Supporting Information

Sustainable photocatalytic production of hydrogen peroxide from water and molecular oxygen

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Table S1: d- spacing obtained from TEM electron diffraction pattern.

d spacing (Å) Measured	d spacing (Å)[S1] TiO_2 (Anatase)	Lattice parameters *(hkl)*[S1]
3.581	3.592	(101)
2.411	2.404	(004)
1.936	1.936	(200)
1.730	1.722	(105)
1.511	1.508	(204)

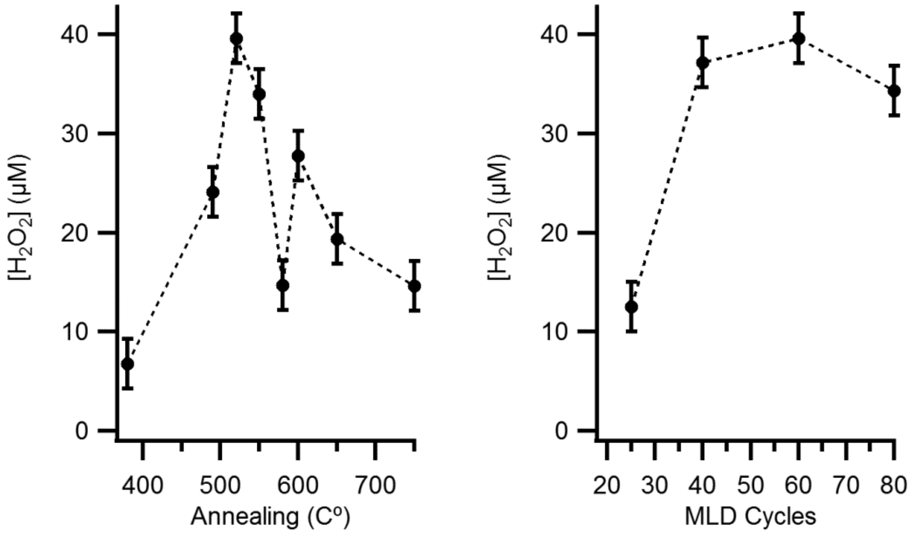

Fig. S1. (a) Maximal steady state concentration (SSC) of H_2O_2 obtained for catalysts prepared with (a) 60 MLD cycles and annealed at the specified temperatures, (b) for catalysts annealed at 520 °C and prepared with the specified number of MLD cycles.

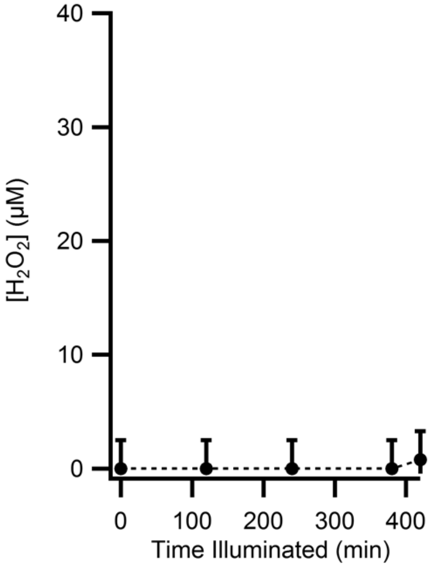

Fig. S2. Maximal steady state concentration (SSC) of H_2O_2 obtained for photocatalysis experiment performed with deoxygenated solutions under argon. Catalyst prepared with 60 MLD cycles and annealed at 520 ^{o}C and gold deposited as described in the text.

