Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information For

Enhanced Photothermal Reduction of Gaseous CO_2 over Silicon Photonic Crystal Supported Ruthenium at Ambient Temperature

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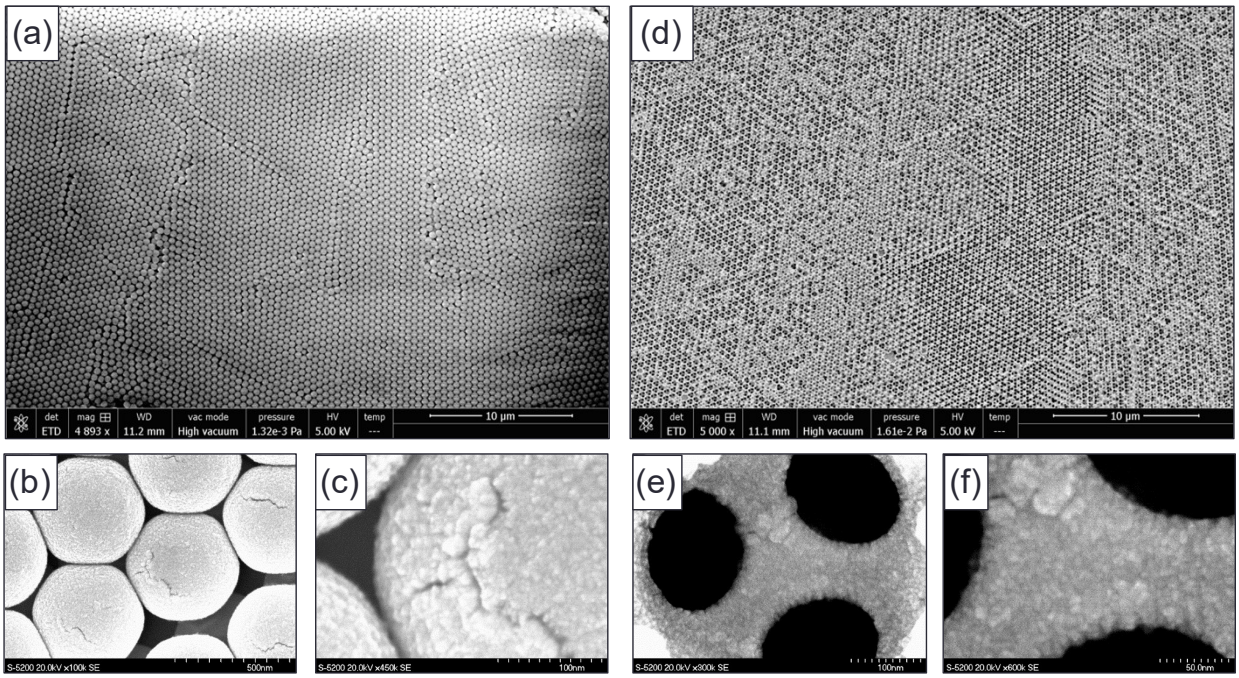

Figure S1 SEM images of the Ru/SiO_2-o sample at (a) 4.9k, (b) 100k, and (c) 450k magnification, and of the Ru/i-Si-o sample at (d) 5k, (e) 300k, and (f) 600k magnification

