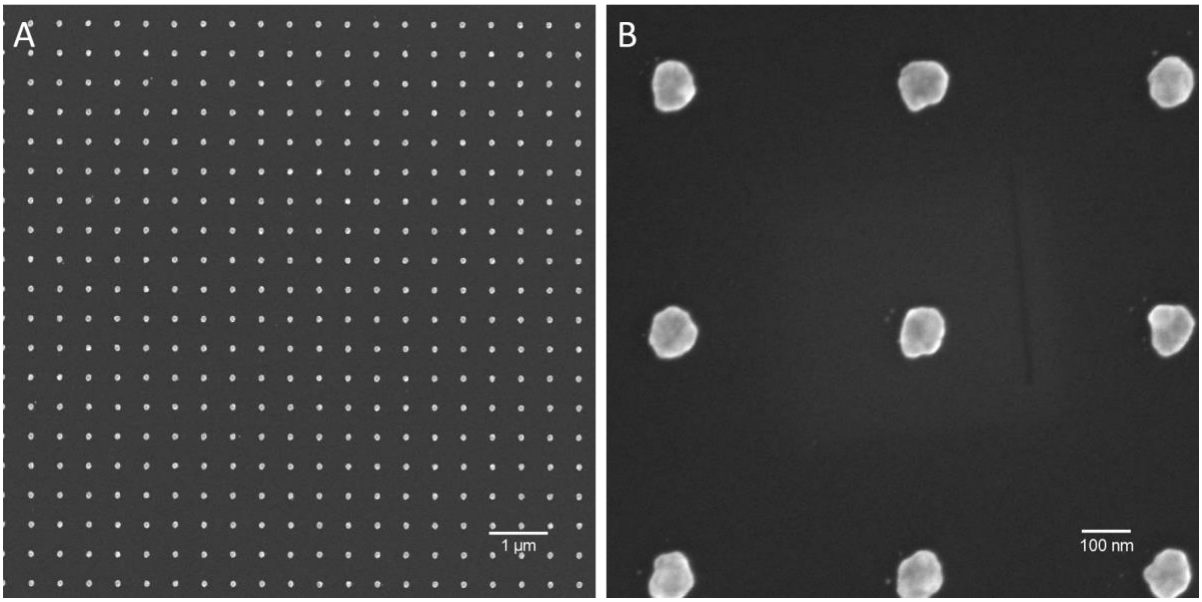

Figure S1. A) SEM image of an Ag ND array fabricated on silicon substrate. B) Zoomed-in image of individual Ag NDs.

S2 | FDTD simulations of anisotropic nanoparticle reshaping

The SEM image of a single Ag ND in x-y plane is imported in the 3D electromagnetic simulator FDTD (Lumerical Inc.) assuming a height of 40 nm. The ND is supported on a glass substrate. It is assumed that an anisotropic ND, when subject to heating, will undergo reshaping into more symmetrical structures such as a composite structure made of disc and hemisphere which can eventually transform into a full sphere. Assuming constant volume for all the three structures, their scattering spectra is simulated using FDTD (see the figure below).