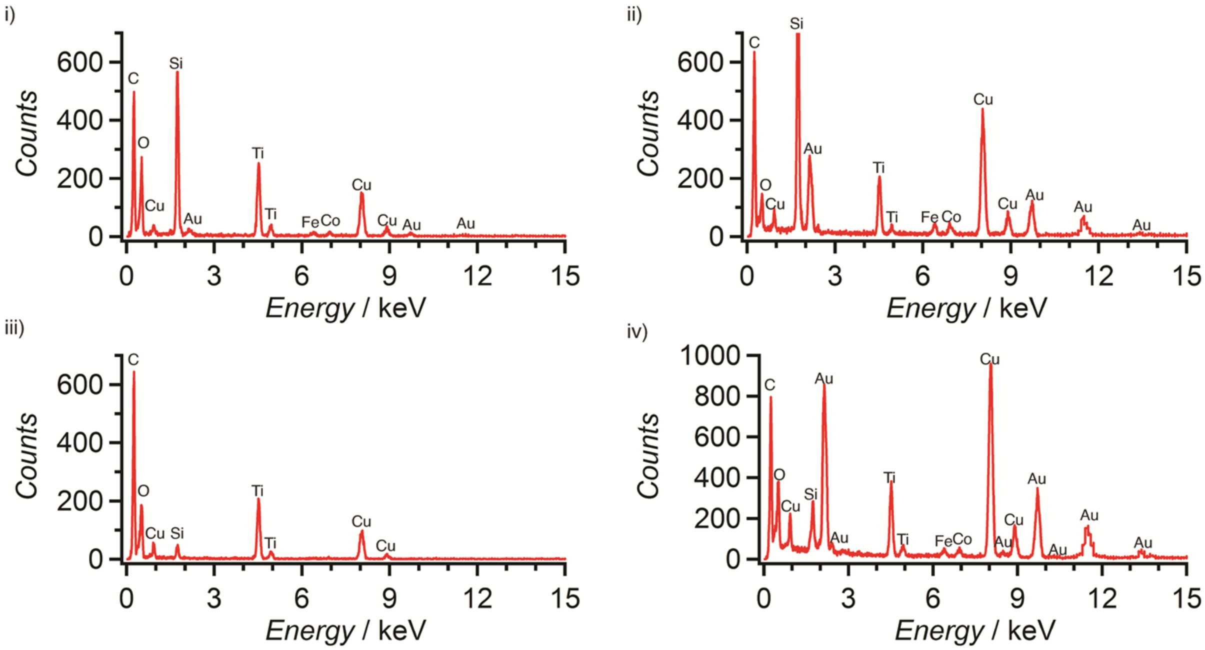

Fig. S3 EDS spectra corresponding to the highlighted regions in figure 3: (i) and (ii) showing filled catalyst region with Si core and Au particles on TiO_2 shell. (iii) hollow TiO_2 tube region, and (iv) hollow TiO_2 tube region with gold deposited inside the tube. All spectra were acquired with 50 sec live acquisition time. Parasitic peaks of C and Cu originate from the supporting grid. Fe and Co peaks originate from the sample holder.

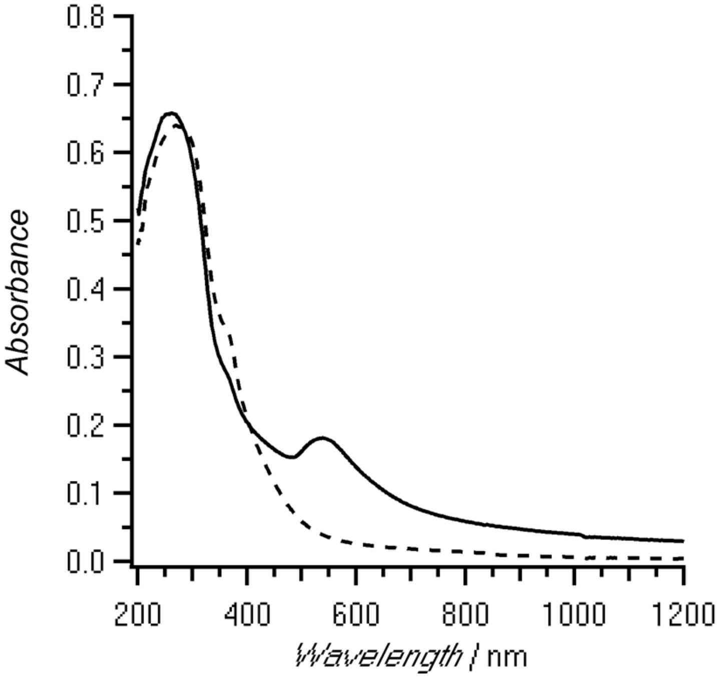

Fig. S4 Optical absorption (UV-VIS-NIR) spectra. Photocatalyst with gold depositon (solid line) and without gold depositon step (broken line). Spectra were collected using a Perkin Elmer Lambda 1050 spectrophotometer equipped with an integrating sphere.

