Supporting Information for

Marrying SPR Excitation and Metal-Support Interactions: Unraveling the Contribution of Active Surface Species in Plasmonic Catalysis

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Figure S1. SEM image (A), UV-VIS extinction spectrum (B), and histogram of size distribution (C) for Au nanoparticles that were obtained by the reduction of $AuCl_{4^-(aq)}$ as the Au precursor in the presence of PVP and ascorbic acid. The scale bar in the inset (in A) corresponds to 100 nm.



Figure S2. Histograms of size distribution for the Au NPs deposited on the SiO₂ (A) and CeO₂ (B) supports. The diameter of the Au NPs corresponded to 21.8 ± 3.1 and 21.9 ± 3.2 nm in the Au/SiO₂ and Au/CeO₂ materials, respectively.



Figure S3. (D) X-ray diffraction patterns of Au/SiO₂ and Au/CeO₂ (black and red traces, respectively). Due to the higher crystallinity of CeO₂ relative to SiO₂, the intensity of the diffraction peaks assigned to Au NPs in the Au/CeO₂ sample has a lower intensity relative to Au/SiO₂. However, the FWHM (full width at half maximum) for Au NPs is similar in both samples.



Figure S4. Characterization of SiO₂ and Au/SiO₂ materials (black and red traces, respectively) by H2-TPR (A), Raman spectroscopy (B), and XPS for the Au 4f and O 1s core levels (C and D, respectively). H₂-TPR profiles displayed a single peak assigned to the bulk SiO₂ reduction, in which a slight shift to lower temperatures was observed after the addition of Au over SiO₂ support. Raman results indicated the presence of an intense band centered in 1000 cm⁻¹ assigned to Si-O-Si bending and asymmetric stretching vibration. XPS spectra of (C) Au 4f and (D) O 1s core levels showing characteristic BE values for Au⁰ (C) and no significant modification in the oxygen BE after addition of Au over the SiO₂ support.



Figure S5. XPS spectra of Ce 3d (A) and Au 4f (B) core levels for the Au/CeO₂ material. The peaks denoted by u' and v' are characteristic peaks of Ce^{3+} ions, whereas those marked by v, u, v'', u'', v''' and u''' are of Ce^{4+} ions.



Figure S6. (A) Diffuse reflectance spectra for Au/CeO₂, Au/SiO₂, Au/TiO₂, and Au/ZrO₂ (red, blue, black, and green traces, respectively). (B) Laser-power-dependent oxidation of PATP, expressed as the DMAB:(PATP+DMAB) ratio, for Au/CeO₂, Au/SiO₂, Au/TiO₂, and Au/ZrO₂ (red, blue, black, and green traces, respectively). Au/CeO₂, Au/TiO₂, and Au/ZrO₂ display SPR bands that are redshifted as compared to Au/SiO₂. Despite the re-shifted LSPR position, both Au/TiO₂ and Au/ZrO₂ samples displayed PATP conversions that were similar relative to Au/SiO₂. This result indicated that the improved conversion for the Au/CeO₂ sample cannot be explained solely based on the shift in SPR position, and that the major contribution for the to the detected activities comes from the activation of oxygen species from the CeO₂ support.



Figure S7. (a) Chopped visible light (light/dark) linear sweep voltammetry in the photoelectrochemical oxygen evolution reaction for CeO₂ and 10 mol % Au/CeO₂ samples. (B) SEM image of the 10 mol % Au/CeO₂ film employed for the photocurrent measurements. Whereas CeO₂ electrode remains unresponsive to illumination, the voltammetry scan using the Au/CeO₂ electrode shows a clear anodic photocurrent, which can be assigned to the injection of SPR-excited hot electrons from Au to CeO₂.



Figure S8. Laser-power-dependent SERS spectra for the Au/CeO_2 materials that had been functionalized with PATP recorded employing 785 nm as the excitation wavelength. The exposure time corresponded to 10 s.

| Sample | Oxygen species | Binding energy (eV) | Percentage (%) | Os/OL |
|---------------------|----------------|---------------------|----------------|-------|
| CeO ₂ | OL | 529.3 | 68 | 0.4 |
| | Os | 531.4 | 29 | |
| | Ow | 533.9 | 3 | |
| Au/CeO ₂ | OL | 529.1 | 53 | 0.9 |
| | Os | 530.7 | 46 | |
| | Ow | 534.3 | 1 | |

Table S1. Binding energies, surface composition, and O_s/O_L ratios for CeO₂ and Au/CeO₂ materials obtained from the XPS analyses.