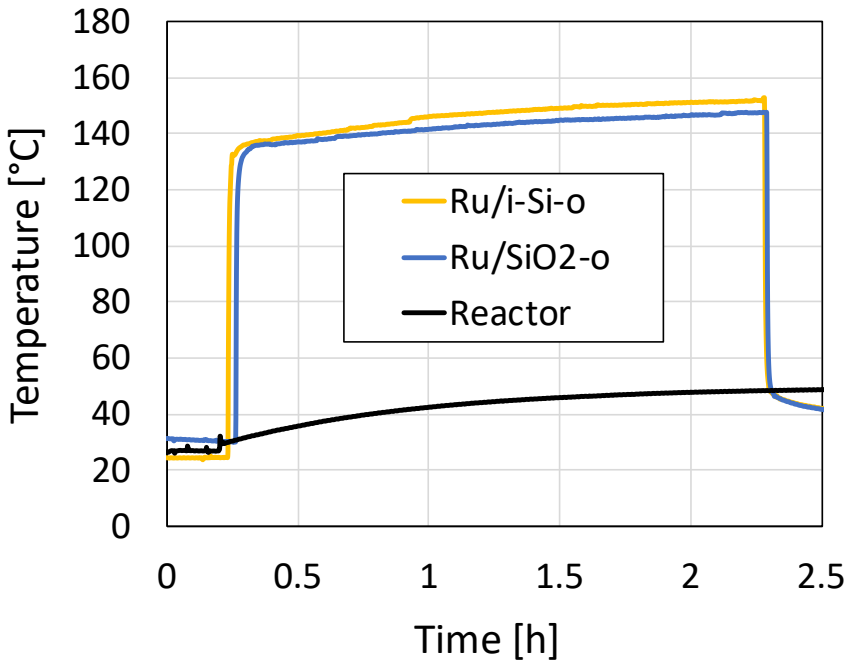

Figure S2 Temperature profiles for reactions carried out under solar-simulated radiation from a 300 W Xe lamp at an intensity of 2,470 mW/cm^2 (24.7 Suns). When the lamp is turned on at the ~0.25 h point the temperature of the Ru/i-Si-o and Ru/SiO_2-o catalysts quickly increase to over 130 °C. The temperatures of these catalysts continue to rise at a slower rate and reaches ~150 °C at the 2 h point when the light is switched off. It should be noted that the thermocouple used for these measurements is located on the rear side of the silicon wafer that the photonic crystals are deposited on (the side that is opposite from the side with the photonic crystals and supported Ru). The actual temperature of the supported Ru is expected to be significantly greater than 150°C during photomethanation reactions. The temperature of the bare reactor, measured without a catalyst present and with the thermocouple placed out of the path of the incident light from the Xe lamp, did not exceed 50 °C after 2.5 h (black line).

