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# **Electronic Supplementary Information**

Tailoring metal-oxide interfaces of inverse catalysts of TiO<sub>2</sub>/nanoporous-Au under hydrogen oxidation

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\*To whom correspondence should be addressed: jeongypark@kaist.ac.kr, kim\_sh@kist.re.kr KEYWORDS: Hydrogen oxidation, nanoporous Au, Au/TiO<sub>2</sub> Interface, catalytic activity.

### Synthesis of nanoporous Au films

Nanoporous gold films were prepared by electrochemical de-alloying of Si out of co-sputter-deposited  $Au_xSi_{1-x}$  films. In a vacuum chamber with a base pressure of  $10^{-6}$  Torr, Au and Si were deposited via co-sputtering on n-doped Si(110) substrates (1 cm × 2 cm) with a Ti adhesion layer and a Au layer etch stop. Au was sputtered in dc mode at 10 W and Si was co-sputtered in radio frequency (RF) mode at 200 W for 40 minutes. By varying the sample position under these plasma powers, we obtained  $Au_xSi_{1-x}$  films with different atomic compositions. In the next step, Si was selectively dealloyed in a 3% HF aqueous solution with a three-electrode system consisting of Ag/AgCl (3 M KCl) as the reference electrode, a Pt wire as the counter electrode, and the  $Au_xSi_{1-x}$  films as the working electrodes in an electrochemical analyzer (CH660, CH Instruments Inc.). The bottom Si(110) substrates of the samples were sealed with silicon glue before they were immersed in the HF solution and dealloyed under a linear potential sweep from 0 to 1.3 V at a scan rate of 10 mV/s. After dealloying, the np-Au films were cleaned under cyclic voltammetry from -0.25 to 1.8 V (vs. Ag/AgCl) at a scan rate of 100 mV/s in a 0.5M H<sub>2</sub>SO<sub>4</sub> solution until reproductive voltammograms were obtained.

#### Deposition of titania over nanoporous Au films

To generate inverse  $TiO_2/np$ -Au catalysts for engineering  $TiO_2/Au$  interfaces and systematic investigation of catalytic activity under H<sub>2</sub> oxidation, we deposited titania using liquid-phase deposition (immersion in a solution of TTIP in ethanol). For the liquid-phase deposition, all of the np-Au samples were cleaned by sonication for 10 minutes in ethanol, followed by immersion in the TTIP/ethanol solution. The samples were kept in the solution for 10 minutes, and then air dried for 15 minutes. Finally, all of the samples were heated in an oven at 473 K for 1 hour.

#### Characterization

To assess the pore/ligament structural morphology, post-oxide deposition of titania, and the structural integrity of the nanoporous Au following the catalytic reactions, we took images using scanning electron microscopy (SEM; Magellan400). To investigate morphological characteristics, including the thickness, amount, and phase of the deposited titania, cross-sectional samples were prepared for transmission electron microscopy (TEM) analysis. For this purpose, a focused ion beam (FIB; Helios Nanolab 450 F1) was used to cut cross sections of the TiO<sub>2</sub>/np-Au catalysts. TEM images and energy-dispersive X-ray spectroscopy (EDS) spectra were taken using field emission transmission electron microscopy (FE-TEM; Tecnai TF30 ST). For investigation of the crystalline phase of the deposited titania, we used multipurpose attachment X-ray diffraction (XRD; SmartLab, RIGAKU). The measurements were taken at a 2 $\theta$  scan range of 10–90°, scan speed of 2.4°/min, and step size of 0.01 Å using CuKa radiation to identify the phases. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo VG Scientific Sigma Probe system equipped with an Al-Ka X-ray source (1486.3 eV) with an energy resolution of 0.47 eV full width at half maximum (FWHM) under ultrahigh vacuum (UHV) conditions of 10<sup>-10</sup> Torr.



**Fig. S1** HR-TEM investigation of the np-Au–TiO<sub>2</sub> interface. The TiO<sub>2</sub> layer is on top of the np-Au for the 0.1 weight% TTIP on np-Au-2. TiO<sub>2</sub> and Au have an average lattice spacing of ~ 0.18 nm and ~0.236 nm, respectively (scale bar refers to 1 nm).

As can be seen in Fig. S1, we found that for all TTIP-loaded nanoporous Au, a Au–TiO<sub>2</sub> interface is formed. HR-TEM images reveal formation of such a Au–TiO<sub>2</sub> interface. For 0.1 weight% TTIP, the Au–TiO<sub>2</sub> interface can be clearly seen (due to the semi-continuous ~ 2-4 nm TiO<sub>2</sub> layer).



**Fig. S2** XRD patterns of TiO<sub>2</sub>: 0.1 weight%, 0.5 weight%, and 1 weight% TTIP deposited on a Si wafer before catalytic H<sub>2</sub> oxidation.

Fig. S2 shows structural information for the  $TiO_2$ . The  $TiO_2$  peaks are identified at 32.8 degrees, which can be assigned to the (200) plane of the brookite phase. This peak is only observed in 0.5 weight % TTIP.

