

Supporting Information

Support-free Bimodal Distribution of Plasmonically Active Ag /AgO_x Nanoparticle Catalysts: Attributes and Plasmon Enhanced Surface Chemistry

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Preparation of Ag/AgO_x nanoparticle structure

The precursor Ag film thickness plays a significant role on the Ag/AgO_x nanostructure formation and composition *via* the high temperature annealing process outlined in the Methods. For example, a 3 nm thick Ag film is fully oxidized during the annealing cycle and shows no observable LSPR band. For a 60 nm Ag film, although a bimodal distribution of Ag/AgO_x NPs results, the large particles have an average size of ~ 490 nm, which is too large to produce the desired LSPR in the visible light range. Figure S1a,b,c displays SEM images of the Ag/AgO_x NP structure obtained from a 60 nm Ag film for a comparison with that obtained from a 20 nm Ag film (Figure 1) at different SEM magnifications. It is noticeable that other than the larger AgNPs, a uniform distribution of small size (on average ~ 10 nm) AgNPs is present and comparable to that

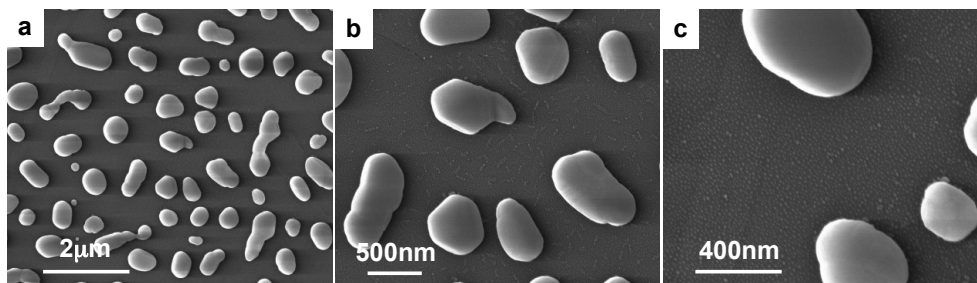


Figure S1 Secondary electron microscopy (SEM) images of a bimodal Ag/AgO_x nanoparticle structure made from a 60 nm precursor Ag film at increased SEM magnifications (a, b, c).

seen in Figure 1f, consistent with the formation of a bimodal nanoparticle structure. The bimodal properties of AgNPs are verified by the UV-vis results shown later.

Characterization

X-ray diffraction (XRD)

Figure S2 shows XRD patterns for a 20 nm thick Ag film before and after annealing. There are no XRD peaks observed with the as-deposited film, while after annealing at 900 °C, a sharp peak appears at 2θ of 38.18° , indicating (111) as the preferred orientation for the formed AgNPs. The Scherrer equation is used to deduce an average size of ~ 108 nm for the Ag nanocrystallites formed, which is smaller than the 160 nm average particle size obtained from SEM imaging. This disparity is likely due to the surface disordered Ag phase, the bimodal characteristics of the Ag nanoparticles and the AgO_x layer being invisible to XRD.

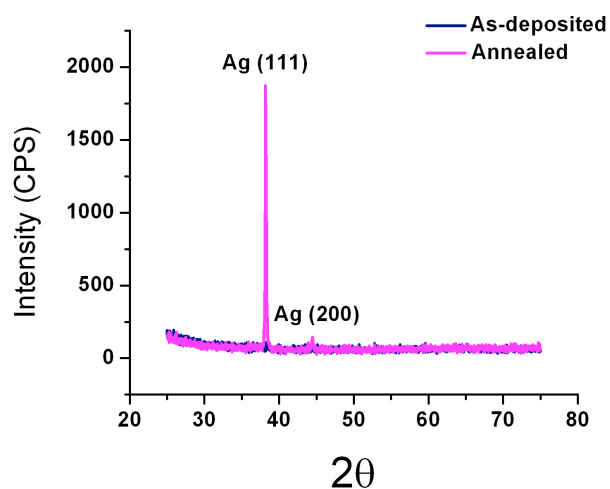


Figure S2 X-ray-diffraction (XRD) patterns of a 20 nm precursor Ag film before and after annealing to make the bimodal Ag/AgO_x nanoparticle structure.