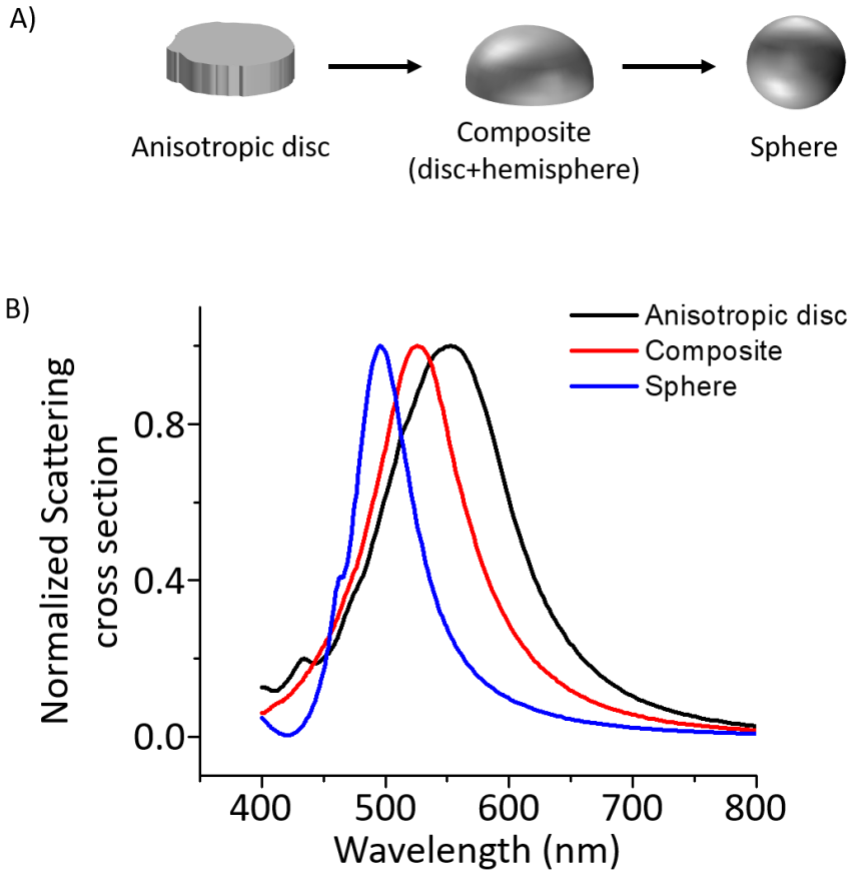

Figure S2. A) Schematic representation of reshaping of an anisotropic Ag ND upon heating. B) Simulated scattering spectra of an anisotropic disc (black line), composite (red line) and spherical (blue line) nanostructure of silver.

S3 | Effect of pure gases on Ag NDs in the absence of laser irradiation

We study the structural stability of silver nanodisks in the absence of laser irradiation and in different gas environments. Single-particle DF scattering spectra are recorded every 15 minutes, while keeping the sample under a given gas atmosphere (air, N_2, H_2 or CO_2) for 1 hour. During the 15 minutes waiting time the excitation source is switched off. LSPR peak positions are extracted by fitting a Lorentzian to the measured DF scattering spectra. Ag NDs do not show any structural change in the absence of laser irradiation in the four different gas environments studied. Fluctuations of 1-2 nm in the λ_{LSPR} observed during the measurement can be attributed to mis-alignment of the nanodisk with respect to the centre of spectrometer slit.

