Electronic Supplementary Information (ESI)

High-Temperature Surface Enhanced Raman Spectroscopy for *in Situ* Study of Solid Oxide Fuel Cell Materials

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Fabrication of Ag@SiO$_2$ nanoparticles

The Ag nanoparticles with SiO$_2$ shell (abbr. Ag@SiO$_2$ NPs) were fabricated through a wet chemical procedure. To form the Ag seeds, 0.75 g of polyvinyl pyrrolidone (PVP, Mw=~55,000 g/mol) was fully dissolved in 3 mL of anhydrous ethylene glycol (EG, 99.8%) and then mixed with 0.25g of AgNO$_3$. The resulting solution was kept at 120 °C for 1 hr under vigorous stirring in which AgNO$_3$ was reduced to Ag nanoparticles. Afterward, 20 mL of ethanol was added to form homogeneous Ag colloidal suspension. Prior to the application of SiO$_2$ coating, 1 mL of concentrated NH$_4$OH was added into the Ag suspension to create a suitable basicity for SiO$_2$ growth. Then, 0.3 mL of Tetraethyl orthosilicate (TEOS) was introduced into the suspension of Ag seeds to develop a uniform encapsulation of SiO$_2$ on Ag, after letting set for 1 hour. Afterward, Ag@SiO$_2$ core@shell nanoparticles were extracted from the colloidal solution by repeated centrifuging at 6000 rpm with ethanol and D.I. water. After each centrifuge step, the supernatant liquid was decanted to remove the excess organic precursors.

Characterization of the Ag@SiO$_2$ nanoparticles

The morphological and optical properties of the Ag@SiO$_2$ nanoparticles were characterized by TEM and UV-Vis extinction spectrometry. To prepare the TEM samples, Ag@SiO$_2$ nanoparticles were dispersed in ethanol using an ultrasonic bath for 30 min and then dropped onto Formvar-coated copper grids using a micropipette. Images were obtained by a JEM-1400 TEM operating at an accelerating voltage of 100 kV. The scanning electron microscopy was also carried out in a thermally assisted field emission SEM (LEO 1530) to verify the shape, size and distribution of Ag@SiO$_2$ nanoparticles. LSPR Extinction spectra of the Ag@SiO$_2$ nanoparticles were collected on a UV-Vis-NIR spectrometer (Ocean Optics) in a wavelength range from 200 to 1200 nm. The samples were prepared by dropping the nanoparticles on the microscope cover slips. The contribution of the glass coverslip was subtracted from the extinction spectra.

Preparation of SERS Samples

R6G: The Ag@SiO$_2$ nanoparticle suspension (10mg/mL) was mixed with R6G solution (10^{-3} M) at 1:1 volume ratio. It was compared with R6G solutions (10^{-1} M or 10^{-3} M) and the blank Ag@SiO$_2$ nanoparticles (10mg/mL). All samples were spin-coated on silicon wafers (1 cm^2) at 1000 rpm. **GDC thin film:** Gadolinium doped ceria was deposited on Si wafers through RF magnetron sputtering to a thickness of ~85 nm. The thin films were annealed at 800 °C for 30 mins prior to SERS study. Ag@SiO$_2$ nanoparticle suspension (10mg/mL, 10µL) was drop-coated on the GDC thin film (0.25cm^2) to provide SERS enhancement. The reference Ag@SiO$_2$ sample was prepared with the same protocol on silicon wafers. **Ni foils:** Ag@SiO$_2$ nanoparticle suspension (10mg/mL, 10µL) was drop-coated on the nickel foils (1 cm^2) before the C$_3$H$_8$ exposure. Equal amount of Ag@SiO$_2$ suspension was loaded on silicon wafers as the reference. **CeO$_2$ powder sample**: Ag@SiO$_2$ (10mg/mL) was mixed with CeO$_2$ suspension (100g/mL) at 1:1 volumn ratio and drop coated onto silicon wafers. **Loading of Ag@SiO$_2$ nanoparticles**: We estimated the loading of the Ag@SiO$_2$ nanoparticles from the corresponding SEM image (Figure S9). By drop coating 10 µL of Ag@SiO$_2$ nanoparticle suspension on 1 cm^2 silicon wafer, ~94 nanoparticles deposit on the unit area of 1 µm^2, resulting in a surface coverage of ~47%.