X-ray photoelectron spectroscopy (XPS)

In addition to XPS of surface/subsurface O 1s and Ag 3d shown in Figure 2, XPS of core level carbon C 1s is collected and presented in Figure S3. The broad peak is deconvoluted with curve fitting into three peaks with binding energies at 283.36, 285.28, and 287.01 eV, respectively. This indicates multiple carbon-based surface species adsorbed on the Ag/AgO_x nanostructure, consistent with the surface carbonate species revealed by the Raman spectrum (Figure 4). This results from the trace hydrocarbon source from the gas manifold, which is readily adsorbed and oxidized on the Ag/AgO_x nanostructure.

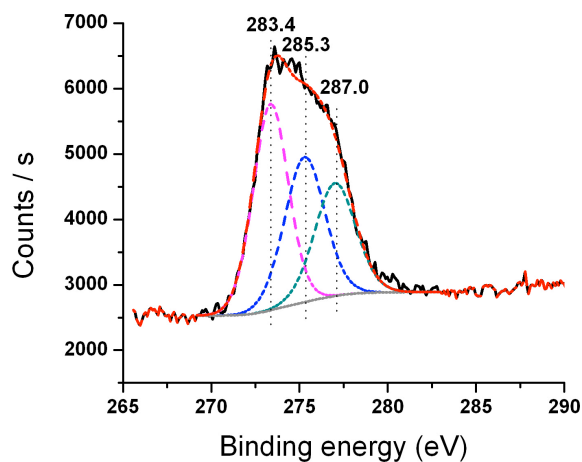


Figure S3 X-ray photoelectron spectroscopy (XPS) of core level carbon C1s of a bimodal Ag/AgO_x nanoparticle structure made from a 20 nm Ag precursor film with deconvolution curve fitting plotted in dashed lines.

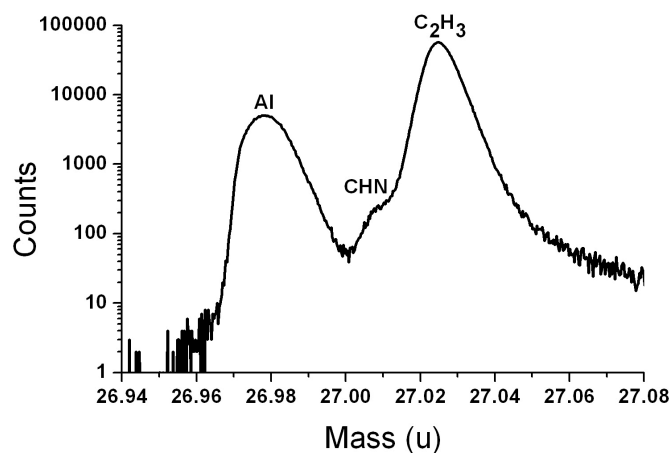


Figure S4 Secondary ion mass spectroscopy (SIMS) spectrum of a bimodal Ag/AgO_x nanoparticle structure.

Secondary ion mass spectroscopy (SIMS)

As detailed in the Methods section, trace Al is introduced into the Ag film *via* re-evaporation of the Al pre-coated on the chamber components during the subsequent Ag thermal evaporation process. Thus it is expected that the trace Al is enriched at the

bottom of the Ag film according to the physical deposition nature. The presence of Al in the sample is confirmed by the secondary ion mass spectrometry (SIMS) spectrum as shown in Figure S4. We propose the following model for the nanostructure growth. Upon annealing, Ag beyond the bottom portion of the film is in the presence of less trace Al and can readily grow into larger Ag particles *via* an Ostwald ripening model along with metal oxidation. Ag closer to the bottom of the film is within the distribution of more trace Al, which is preferentially oxidized and produces a thermodynamic barrier towards the growth of AgNPs. This leads to the formation of a uniform distribution of smaller sized AgNPs dispersed in an AlO_x (trace)- AgO_x “blanket”. This model accounts for the growth of a bimodal distribution of AgNPs within the Ag/ AgO_x nanostructure, which is clearly visible from the SEM images in Figures 1 and S1 and the LSPR spectra in Figures 3 and S5. It is interesting to note that some small particles appear parasitic on the large particles and remain present even after repeated exposures to catalytic reaction environments (see Figure 1c and 1f). They are likely AgNPs with a capping of AgO_x -trace AlO_x and have been brought up on the larger particles during the nanostructure growth. This self-consistently supports the role of Al and the growth model for the Ag/ AgO_x nanostructure we have proposed. A detailed growth mechanism is under further study.