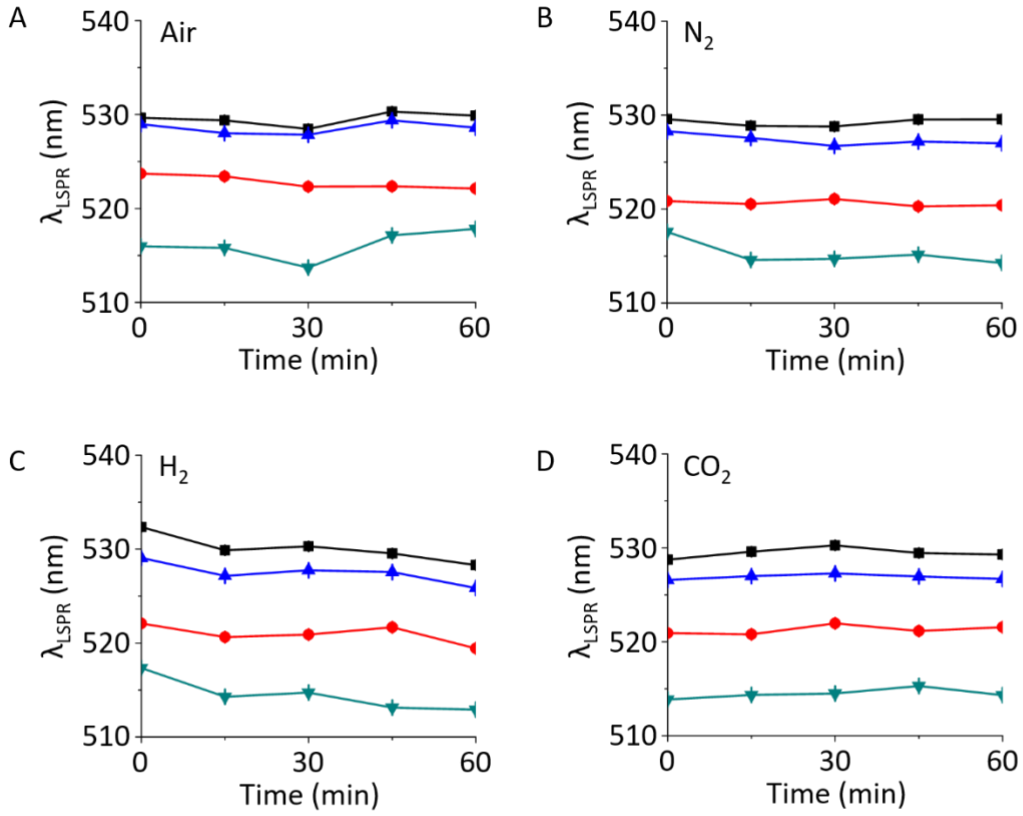

Figure S3. Measured LSPR shifts on four individual Ag NDs depicted by black, blue, red and teal colour curves respectively in A) air, B) N_2, C) H_2, D) CO_2 at room temperature and in absence of laser irradiation, over a period of 1 h.

S4 | FDTD simulation of Ag and Ag-Ag_2O NDs

Here we show that the reduction of a 1 nm native silver oxide on the surface of a Ag ND is expected to lead to a blue shift of its plasmon resonance. An Ag-Ag_2O ND with Ag core diamter of 93 nm and height 39 nm, and a 1 nm shell of silver oxide was designed in FDTD. Ag mass conservation calculations indicate that the reduction of the 1 nm silver oxide shell results in a 0.3 nm silver additional layer over the original silver core. Hence, in order to compare the LSPR shifts, a second simulation of Ag ND of diamter 93.6 and height 39.3 was also perfomed. The LSPR of the reduced Ag ND clearly shows a blue a shift in comparison to that of the oxidised Ag-Ag_2O ND.

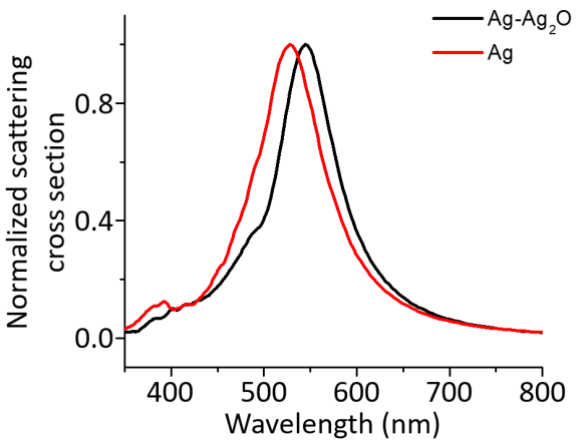

Figure S4. Simulated scattering spectra of Ag ND with a conformal coating of 1 nm of silver oxide (black curve), and Ag ND formed upon uniform reduction of surface silver oxide (red curve).

S5 | TEM images of Ag nanoparticles before and after laser irradiation in hydrogen atmosphere

For TEM measurements, Ag nanoparticles synthesized via the Lee Meisel method[1] are drop casted on a carbon coated Cu grid. TEM micrographs are acquired on a JEOL 2100 at an operating voltage of 200 kV. For pre and post-photocatalysis imaging, the TEM grid is attached to a glass slide and then incorporated into the flow cell. The grid is illuminated with a 532 nm laser, at a power density of around 30 mW/mm^2. Although the irradiance is four orders of magnitude lower in comparison to single particle spectroscopic studies, additional thermal contributions from the copper grid may compensate for the low irradiation intensity. Colloidal nanoparticles show dramatic surface restructuring and superficial cluster formation in hydrogen under laser irradiation, as evidenced by the TEM images below. A direct comparison between colloidal nanoparticles and nanolithographically-made nanodisk is not possible, given their different absorption cross-sections and surface chemistry. However, a similar surface restructuring with formation of silver clusters is responsible for the strong intermittent luminescent signal measured when irradiating Ag NDs in a reducing gas atmosphere.