Raman spectroscopy

Raman spectra were obtained using a Renishaw RM 1000 spectromicroscopy system (~2 µm spot size). An air-cooled Ar laser (CVI Melles Griot) emitted at 488 nm and 514 nm and a solid state diode laser (Thorlabs) with 633nm emission line were used for excitation of Raman signal in this study, with a total power of 30mW, 5mW, and 10mW, respectively. The laser bleaching effect was negligible, as shown in Figure S4. GDC thin films loaded with Ag@SiO$_2$ nanoparticles were inspected with 488nm laser of different power: 3 mW and 30 mW . The samples were kept at 450°C in air for 30 mins prior to the inspection. In both cases, the 465cm^{-1} peak of GDC showed stable intensity, showing minimal degradation over time.

Different excitation wavelengths were used for different materials systems to optimize the signal-to-noise ratio. While the Raman band position is independent of the wavelength of the excitation laser, the intensity of Raman band is sensitive to excitation wavelength, particularly in the SERS study. On each material system, the SERS data were properly referenced with the Raman data collected from the controlled groups with the same excitation wavelength.

A Harrick environmental chamber described in our earlier publications was used for *in situ* Raman tests.[1,2] All *ex situ* Raman spectra presented in this study were averaged from 8–9 points collected by a mapping function provided by Renishaw system to increase reliability. The *in situ* time-resolved studies were each conducted on the same spot, with the laser slightly off focus to cover a larger area of about 5 um in diameter. An automated MATLAB program was used to remove the fluorescence background present in the Raman spectra, with a polynomial background fitting protocol developed by Lieber et al[3]. Figure S12 presents the diagram of the in situ Raman testing chamber and the effect of fluorescence background removal protocol.

Calculation of Enhancement Factors

SERS enhancement factors (EF) of the Ag@SiO$_2$ nanoparticles were evaluated with SOFC materials (GDC thin film and carbon deposition on nickel) and probe molecules (Rodamine-6G). Since the GDC thin film lies underneath the nanoparticles and the R6G molecules absorb on the surface of nanoparticles, the enhancement factors generated in these two scenarios are not the same. The EF generated from the GDC thin film was calculated from the ratio of the characteristic peak intensity after SERS treatment to that without SERS treatment.

$$EF_{net} = \frac{I_{SERS}}{I_{Blank}}$$

I$_{SERS}$ denotes the peak value of characteristic Raman band after the sample is loaded with Ag@SiO$_2$ NPs, while I$_{bulk}$ represents the same peak value collected from the blank substrate. All enhancement factors were generated after the baseline subtraction. A stepwise schematic of EF calculation is presented in Figure S8.

To compare our work with the previous SERS studies, we employed R6G as another reporter. The enhancement factor of Ag@SiO$_2$ NPs with R6G probe molecules was calculated by comparing the Raman signal intensities of the pure R6G sample and the mixture of R6G solution and Ag@SiO$_2$ nanoparticles. The calculation method developed by Le Ru[4] and Van Duyne[5] is as follows:

$$EF_0 = \frac{I_{SERS}}{I_{Bulk}} \times \frac{\sigma_{Bulk}}{\sigma_{SERS}}$$

I$_{SERS}$ is the peak value of 1646cm^{-1} Raman band from the R6G sample mixed with Ag@SiO$_2$ nanoparticles, I$_{bulk}$ represents the same peak value collected from pure R6G molecules. The signals were normalized by the surface concentrations of R6G molecules in each sample: σ$_{bulk}$ and σ$_{SERS}$. Since the volumn of R6G solutions (10μL) and the sample area (1 cm^2) were constant across all tested samples, the value of surface concentration was proportional to the concentration of R6G solutions. In the samples prepared for Figure 2 (C), the concentrations of R6G molecules were 0.1M (Bulk) and 0.005M (SERS solution mixed with the 0.01M R6G solution), resulting in a normalization factor of 200. With the concentration factor accounted, the final enhancement factor was found to be ~150.

Factors such as the increase of surface area by Ag@SiO$_2$ NPs and the area density of Ag@SiO$_2$ NPs were not taken into consideration. Therefore, the enhancement factor calculated on R6G molecules only presents a semi-quantitativive indicator for benchmarking future study and comparison with other works.