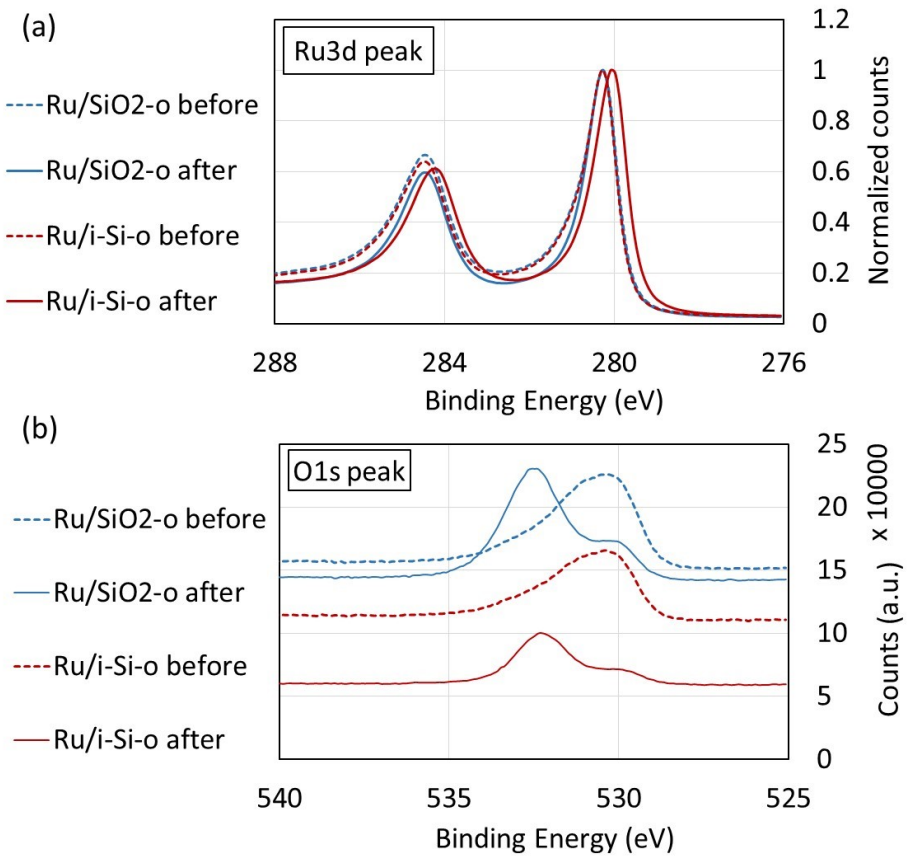

Figure S3 Comparison of the XPS (a) Ru3d and (b) O1s peaks for the Ru/SiO_2-o (blue lines) and Ru/i-Si-o (red lines) measured before (dashed lines) and after (solid lines) the Sabatier reaction rate tests were performed.

The binding energy of the $Ru3d^{3/2}$ peak is in the vicinity of 284.5 eV, and the binding energy of the $Ru3d^{5/2}$ peak is closer to 280.5 eV. More specifically, the $3d^{5/2}$ peak for metallic Ru lies between 279.96 eV and 280.3 eV, while the binding energy for ruthenium dioxide lies between 280.68eV and 281.0 eV.[s1] The $Ru3d^{5/2}$ binding energy peak position for the Ru/SiO_2-o sample is located at 280.3 eV before and after the Sabatier reaction rate tests were performed, indicating the sputtered Ru is metallic. On the other hand, the $Ru3d^{5/2}$ binding energy peak position for the Ru/i-Si-o sampe shifts from 280.3 eV before the reaction to 280.0 eV after the reaction. This indicates that under reaction conditions, in an H_2 environment under high intensity illumination, the Ru/i-Si-o sample is in a highly reduced state.

The Ru/SiO_2-o and Ru/i-Si-o samples exhibit a broad peak associated with ruthenium oxide (529.45 eV) and ruthenium hydroxide (530.75 eV) before testing. However, after the Sabatier reaction tests were run these intenisty of these peaks diminishes while another peak located at approximately 532.4 eV arises, which can be attributed to adsorbed C/O species. [s2]

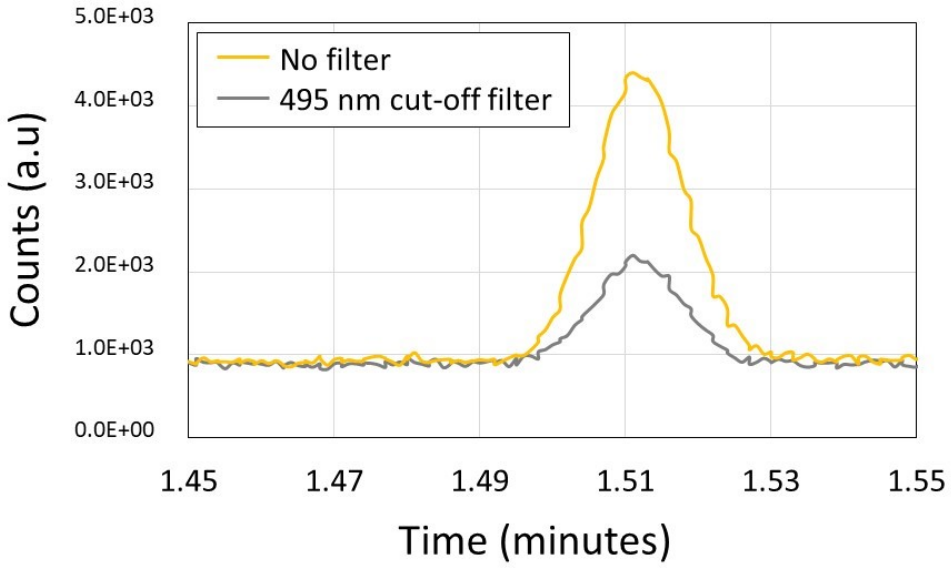

Figure S4 The ion mass 17 peak for photomethanation experiments carried out over the Ru/i-Si-o catalyst under solar simulated radiation produced from a 300 W Xe lamp with an intensity of 2,470 mW/cm^2 (24.7 Suns). These ion mass 17 peaks were acquired using an Agilent 7890A gas chromatographic mass spectrometer.