Table S2 Quantified EDS Results based on Figure 3 and S1.

Figure		3b				3d			
Region		(i)		(ii)		(iii)		(iv)	
Element	Quant. peak	%wt.	%at.	%wt.	%at.	%wt.	%at.	%wt.	%at.
O	K	21.7	38.6	9.2	32.0	39.5	64.5	10.0	44.1
Si	K	42.5	43.1	15.7	31.1	7.1	6.6	5.3	13.4
Ti	K	29.3	17.4	17.9	20.7	52.9	28.8	10.9	16.0
Au	L	6.5	0.9	57.2	16.2	0.5	0.1	73.8	26.5

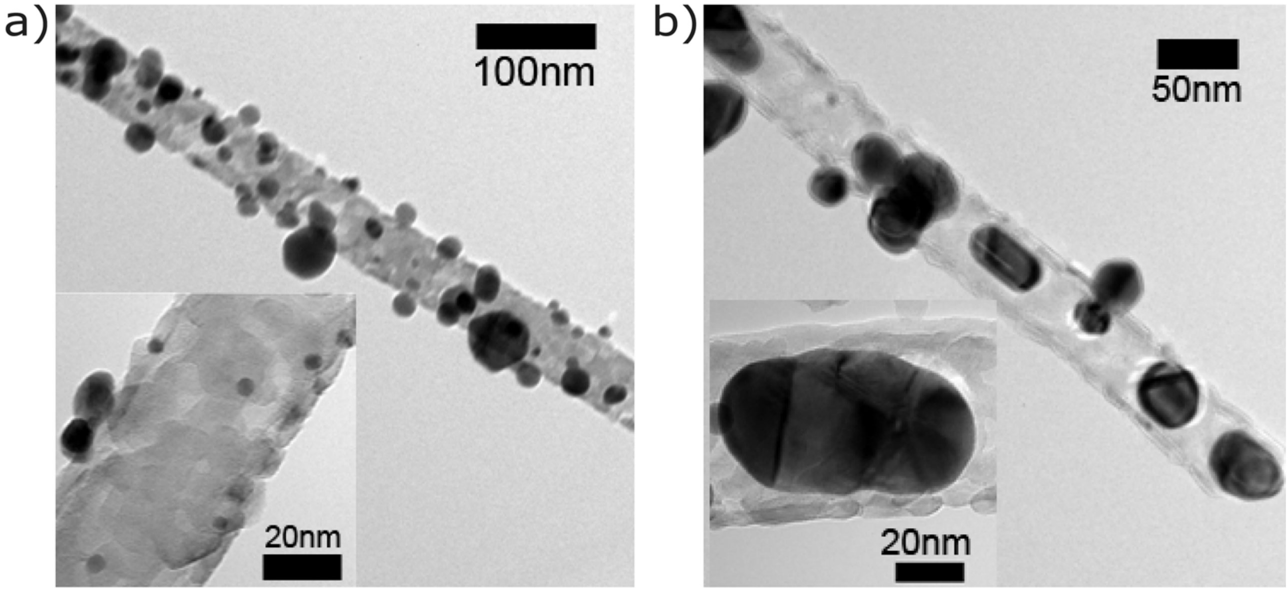

Fig. S5 TEM images of Si-TiEG-Au hybrid nanostructures. (a) Deposition of gold clusters mainly at the external surface while minimizing internal deposition obtained by illumination and preparation conditions as specified below. (b) Deposition of gold clusters mainly at the internal surface creating hollow tubes with pea pod-like structures obtained by gold depostion in the dark and preparation conditions as specified below. Synthesis conditions for both were identical except for the illumination condition during gold deposition step. Si NW diameter 30 nm, growth time 15 min, Ti-EG MLD layer 40 cycles, annealed at 700 °C for 30 min; gold deposition from aqueous solution ($AuCl_3$:HF 1mM:200mM) for 5 min in the specified illumination condition.