References

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2. K. S. Blinn, H. Abernathy, X. Li, M. Liu, L. A. Bottomley and M. Liu, *Energy & Environmental Science*, 2012, **5**, 7913-7917.
3. C. A. Lieber and A. Mahadevan-Jansen, *Appl. Spectrosc.*, 2003, **57**, 1363-1367.
4. E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *Journal of Physical Chemistry C*, 2007, **111**, 13794-13803.
5. R. P. Van Duyne, J. C. Hulteen and D. A. Treichel, *The Journal of Chemical Physics*, 1993, **99**, 2101-2115.

Figures
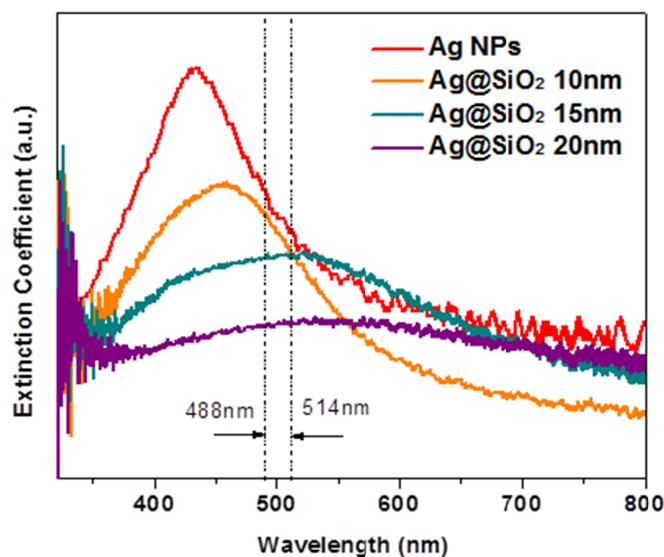
Figure S1 UV-Vis extinction spectra of bare Ag seeds and Ag@SiO$_2$ nanoparticles with different SiO$_2$ shell thicknesses. The Ag nanoparticles with 10 nm