UV-vis extinction spectroscopy

UV-vis extinction spectra are collected in transmission mode on a Varian Cary 50 UV-vis spectrometer. Figure S5 exhibits UV-vis extinction spectra for the nanostructures made from thermal annealing of 3 and 60 nm precursor Ag films, respectively, for a

comparison to Figure 3 for the Ag/AgO_x NP structure obtained from a 20 nm Ag film. It

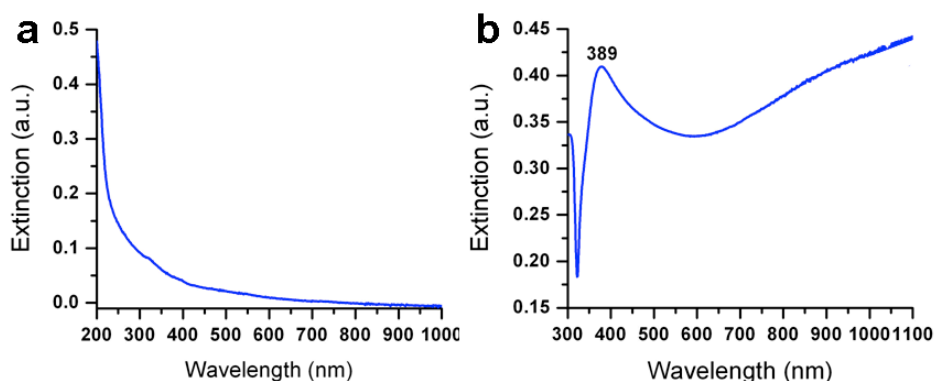


Figure S5 UV-vis spectra of bimodal Ag/AgO_x nanoparticle structures made from Ag precursor films of different thickness (a) 3 nm and (b) 60 nm, characterized at room temperature and ambient air conditions.

can be seen that there is no LSPR band observable in Figure S5a, illustrating a complete oxidation of the extremely thin 3 nm Ag film during the annealing process. For the 60 nm Ag film, there is a sharp extinction peak present in Figure S5b, which is centered at 389 nm. The peak position corresponds well with the small sized (on average ~ 10 nm) particles visible from Figure S1c, verifying that the nature of the observed small size particles is indeed metallic Ag instead of AgO_x. This agrees well with the case for the 20 nm Ag based system, reinforcing that the small size (averagely ~ 6 nm) particles shown in Figure 1c are metallic AgNPs contributing to the extinction band at 367 nm shown in Figure 3. This in turn provides further support to the formation of a bimodal AgNP distribution discussed in the main text of this report. Note that in Figure S5b the rising slope toward 1100 nm is likely a part of a LSPR band centered in the near infrared region resulting from the large size set of AgNPs shown in Figure S1.

It is clear that the precursor Ag film thickness has a strong effect on the size of the large AgNPs formed and thus the associated LSPR. However, Ag film thickness has less

of an affect on the small particles and their corresponding LSPR. The small particles appear to be highly dependent on the presence of trace Al.

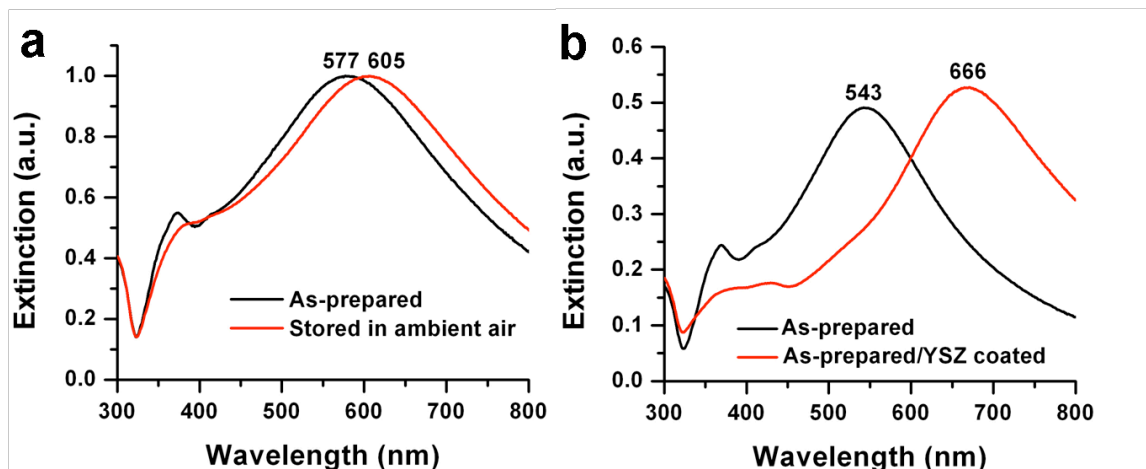


Figure S6 UV-vis extinction spectra of as-prepared samples before and after storage in ambient air (a) and before and after deposition of surface coating of YSZ (b).