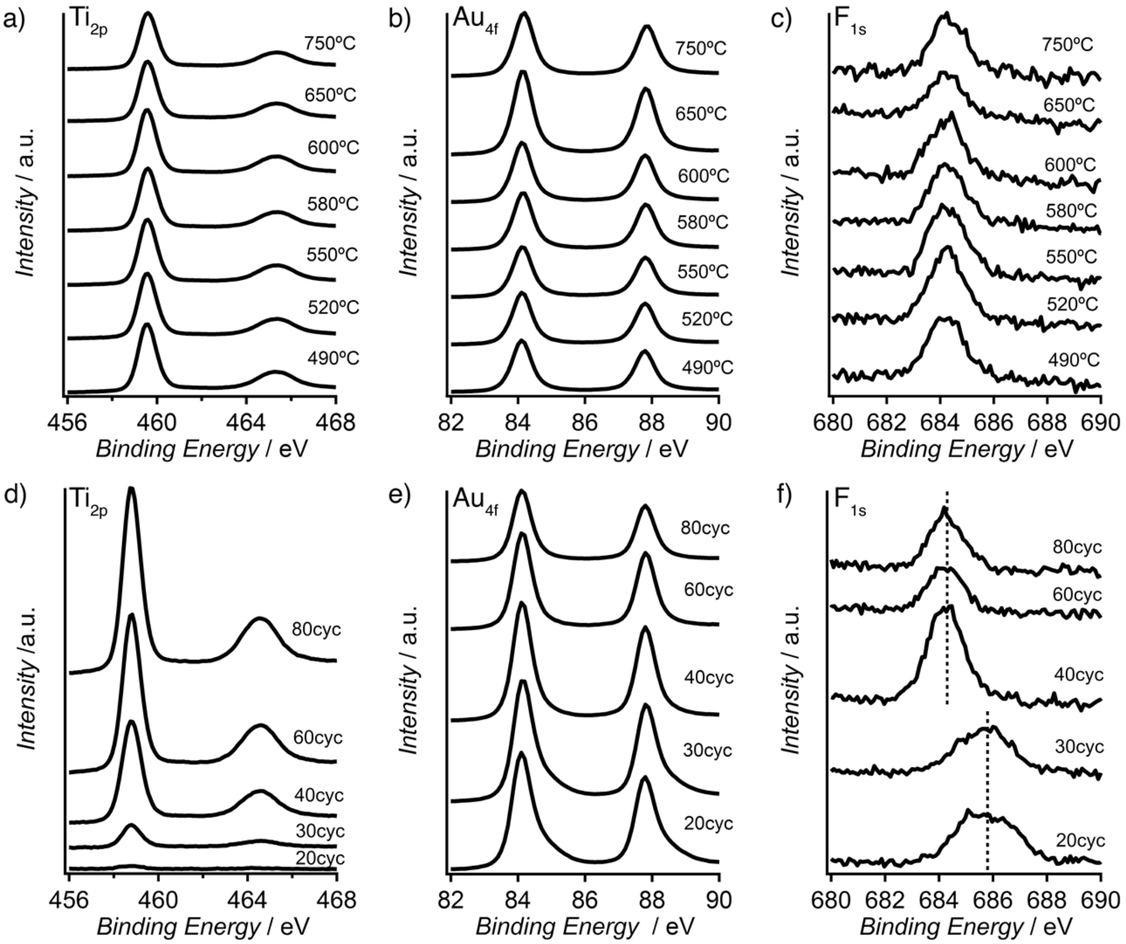

Fig. S6 XPS spectra for catalyst preparations with various anneal temperatures (a-c) and TiEG MLD layer thickness (d-f). Note the change in F_{1s}. binding energy from 685.8 eV to 684.3 eV with increasing MLD cycles.

Experimental Section

Nanowire film synthesis. Gold colloid solution (30nm Au nanoparticles solution, Ted Pella, Inc.) was deposited for 2 min. on substrates that were pre-treated with Poly-L-lysine solution as described elsewhere.[15] Si NWs were grown by placing the samples with the deposited gold colloids in a custom built CVD system. Prior to Si NW growth samples were treated with O_2 plasma to remove organic contaminants. The CVD was performed with temperature set to 440 ˚C, and 35 torr pressure, 50 sccm H_2, and 2 sccm SiH_4 gas flow. NWs (~2-3 micron long) were prepared on quartz slides and TEM membranes (50nm thick Si_3N_4 Ted Pella, Inc.) for catalysis experiments and direct TEM characterization, respectively.