SiO$_2$ shell were used in this study. The wavelengths of the laser excitations are indicated with the dotted lines.
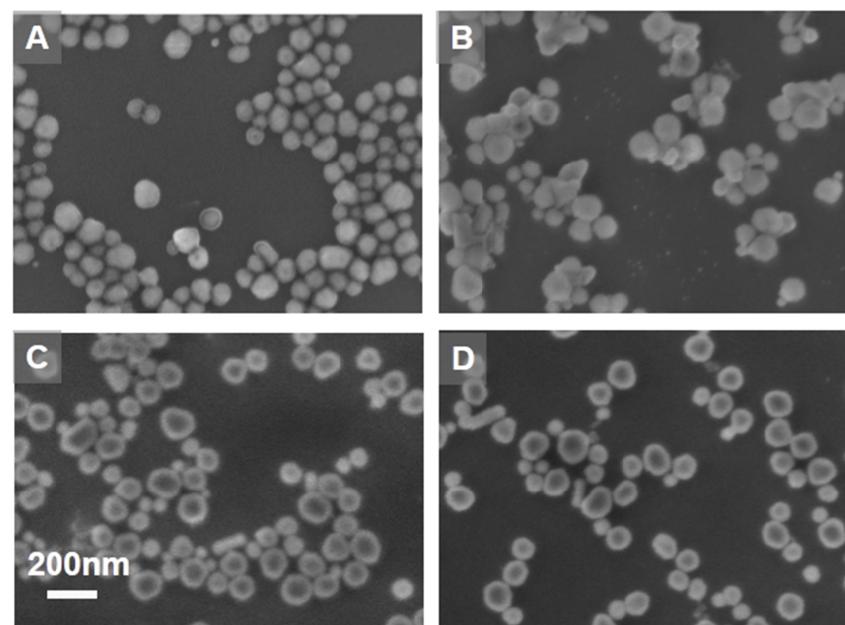
Figure S2 SEM images of the Ag@SiO$_2$ nanoparticles loaded on silicon wafers. (A) As deposited. (B) Annealed in air at 450 °C for 1 h. (C) Annealed in 10% H$_2$ in Ar at 450 °C for 1 h. (D) Annealed in 15% C$_3$H$_8$ in Ar at 450 °C for 1 h.
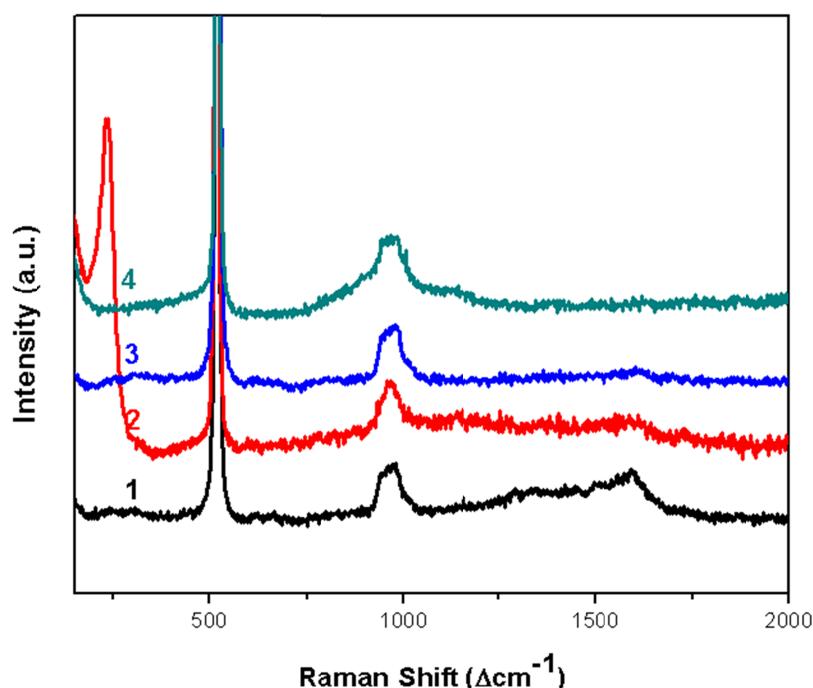
Figure S3 Background Raman spectra of the Ag@SiO$_2$ nanoparticles loaded on silicon wafers. 1) As deposited, 2) Annealed in air at 450 °C for 1 h, 3) Annealed in 10% H$_2$ in Ar at 450 °C for 1 h, 4) Annealed in 15% C$_3$H$_8$ in Ar at 450 °C for 1 h. Spectra are taken with the 488 nm