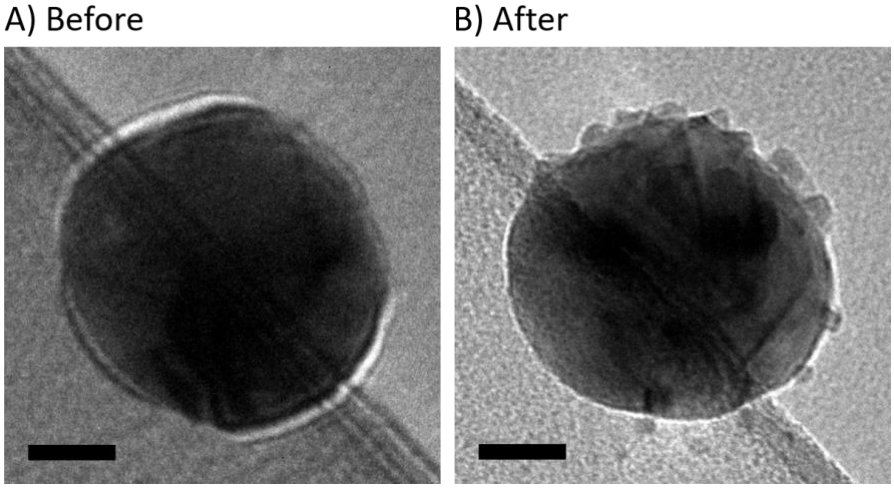

Figure S5. TEM image of colloidal silver nanoparticles dropcasted on carbon coated Cu grid A) before and B) after laser illumination in hydrogen atmosphere. A 532 nm laser is used to illuminate the sample at 0.03 $\mu W/\mu m^2$ for 1 h. Silver surface undergoes photocatalyzed surface reaction in hydrogen atmosphere to form the tiny protrusions and islands. The scale bar in both A and B is 20 nm.

S6 | LSPR broadening for Ag ND under laser irradiation in hydrogen atmosphere

In hydrogen under laser illumination condition, we observe that the LSPR red shifts due to restructuring. In addition, we see that the full width at half maximum (FWHM) also increases, indicating increased plasmon damping. Hydrogen gas is a reducing agent and it can therefore reduce the surface silver oxide of Ag ND to form islands/clusters of metallic silver. This process increases the surface roughness of the NDs. Owing to this roughness, the new structure will have a non-homogenous surface and regions of enhanced electric fields or hot spots on its surface. These hot spots and their interaction with the substrate or the surrounding medium lead to a red shift and to a damping of the NDs plasmon resonance, in agreement with our experimental observation.[2]

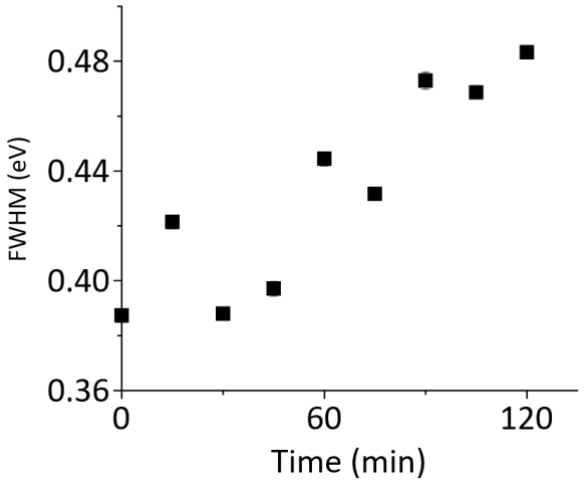

Figure S6. Full width at half maximum of the LSPR observed in Ag ND during 532 nm irradiation at 1 $mW/\mu m^2$ in H_2 atmosphere. The data is obtained after fitting a Lorentzian curve to curves in figure 3b of main text.

