

Supporting Information

Complete Surface Reconstruction of Nanoporous Gold During CH₄ Pyrolysis

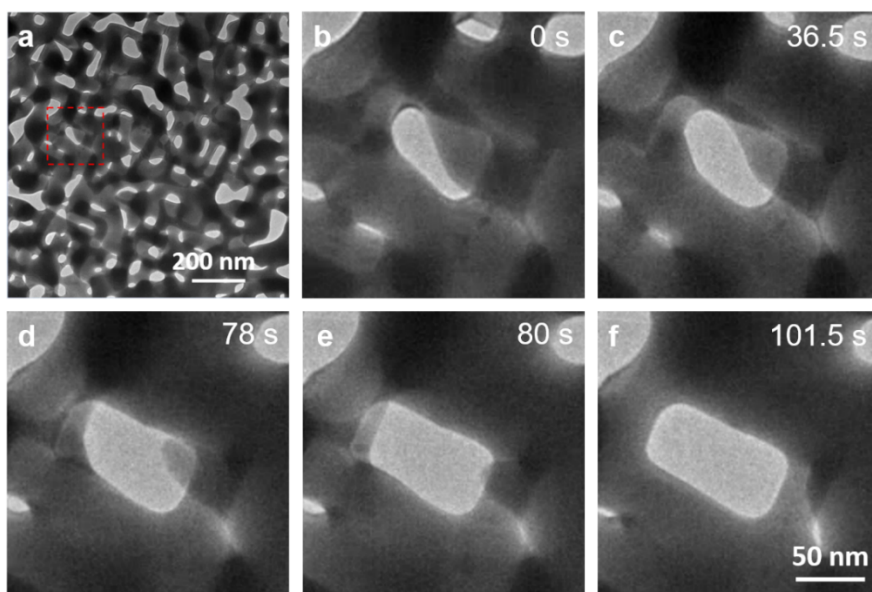


Figure S1 The morphology changes of a single complete hole during CH_4 pyrolysis. (a) Low-magnification TEM image of NPG at 300 °C. The boxed region was thereafter *in situ* characterized in atmospheric-pressure pure CH_4 . (b–f) High-magnification TEM images of the boxed region at different times, during CH_4 pyrolysis at 346 °C. The images (b–f) have the same scale bar.

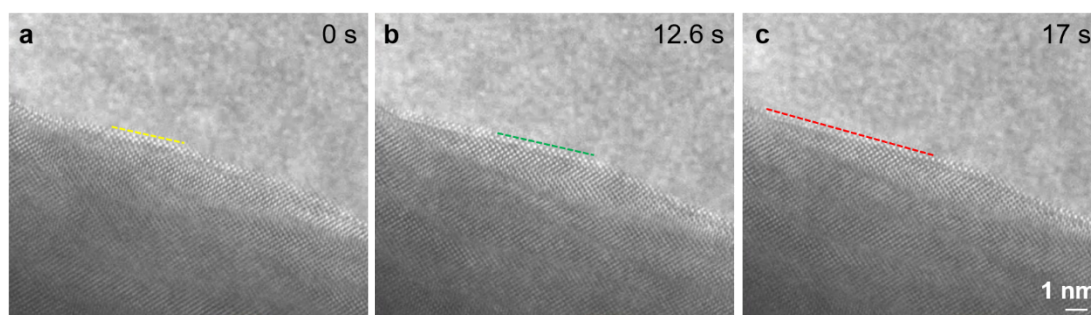


Figure S2. Atomic resolution evolution of ligament surface reconstruction in NPG. (a–c) High-resolution TEM images of the ligament surface at different times in atmospheric-pressure pure CH_4 . The crystal facets of each time were marked with yellow, green, red lines, respectively. The images have the same scale bar.

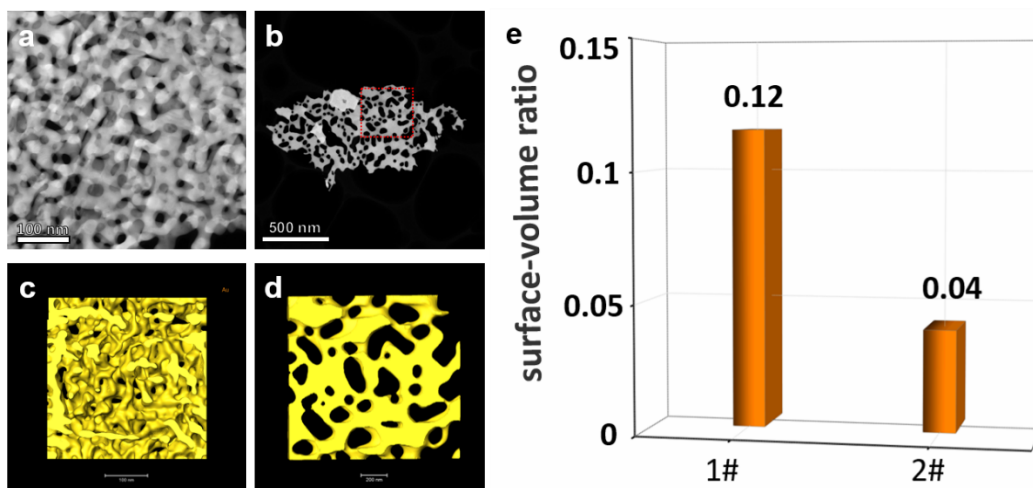


Figure S3 Morphology of the material before and after reconstruction. HAADF images of the material before (a) and after reconstruction(b). (c) and (d) The tomography of the red-framed region in (a) and (b), respectively. (e) The surface–volume ratio of the 3D structures in (c) and (d), where 1# represents the as-prepared NPG, and 2# represents the one after forming crystal facets.