laser at 30 W with an acquisition time of 10 s. The carbonaceous features shown on Line-1 are due to the residue organics or adventitious carbon on the surface of the Ag@SiO$_2$ nanoparticles, which disappeared after heat treatments.
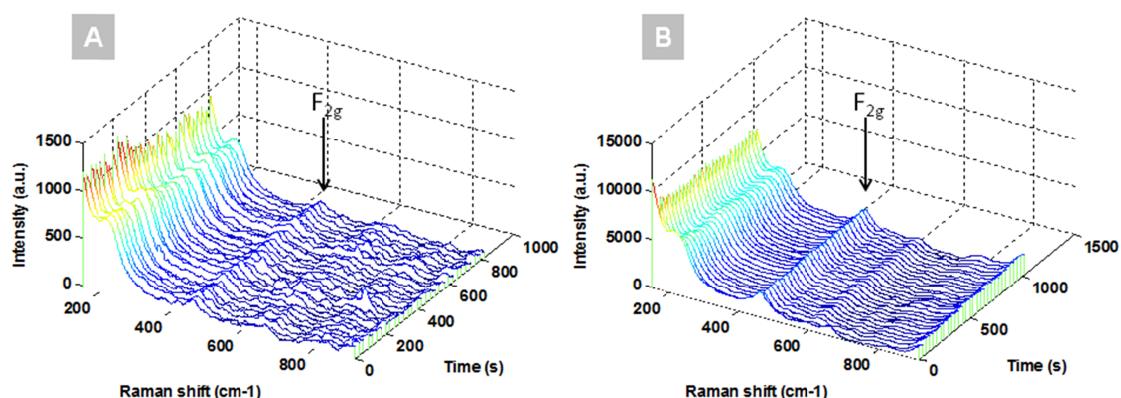
Figure S4 Robustness of Ag@SiO$_2$ nanoparticles against laser bleaching. Raman spectra of the Ag@SiO$_2$ NPs loaded on GDC thin films. (A) Collected continuously with 488 nm laser of 3mW power. (B) Collected continuously with 488 nm laser of 30mW power with an acquisition time of 10 s.
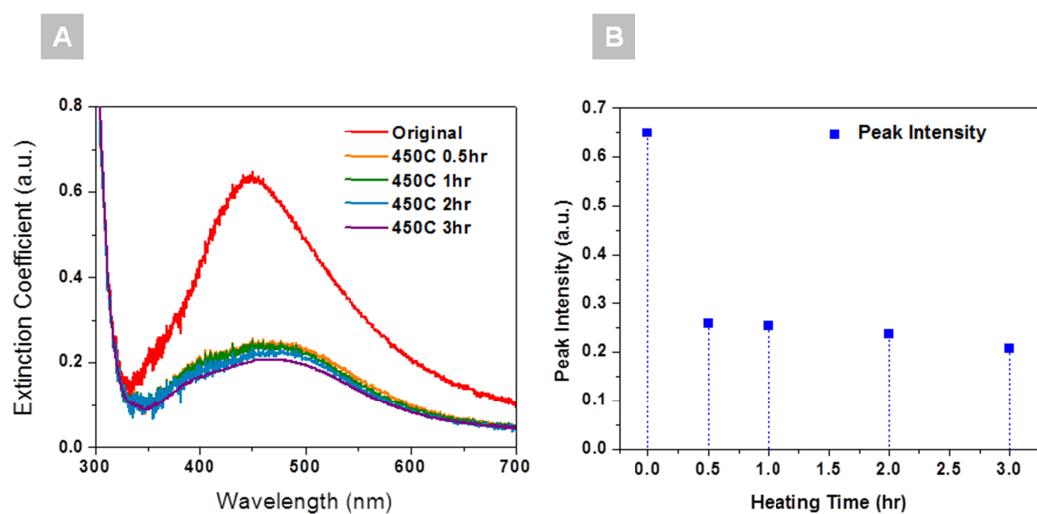
Figure S5 (A) UV-Vis extinction spectra of Ag@SiO$_2$ NPs loaded on glass slides, before and after annealing at 450°C for 0.5-3hrs. (B) Dependence of the LSPR peak intensity on heating time.