S7 | Reshaping and restructuring under laser irradiation in CO_2 + H_2 mixtures

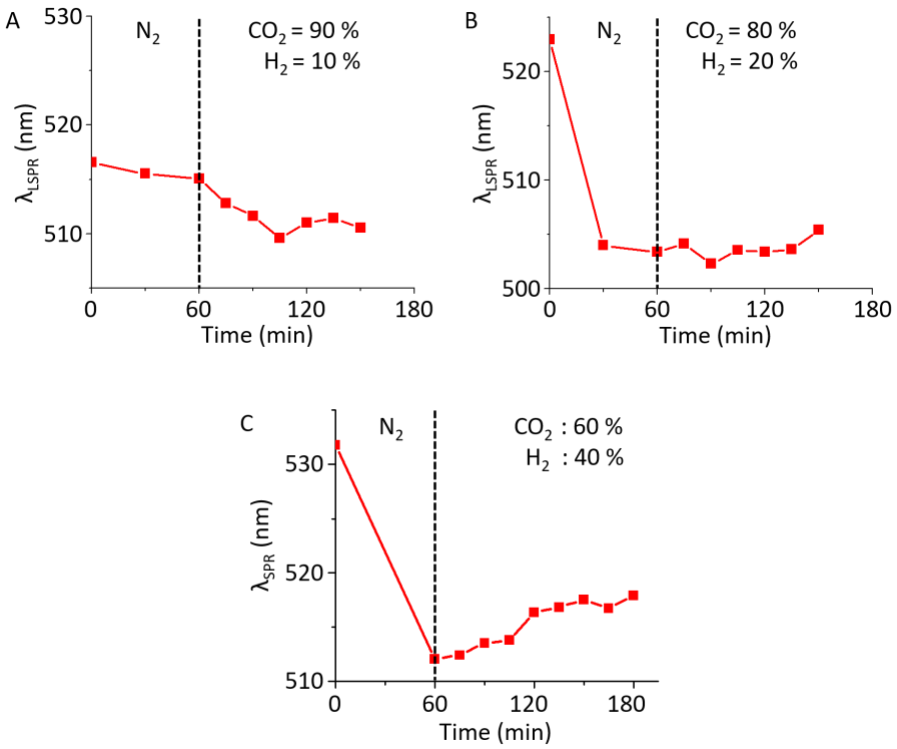

Figure S7. Time evolution of the LSPR of a single Ag ND in various volume mixtures of CO_2 and H_2 gases under laser irradiation. The Ag ND is pretreated with N_2 for the first 60 min after which the reaction chamber is flushed with CO_2 and H_2 at A) 90:10, B) 80:20 and C) 60:40 ratio. 532 nm laser at 1 mW/μm^2 is focussed on the Ag ND catalyst. The blue shift in nitrogen is due to the photothermal reshaping of the Ag NDs

S8 | Size and photoluminescence of *in-situ* formed silver clusters on Ag NDs

Metal clusters have molecule-like electronic levels. Depending on their number of atoms, these clusters have distinct HOMO-LUMO gaps. Excitation of electrons between these electronic levels can give rise to luminescence. In our study, we observe that during photocatalytic CO_2RR using 532 nm laser excitation, Ag ND restructure and show intermittent luminescence, indicating formation of silver cluster. We use the spectral position of this luminescence or emission energy to calculate the size of the cluster formed, using equation (4) in the main text. From Figure S8 it can be seen that, as the size of the clusters increases from 13 to 24 atoms, the emission energy decreases (or red shifts) implying a narrowing of HOMO-LUMO gap. This red shift is typically accompanied by broadening of PL spectrum, indicating availability of multiple transitions and decay channels for excited electrons in larger clusters.