Ti-EG layer formation on NW films by MLD process. Ti-EG films were prepared using $TiCl_4$ (Acros, 99.9%) and ethylene glycol (Aldrich, > 99%). Ultrahigh purity Ar gas was used as the carrier gas in viscous flow reactor and for purge between reactant exposures. MLD films were prepared by dosing the reactant precursors into Ar carrier gas. The duration of precursor dosing was controlled using computer controlled pneumatic valves ($TiCl_4$ 0.3 s, purge 9 s, EG 70 s, purge 30 s). A steady state pressure of 2.5×10^{-1} mbar was maintained during the process. The EG precursor chamber temperature was set to 70 °C, and the sample reaction chamber temperature was set to 100 °C. Ti-EG films were prepared on Si NW films formed on quartz slides. Prior to MLD film formation the NW film was subject to O_2 plasma for 1 min. Samples were prepared and characterized for a range of Ti-EG film thicknesses between 20 and 80 MLD cycles. Immediately after completion of the MLD process the NW films coated with Ti-EG layer were thermally annealed in a pre-set furnace in the temperature range of 480 to 750 °C for 30 minutes. Oven temperature is pre-equilibrated to avoid kinetic effects of temperature ramp.

Gold deposition. 1mM AuCl3 solution with 200 mM HF is used for the deposition of Au nanoclusters. Samples were immersed in solution for 6 min under hood light (unless otherwise specified) followed by careful rinsing with DI water.

Photocatalysis experiments. Substrates with catalyst film were placed in a quartz cuvette with 2mL of 0.01M HCl and illuminated by UV 9W lamp (365 nm) or simulated sunlight illumination (AM 1.5 G; 100 mW cm^{-2}). Freshly prepared catalyst films were treated with Ozone for 3min. using a UVOCS cleaning system prior to photocatalytic experiments.

Spectroscopic quantification of H_2O_2. Measurements of the H_2O_2 concentration were made using the Iodide/triodide method[S2,S3] Buffer solutions containing potassium hydrogen phthalate, sodium hydroxide, potassium iodide, and ammonium molybdate were used to quantify H_2O_2 by iodide absorbance the peak from 350 nm. All measurements were performed using a double beam spectrophotometer. Concentration was determined using a calibration curve (figure S5).

XPS analysis. The atomic compositions for Ti, Si and Au were quantified by drop casting the catalyst on an aluminum foil. F was quantified for catalyst on SiO_2/Si wafer.

Transmission Electron Microscopy Measurements. TEM imaging and analysis were preformed with an FEI Tecnai F20-G^2 microscope at 200kV with EDAX EDS detector.

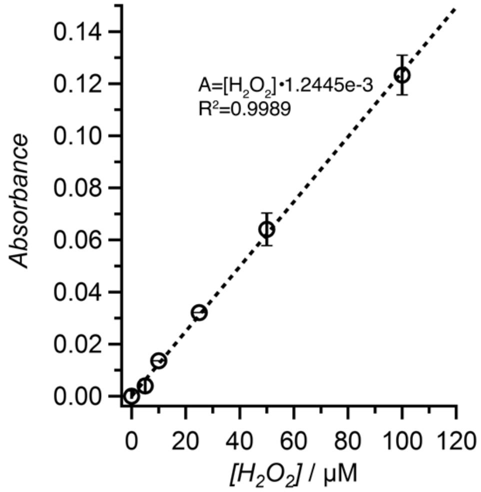

Fig. S7 Calibration curve for spectroscopic determination of H_2O_2 concentration. Error bars represent the standard deviation obtained of multiple measurements.

Citations:

(S1) T. E. Weirich, M. Winterer, S. Seifried, J. Mayer, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2002, **58**, 308-315.

(S2) C. Aria, F. Mata, J. F. Perez-Benito, *Can. J. Chem.*, 1990, **68**, 1499-1503.

(S3) T. C. J. Ovenston, W. T. Rees, *Analyst* 1950**, 75,** 204-208.