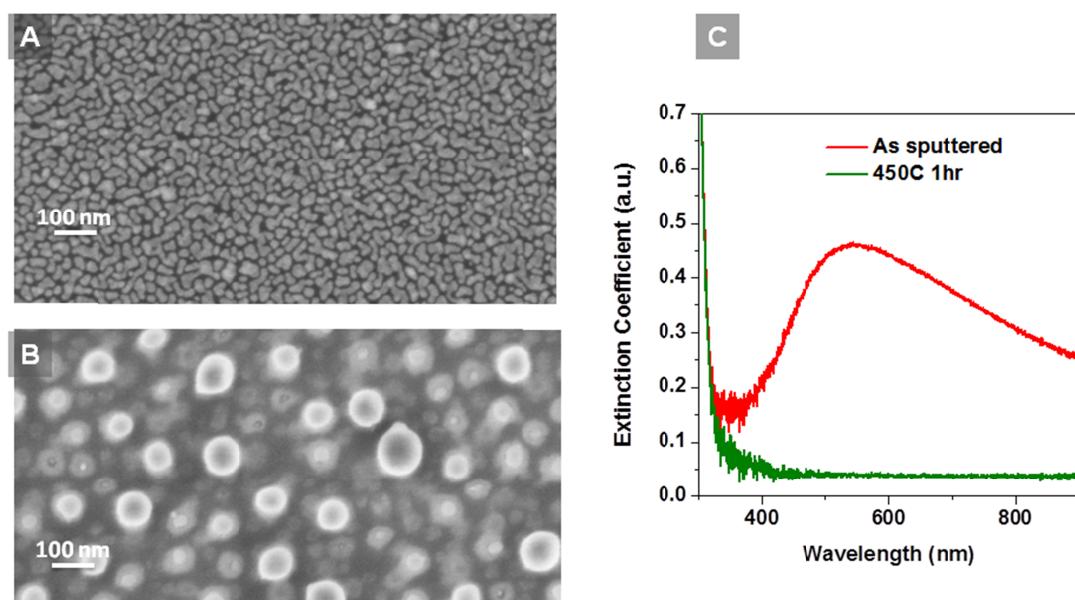
Figure S6 SEM images of sputtered Ag NPs (A) before and (B) after heat treatment at 450°C for 1hr in air. (C) UV-Vis extinction spectra of sputtered Ag NPs, before and after annealing at 450°C for 1hr.
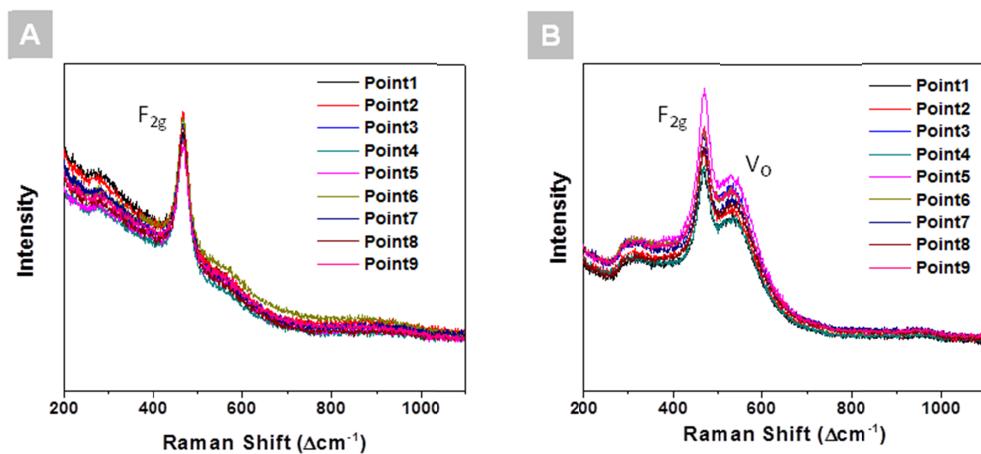
Figure S7 Statistical reliability of the SERS signal of the oxygen species on the CeO_2 surfaces. (A) *In situ* SERS spectra collected from 9 different spots on the CeO_2 surface purged with air at 450°C and (B) purged with 4% H_2 at 450°C.
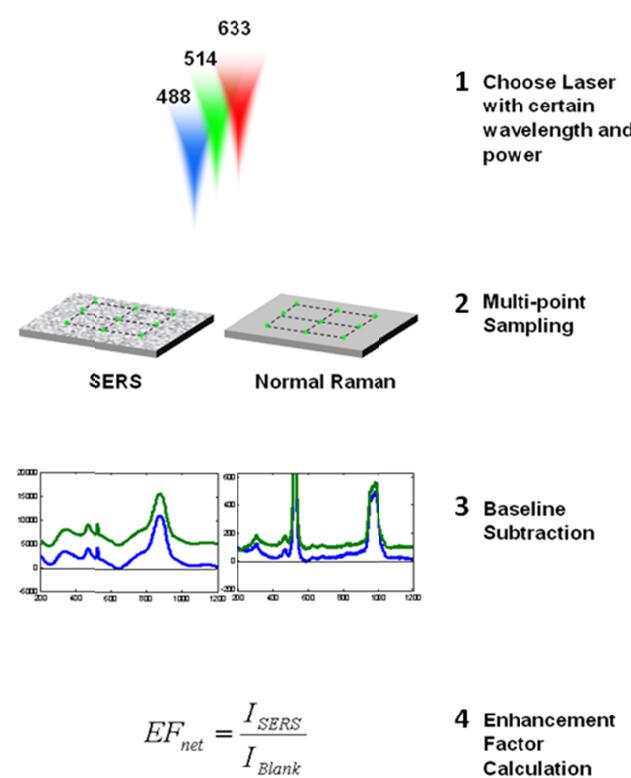
**Figure S8** Stepwise schematic for evaluation of enhancement factor of Ag@SiO$_2$ NPs.