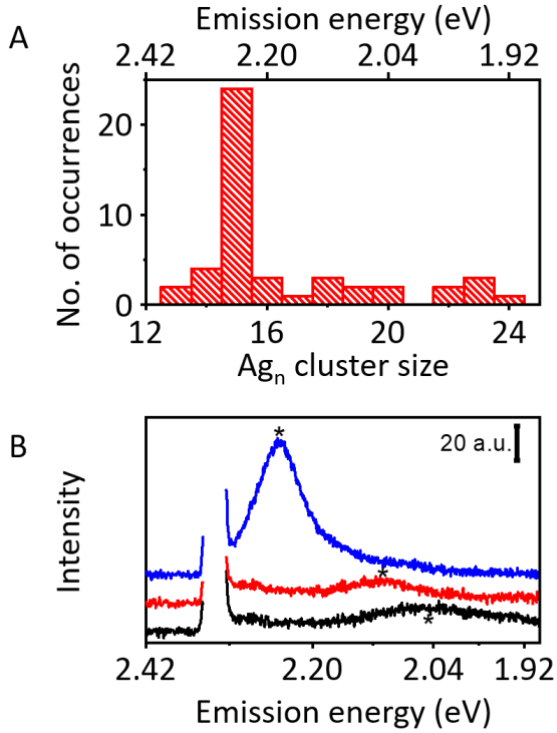

Figure S8. A) No. of occurrences (or observations) of Ag_n cluster formation of varying size on Ag NDs during photocatalytic CO_2RR. B) Three representative examples of Ag_n cluster emission showing decrease in emission intensity with decreasing emission energy or increase in cluster size. Asterisks mark the extracted emission energy.

S9 | LSPR shifts under photocatalytic CO_2RR

The LSPR shifts measured over individual Ag NDs during photocatalytic CO_2RR varies from particle to particle. This variation is attributed to the heterogeneity in size, shape, granularity (number of granules in a single Ag ND), and chemical compositions (such as oxidation of silver surface) of Ag NDs, which determines the extent of their reshaping and restructuring. Furthermore, drift in particle position with respect to laser spot can lower the power absorbed by the particle and hence their photocatalytic restructuring.

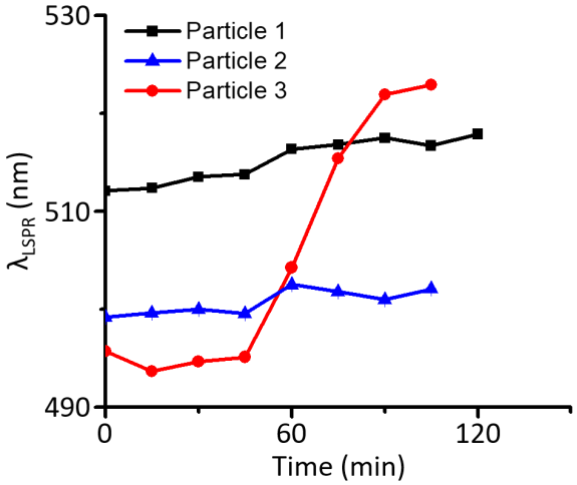

Figure S9. Time evolution of the LSPR of three individual Ag NDs under photocatalytic CO_2RR in a 60/40 CO_2/H_2 gas mixture for 532 nm excitation at 1 mW/μm^2. The Ag NDs are pre-treated with N_2 under laser illumination after which the reaction chamber is flushed with the CO_2/H_2 gas mixture.