The other  $TiO_2$  peaks are identified at 61.9 degrees, which is assigned to the (250) plane of  $TiO_2$ . A small peak of brookite emanating from the (133) plane also appears at 64.6 degrees.

From the XRD results, it is expected that the deposited  $TiO_2$  is largely amorphous with a crystalline titania phase embedded in the matrix.



**Fig. S3** XPS oxidation states of np-Au after titania deposition. (a) Au4f, (b) Si2p, (c) Ti2p, and (d) O1s spectra for (i) 1.0 weight%, (ii) 0.5 weight%, and (iii) 0.1 weight% TTIP-impregnated catalyst. Au is in the metallic Au (0) oxidation state while Ti shows Ti (4+) along with the  $O^{2-}$  component in the O1s spectra confirming the TiO<sub>2</sub> layer on the np-Au. Si2p shows residual Si after de-alloying the AuSi alloy film. The Si (4+) oxidation state signals oxidation into SiO<sub>2</sub>.

The XPS spectra have been analyzed for oxidation states of Au4f, Ti2p, and O1s for all catalysts. For quantitative analysis of the peak positions, line widths, and relative areas of the species, the raw XPS spectra were fitted to Gaussian–Lorentzian functions using CASAXPS software. For peak deconvolution, the C1s peak centered at 284.6 eV was used as the reference for the binding energy scale calibration. Shirley background subtraction was used for the Au4f and Ti2p spectra, while linear background subtraction was used for the O1s and C1s spectra.

We found that Au primarily remains in its noble metallic state, evident by the Au spectra for all systems that shows peaks centered at 84 eV, which is attributed to Au (0) (see Fig. S3a). Fig. S3b,c shows Ti2p and O1s XPS spectra, respectively. The Ti2p spectra show peaks at a binding energy of 458.8 eV, which is characteristic of Ti (4+) and suggests the stoichiometric formation of TiO<sub>2</sub>. The O1s spectra can be deconvoluted into two peaks centered at binding energies of 531.5 eV and 532 eV, which are assigned to absorbed O/OH and O<sup>2-</sup> oxidation states. The O<sup>2-</sup> peak corresponds to the signature peak of TiO<sub>2</sub>, thus confirming TiO<sub>2</sub> on the np-Au film.<sup>1</sup>

#### **Catalytic reaction**

The H<sub>2</sub> oxidation reaction was performed in an UHV batch reactor (1L) with a base pressure of  $5.0 \times 10^{-7}$ Torr. The reaction chamber was evacuated and isolated with a gate valve before it was charged with 15 Torr H<sub>2</sub> and 975 Torr O<sub>2</sub> at room temperature. The reaction mixture was circulated continuously through the reaction line by a Metal Bellows recirculation pump at a rate of 2 L/min. H<sub>2</sub> oxidation was monitored as a function of reaction temperature (130–180 °C). After equilibrating for 1 hour, the reaction mixture was continuously analyzed through an online gas chromatograph. The reaction mixture was separated for analysis using a DS iGC 7200 gas chromatograph equipped with a thermal conductivity detector and a 6 ft-long, 1/8" outer diameter stainless steel 80/100 mesh-size column. H<sub>2</sub>O conversion was reported in terms of turnover frequency (TOF) and was calculated on the basis of the product molecules of H<sub>2</sub>O produced per metal surface site per second of reaction time. For the TOF calculations, the active sites were counted based on the true surface area of the np-Au, which was obtained from the roughness factor measured for the np-Au catalysts.

### Stability of TiO<sub>2</sub>/nanoporous Au films



**Fig. S4:** FE-SEM images of TiO<sub>2</sub>/np-Au (a,b,c) before and (d,e,f) after H<sub>2</sub> oxidation. (a,d) 0.1 weight%, (b, e) 0.5 weight%, and (c, f) 1.0 weight% TTIP-impregnated np-Au films. Deposition of TiO<sub>2</sub> on the np-Au film results in a substantial resistance to structural coarsening of the Au ligaments. After the reaction, the np-Au skeletal structure remains largely intact; however, a slight coarsening of the Au ligaments occurs (scale bar refers to 200 nm).

Bare np-Au underwent severe structural coarsening. Such structural coarsening resulted in the loss of active sites and ultimately irreversible catalyst deactivation occurred.<sup>2, 3</sup> Such degradation is ascribed to curvature-driven diffusion of the surface Au atoms<sup>4, 5</sup> and can be effectively suppressed by deposition of a thermally stable oxide, such as titania.<sup>6, 7</sup>After titania deposition, the structural integrity was enhanced for all np Au films.



**Figure S5:** Turnover number of  $H_2O$  molecules per site with reaction time at a higher reaction temperature of 170 °C for (a) 0.1 weight%, (b) 0.5 weight%, and (c) 1.0 weight% TTIP-loaded np-Au catalysts.

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