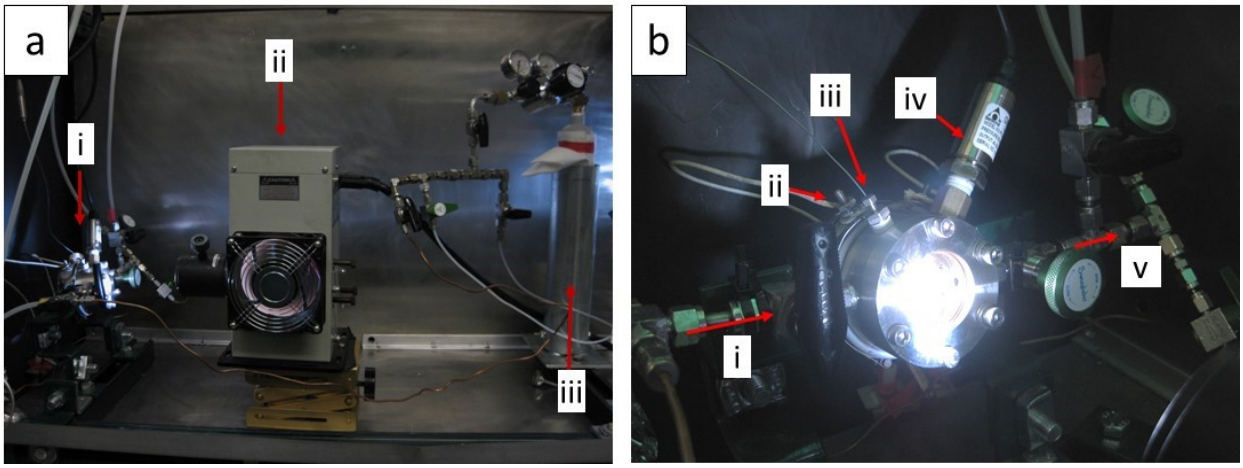

Figure S5 (a) photograph of custom built photoreactor set-up including a (i) stainless-steel batch reactor, (ii) Xe lamp, and (iii) $^{13}CO_2$ tank. (b) Photograph of the stainless-steel batch reactor including (i) gas inlet lines, (ii) heating band, (iii) thermocouple, (iv) pressure transducer, and (v) gas outlet line.

Table S1 Calculated bond lengths, Bader charges, and binding energies of adsorbed H_2 on neutral and charged Ru(0001) surfaces

Surface charge	Bond length (Å)		Bader charge (e)		Binding energy, E_b (eV)
	H1-Ru	H2-Ru	H1	H2	
$[Ru(0001)]^{-1.0}$	1.66	1.66	-1.36	-1.07	-0.705
[Ru(0001)]	-	-	-0.97	-1.04	-0.013
$[Ru(0001)]^{+1.0}$	1.76	1.76	-0.99	-1.03	-0.856

References

[s1] C. Mun, J. J. Ehrhardt, J. Lambert, C. Madic, XPS Investigations of Ruthenium Deposited onto Representative Inner Surfaces of Nuclear Reactor Containment Buildings. Appl. Surf. Sci., 2007, 253, pp. 7613-7621. <10.1016/j.apsusc.2007.03.071>. <irsn-00176550>

[s2] J. L. Hueso, J. P. Espinós, A. Caballero, J. Cotrino, A. R. González-Elipe, XPS Investigation of the Reaction of Carbon with NO, O_2, N_2 and H_2O plasmas, Carbon 45 (2007) 89-96.