200nm
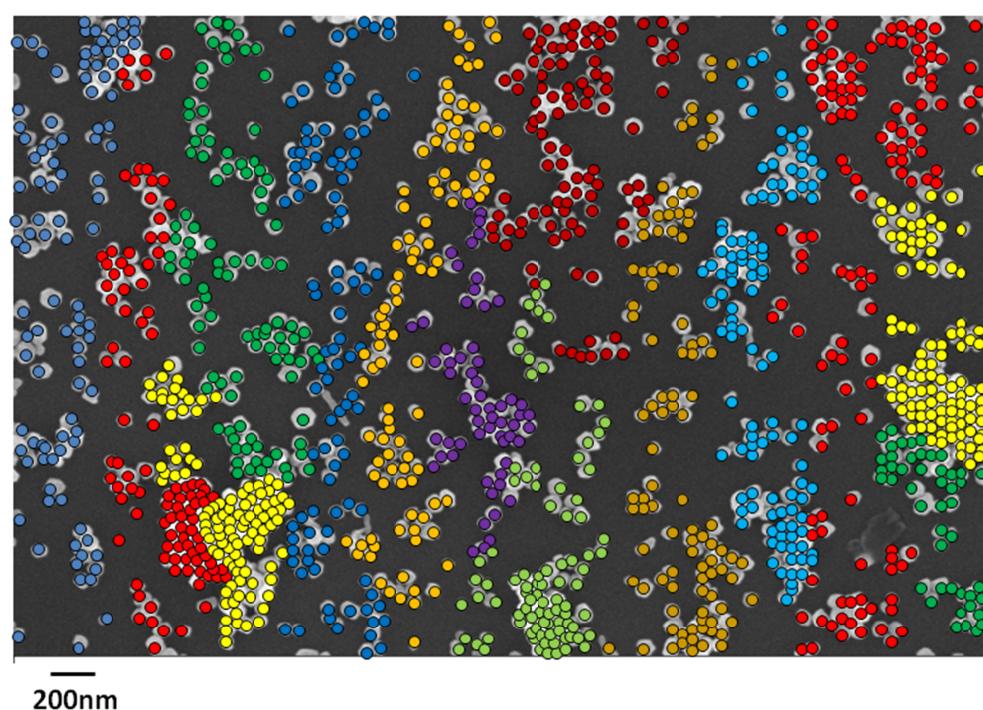
**Figure S9** Evaluation of the loading of Ag@SiO$_2$ nanoparticles by number count of the SEM micrograph.
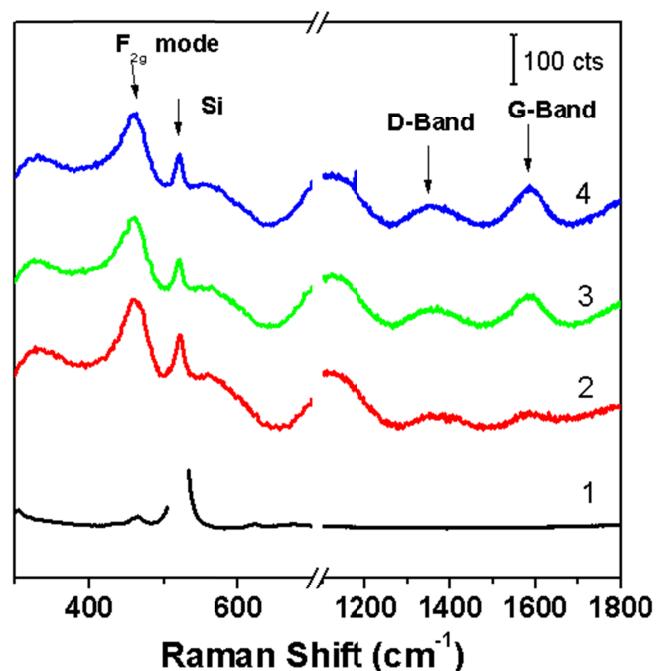
Figure S10 Impact of propane exposure on the SERS effect of Ag@SiO$_2$ nanoparticles. (1) Blank GDC thin film at room temperature, (2) Ag@SiO$_2$ loaded GDC thin film under 4% H$_2$ at 450°C for 30 mins before propane exposure, (3) Ag@SiO$_2$ loaded GDC thin film after exposure to pure wet propane at 450°C for 3hr, and (4) 5hr. All spectra were taken with the 514 nm laser normalized to laser power of 5mW with an acquisition time of 10s.
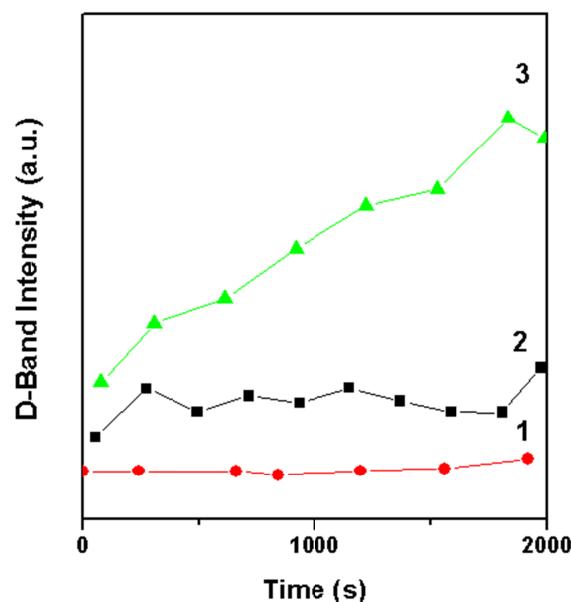