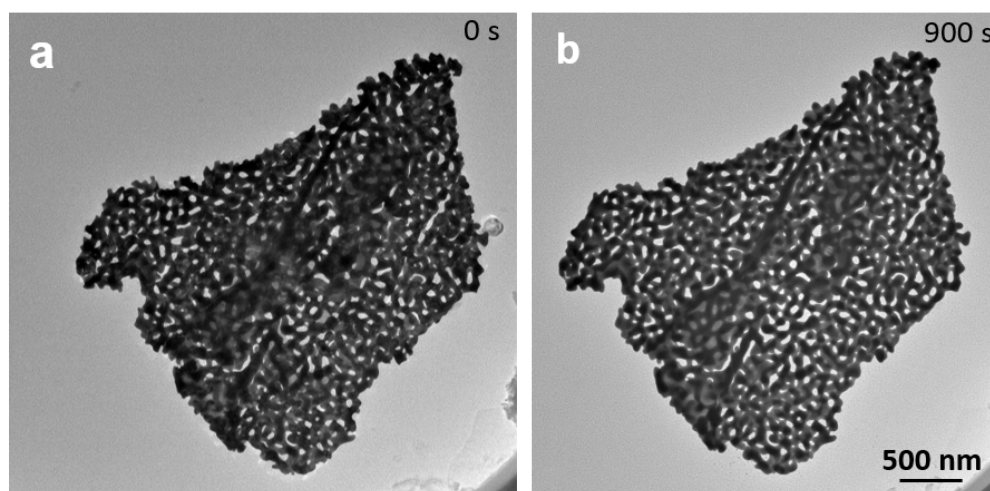


Figure S4 HRTEM images before (a) and after 900s under Ar gas environment (b). The temperature was increased from 23 °C (a) to 450 °C (b) at a rate of 30 °C min⁻¹. The two images have the same scale bar.

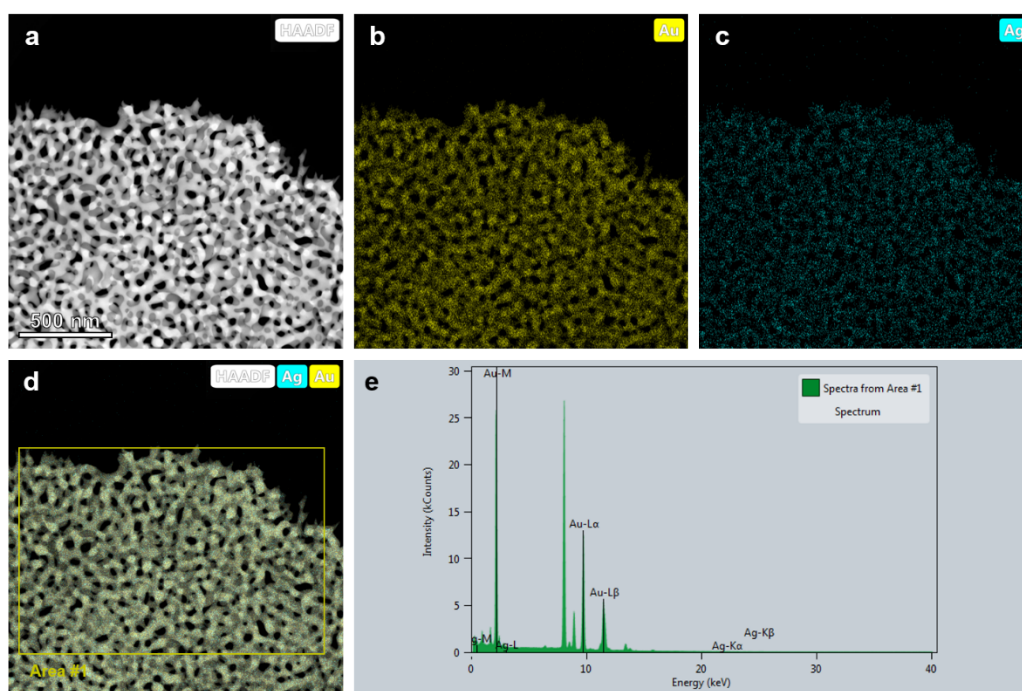


Figure S5 EDS mapping of as-prepared NPG. (a) HAADF image of the NPG. (b–c) EDS mapping images using the Au and the Ag signals from the region in (a). (d) Overlay of (a–c). (e) EDS spectrum from the region in (d).