Figure S6 shows LSPR spectra of two separate as-prepared systems made from 20 nm Ag films before and after storage in ambient air and sputter deposition of a surface coating of yttria stabilized zirconia at room temperature, respectively. It is known that a shift in LSPR can result from either a change in particle size or in the surrounding dielectric constant or both. Since the samples did not undergo any catalytic tests at high temperature, the observed red shift in the LSPR relative to that of the as-prepared samples should originate from the change in the surface dielectric environment.

***In situ* Raman spectroscopy**

Examination of surface species and their catalytic properties within the bimodal Ag core /AgO_x shell nanostructure is carried out through *in situ* Raman spectroscopy. Table S1 summarizes all of the Raman peaks exhibited in Figure 4 and their potential

TABLE S1. Vibrational Frequency (cm^{-1}) and Assignment of Various Chemisorbed Oxygen Species Detected in This Study

Raman shift (cm^{-1})	species	assignment	references
232	Ag-O_2^{-1}	ν (Ag-O_2)	1,2
352	Ag-O_γ	δ (Ag-O)	1,2
463	Ag-O_α	ν (Ag-O)	1,3
492	Ag-OH	ν (Ag-OH)	1,4
618	Ag-O_β	ν (Ag-O)	1,2,5
776	$\text{Ag}^{\text{III}}=\text{O}$	ν (Ag-O)	6
803	Ag-O_γ	ν (Ag-O)	1,2
855	Ag-O-Ag		7
883	Ag-O_γ^{-1}	ν (Ag-O)	8, 9
965	Ag-O_2^{-1}	ν (O-O)	1,2
1011	$\text{Ag}[\text{O-O}]^{-1}$		10
1041	$\text{Ag}^+\text{O}_2^{-1}$		11
1199	Ag-O_2^{-1}	ν (Ag-O_2) + ν (O-O)	1
1376	CO_3	$\nu_{\text{as}}(\text{CO}_3)$	1,12
1582	C related		12
1605	Ag-O_γ	2ν (Ag-O)	
1775	?		

assignments as noted from previous studies. Figure S7a displays optical microscope images, which highlight the film morphologies with and without scratching the Ag/AgO_x film. The scratch induced thicker film minimizes Raman signal resulting from the substrate while increasing the signal from the Ag/AgO_x film, which provides a convenience for Raman based high temperature catalytic characterizations without a need to do substrate background subtraction. Figure S7b compares the Raman spectra collected at room temperature from the thin and the scratch induced thick areas of the

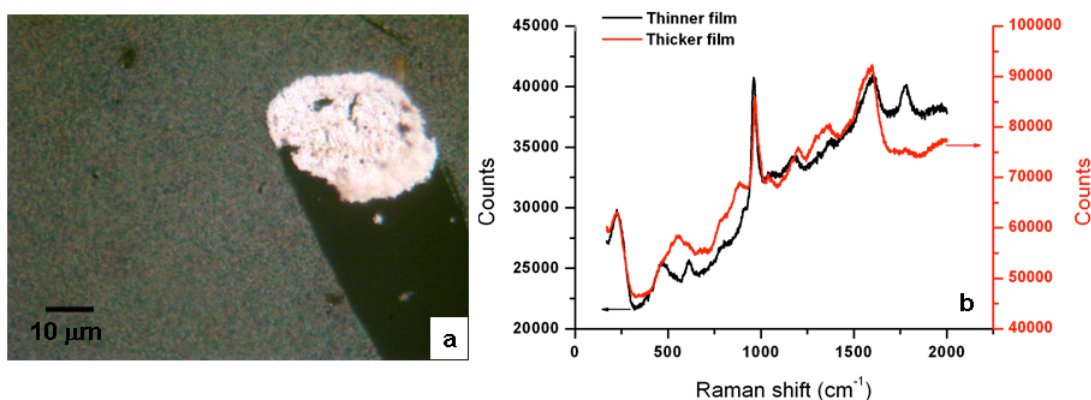


Figure S6 Comparison of optical microscope morphology (a) and Raman spectra at room temperature (b) of thin and thick film areas of a bimodal Ag/AgO_x nanoparticle structure made from a 20 nm Ag precursor films.

Ag/AgO_x nanostructure. The spectra are both comparable with the thicker area showing a factor of ~2.1 enhancement in the Raman signal.

Supporting Information References

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