Electronic Supplementary Information for: Exploring surface science and restructuring in reactive atmospheres of colloidally prepared bimetallic CuNi and CuCo nanoparticles on SiO_2 *in situ* using ambient pressure X-ray photoelectron spectroscopy

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1. Calculation of probing depths

The given values of probing depths or mean free paths of escaping photoelectrons for the Cu, Ni and Co 3p XP spectra are calculated by using the universal escape depth obtained by M. P. Seah and W. A. Dench (*Surf. Interface Anal.* 1979, **1**, 2). For the 3 incident photon energies used in this work this gives:

Incident Photon Energy / eV	*Probing Depth (or inelastic mean free path of an electron in an inorganic solid) / nm*
380	0.8
630	1.0
800	1.2

2. SEM before and after AP-XPS measurements

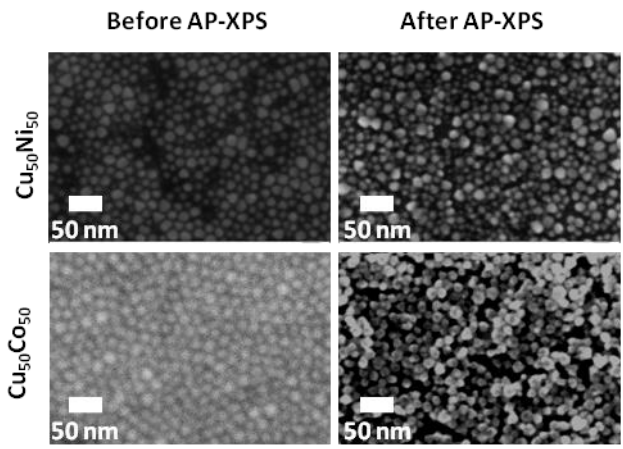

Fig. S1 SEM images representative of nanoparticles on SiO_2 wafer samples before and after ambient pressure XPS measurements were conducted, indicating no significant agglomeration of individual particles.

3. AP-XPS measurements of CuNi nanoparticles from vacuum to 450 °C in H_2

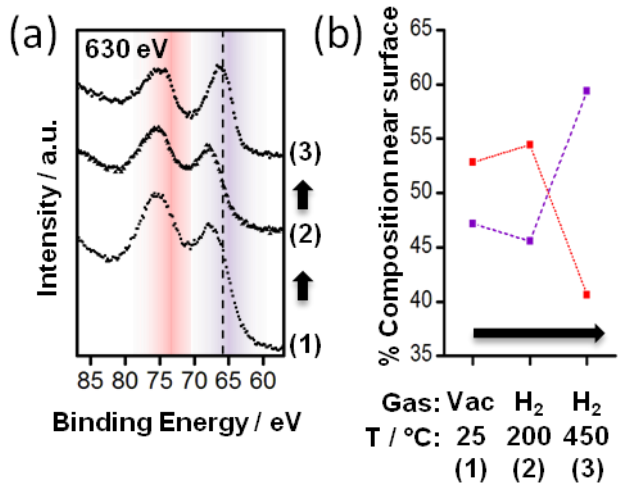

Fig. S2 (a) Ambient pressure Cu (red) and Ni (purple) 3p XP Spectra of CuNi nanoparticles supported on the native oxide layer of a silicon wafer in vacuum and on exposure to 0.1 torr of H_2 at 200 °C and 450 °C as indicated, using an incident photon energy of 380 eV (corresponding to a mean free path of escaping electrons of 0.8 nm). (b) Graph showing the corresponding % of Cu (red) and Ni (purple) in this top 0.8 nm surface layer of the nanoparticles for each condition in (a) (after correction for the relevant photon energy photoelectron cross sections and removal of a Shirley background).

4. AP-XPS measurements of CuNi nanoparticles with different probing depths

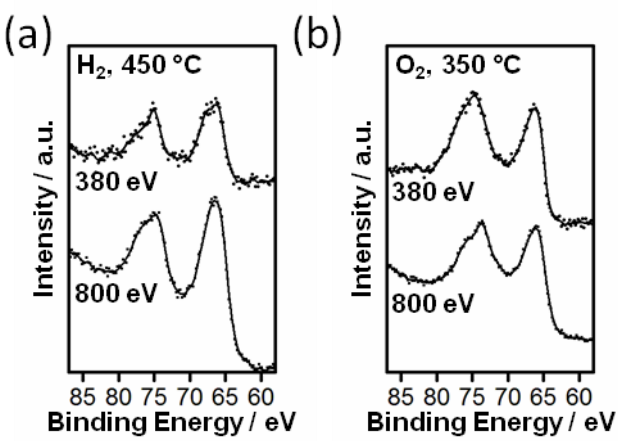

Fig. S3 (a) Ambient pressure Cu and Ni 3p XP Spectra of CuNi nanoparticles supported on the native oxide layer of a silicon wafer in vacuum on exposure to 0.1 torr of H_2 at 450 °C recorded at two different probing depths by varying the incident photon energy. $E_{incident}$ of 380 eV gives a probing depth of 0.8 nm, and $E_{incident}$ of 800 eV gives a probing depth of 1.2 nm. (b) Spectra obtained as in (a) but at 350 °C in O_2.

5. AP-XPS measurements of CuCo nanoparticles from vacuum to 450 °C in H_2

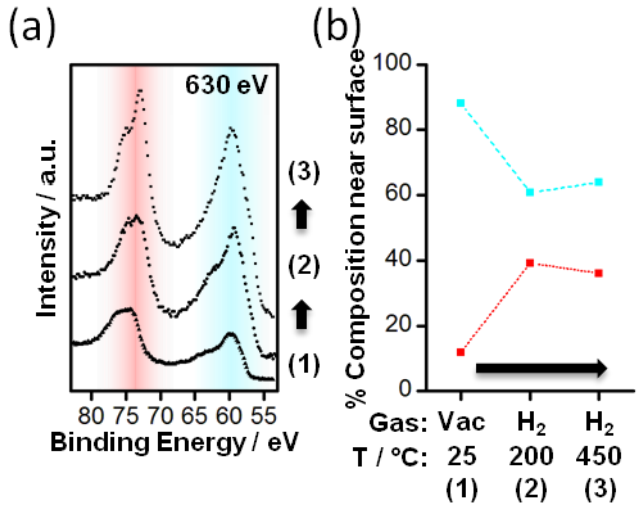

Fig. S4 (a) Ambient pressure Cu (red) and Co (blue) 3p XP Spectra of CuCo nanoparticles supported on the native oxide layer of a silicon wafer in vacuum and on exposure to 0.1 torr of H_2 at 200 °C and 450 °C as indicated, using an incident photon energy of 380 eV (corresponding to a mean free path of escaping electrons of 0.8 nm). (b) Graph showing the corresponding % of Cu (red) and Co (blue) in this top 0.8 nm surface layer of the nanoparticles for each condition in (a) (after correction for the relevant photon energy photoelectron cross sections and removal of a Shirley background).