Figure S11 Effect of SiO_2 on the early stage of carbon deposition. Integrated carbon D-band (1350 cm^{-1}) area collected from (1) SiO_2 coated Ni foil, (2) blank Ni foil, and (3) Ag@SiO_2 loaded Ni when exposed to wet propane at 450^{0}C. (2) and (3) are extracted from Figure 3B and 3E. All spectra were collected with green laser (514nm) excitation normalized to the power of 5mW and the acquisition time of 10s. The SiO_2 coated Ni foil was prepared by mixing TEOS (0.5mL) with diluted NH_4OH in EtOH (1mL/10mL) for 1 h followed by spin coating onto Ni foil at 2000 rpm.
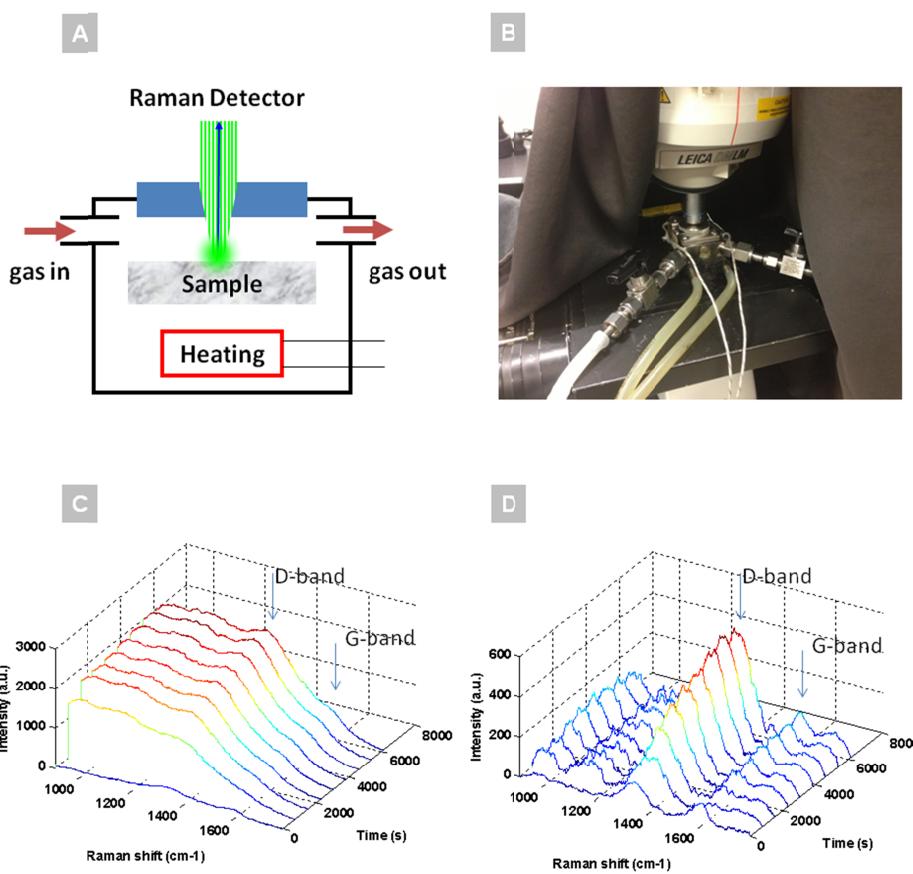
Figure S12 (A) The diagram and (B) the picture of the *in situ* Raman testing chamber. (C) The SERS spectra in Figure 3B in original state and (D) after the fluorescence background removal.