S10 | SERS and photoluminescence of *in-situ* formed silver clusters on Ag NDs

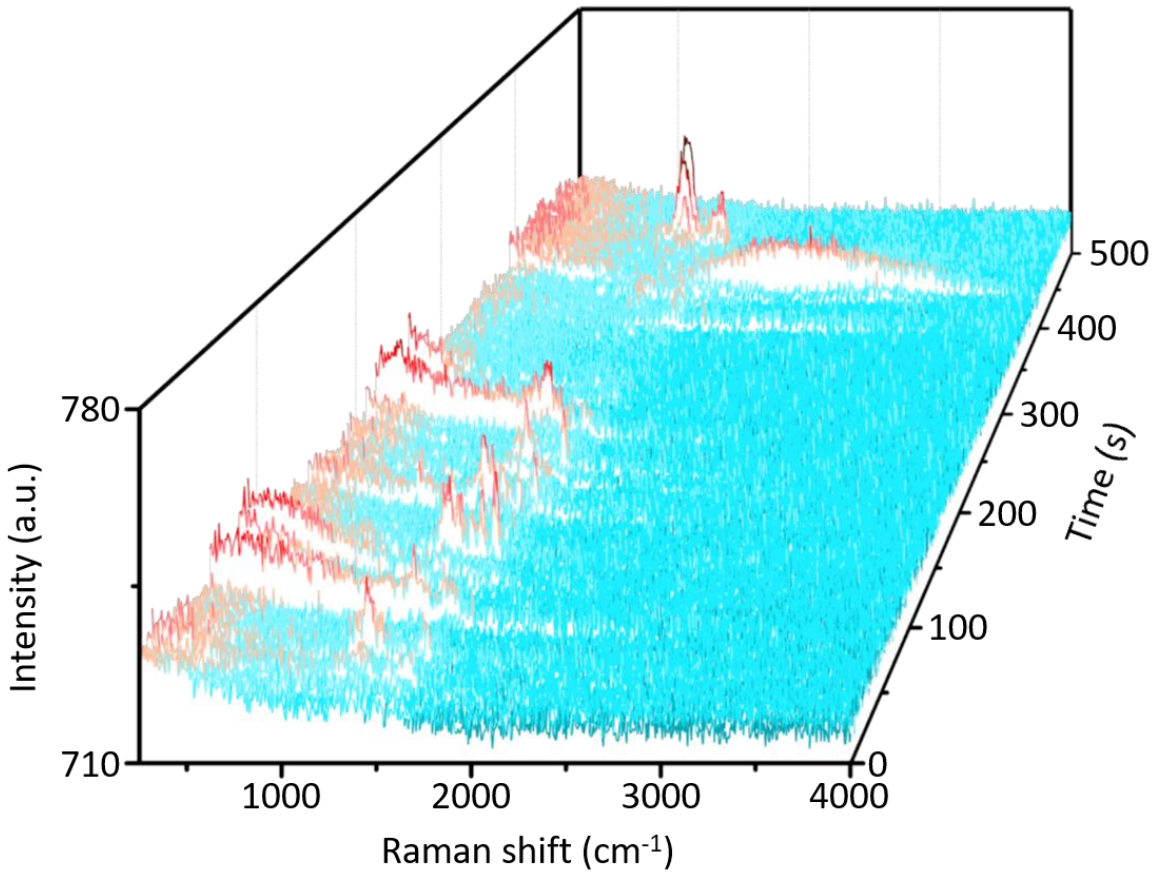

Figure S10. Time evolution of SERS spectra showing the dynamic spectral changes corresponding to the photocatalytic CO_2RR on a single Ag ND in a 60/40 CO_2/H_2 mixture under 532 nm excitation at 1 mW/μm^2. The accumulation time is 1 frame per second. The sharp peaks correspond to the vibrational modes of CO_2RR product molecules, while the broad peaks and the large background signal is due to the luminescence from the silver clusters formed by photocatalytic reduction of the native silver oxide.

References

(1) Lee, P. C. and MeiseL, D. Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols. *J. Phys. Chem* **1982**, 86, 3391–3395. https://doi.org/10.1016/j.cplett.2011.01.025.

(2) Rodrıguez-Fernandez, J.; Funston, A. M.; Perez-Juste, J.; Alvarez-Puebla, R. A.; Liz-Marzan, L. M.; Mulvaney, P. The Effect of Surface Roughness on the Plasmonic Response of Individual Sub-Micron Gold Spheres. *Phys. Chem. Chem. Phys.* **2009**, 11 (28), 5909–5914. https://doi.org/10.1039/b911746f.