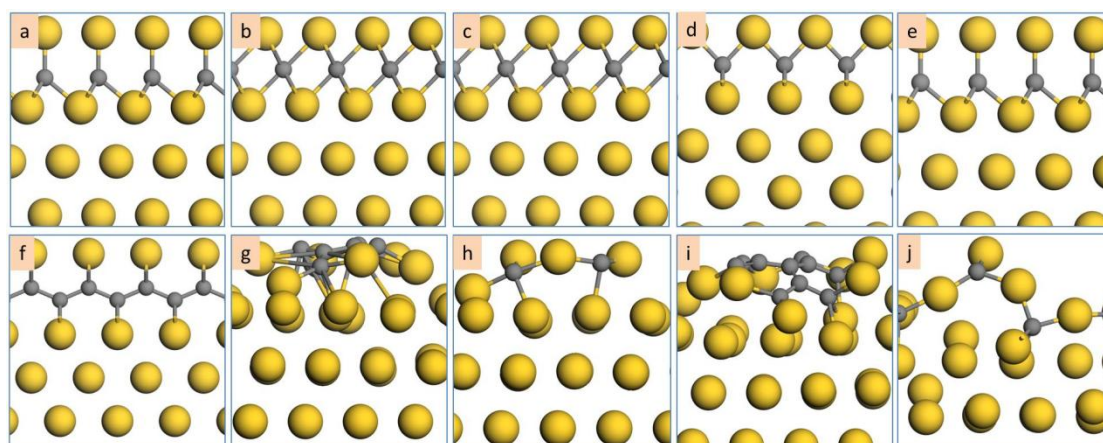


Figure S6 Optimized structure for C atoms located in different positions of sub-layer Au(111), Au(200) and unsaturated Au atom (CN = 6 or 7) structures. (a) Sub-layer C-fcc-Au(111), (b) Sub-layer C-hcp-Au(111), (c) Sub-layer C- Au(111), (d) Sub-layer C-Au(200), (e) Sub-layer C-Au(200)-1, (f) Sub-layer C-Au(200)-1,(f) CN7 (perimeter and bottom), (g) CN7 (perimeter), (h) CN6 (perimeter and bottom), (i) CN6 (perimeter), (Yellow sphere: Au, Gray sphere: C).

Table S1 Calculated Activation Energies (eV)§ for C–H bond cleavage

Elementary reaction	Ag ₁₀	Au ₁₀
CH ₄ *→CH ₃ *+H*	1.54	1.42
CH ₃ *→CH ₂ *+H*	1.60	1.45
CH ₂ *→CH*+H*	1.61	1.17
CH*→C*+H*	1.90	1.95

*: Surface of the catalyst

§: Au et al. *Journal of Catalysis* 185: 12-22 1999; Liao et al. *Journal of Molecular Catalysis A: Chemical* 136: 185–194 1998.

Table R2 Average-stripping energy and top-layer Au strain for C atoms located in different position of Au(111) and Au(200) structures.

	Average-stripping energy (eV)	Top-layer Au strain (%)
Sub-layer C-fcc-Au(111)	0.8454	47.01
Sub-layer C-hcp-Au(111)	0.7117	40.77
Sub-layer C-Au(111)	0.0181	229.19
Sub-layer C-Au(200)	1.7932	48.90
Sub-layer C-Au(200)-1	1.1567	52.40
Sub-layer C-Au(200)-2	1.1583	97.87

The structure of Au (111), Au (200) and the Au surface contain unsaturated Au atoms (coordination numbers of 7 and 6) with C atoms in the sub-layer were optimized. The specific structure is shown in Figure S6. From the calculation results shown in Table S2, it can be observed that for Au (111) structures, when the C atom is located under the top-layer Au atoms ((1) FCC, (2) HCP, (3) FCC and HCP), the surface Au atoms significantly expand by 40%–200% (Figure S6a–c); the average-stripping energy was estimated to be 0.85–0.02 eV (Table S2). In fact, when all HCP and FCC positions in the sub-layer were occupied by C atoms, the surface Au atoms were completely separated from the bulk phase (Figure S6c). For Au (200) structures, C atoms were located in a) the bridge position between two Au atoms, b) in the middle of a quadrilateral composed of four Au atoms, or both a) and b). From Table S2 it can be observed that the distance between top- and sub-layer Au atoms expand by 50%–100% (Figure S6d–f); the average-stripping energy was estimated to be 1.79–1.15 eV (Table S2). It can be seen that all the theoretical

structures which contained sub-layer C atoms were inconsistent with the experimental results. Therefore, we can speculate that under the current experimental conditions, it is not easy for C atoms to enter the interior of Au surface. For unsaturated Au atoms (CN = 6 or 7), when C atom was located in the perimeter and bottom of top-layer unsaturated Au atoms, it was easier to form amorphous C–Au compounds (Figure S6g-j), and this kind of structure was not found during the experiment. Therefore, it can be speculated that under the current experimental conditions, it is difficult for C atoms to enter the interior of Au bulk, and the C species adsorbed on the surface may be the main driving force for the surface reconstruction of NPG.