

Supporting information

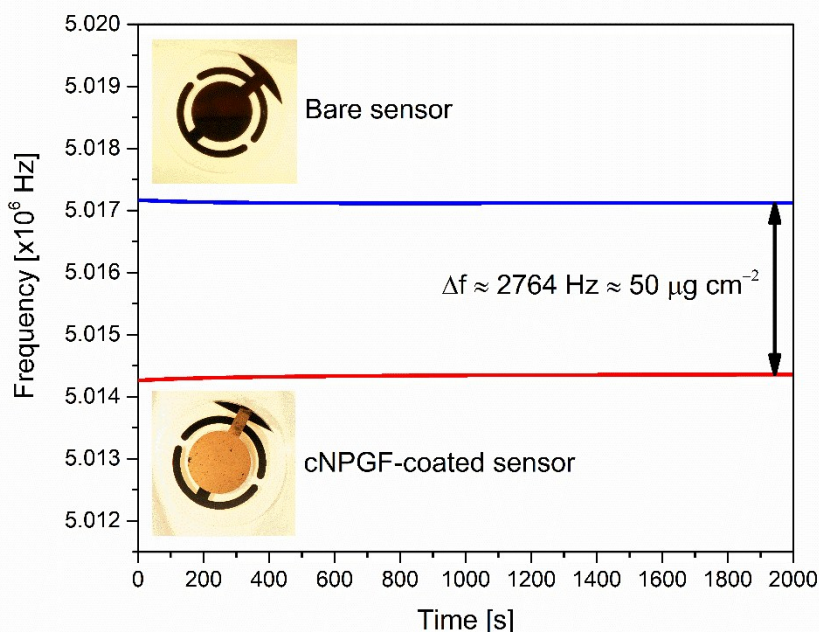


Figure S1. Typical massograms obtained during recording of QCM signals of bare (blue line) and cNPGF-coated (red line) sensors in air. The difference in frequency of oscillating sensors yields apparent areal density of deposited film.

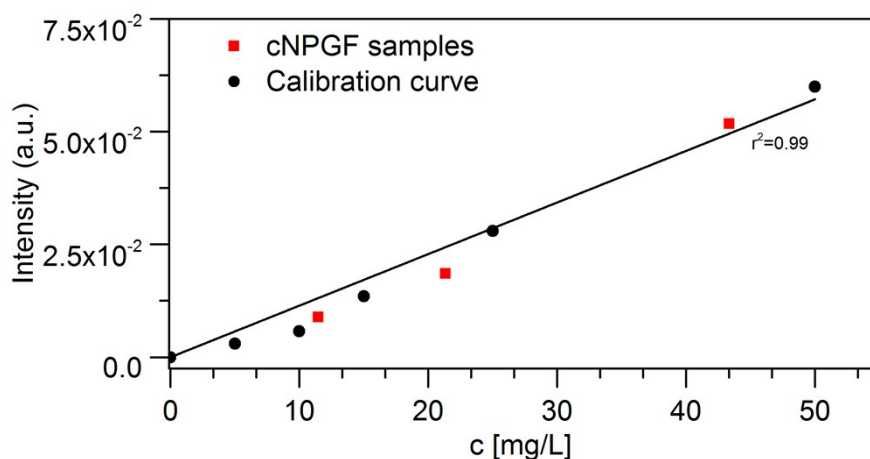


Figure S2. AAS measurements showing the standard curves and the measured samples.

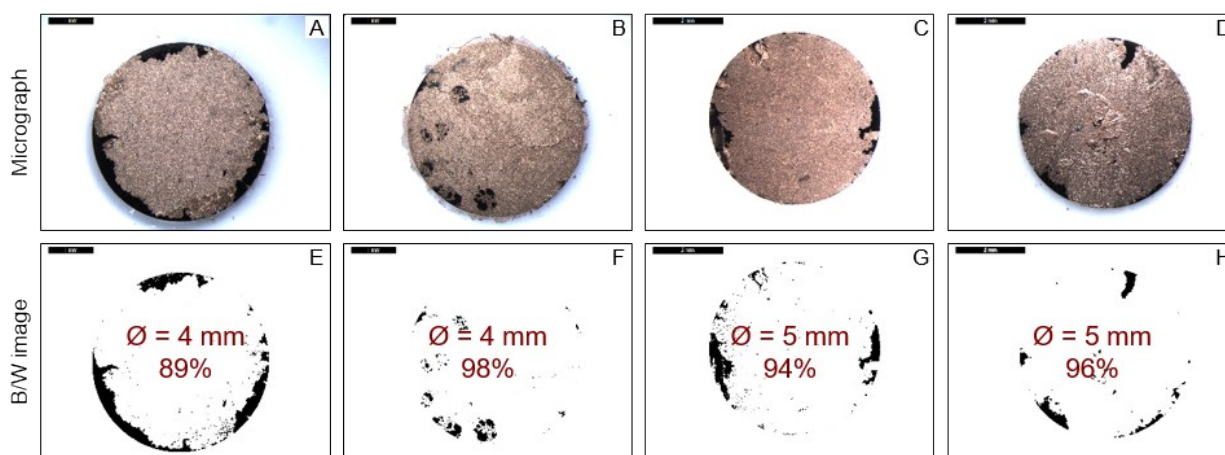


Figure S3. Micrograph images of GC electrodes under an optical microscopy after electrochemical and catalysis testing (A-D) Images processed in software to become black and white, for area determination treatment (E-H). cNPGF coverages of GC area are shown in images.

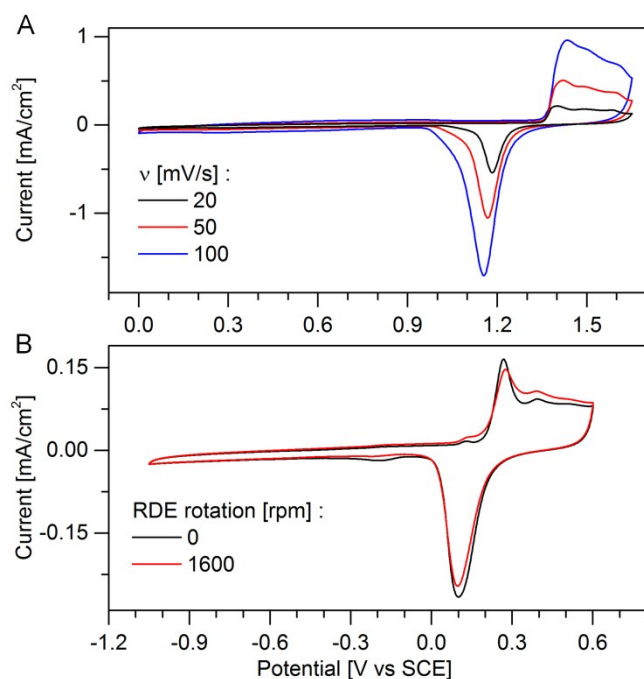


Figure S4. Cyclic voltammograms of cNPGF film deposited on RDE ($A = \text{ca. } 0.18 \text{ cm}^2$) in Ar-purged (A) 0.10 M H₂SO₄ solution recorded at different scan rates, (B) 0.10 M KOH solution recorded at 20 mV/s at stationary conditions (black line) and at electrode rotation rate of 1600 rpm (red line). Current densities are normalized per geometrical area of the electrode.

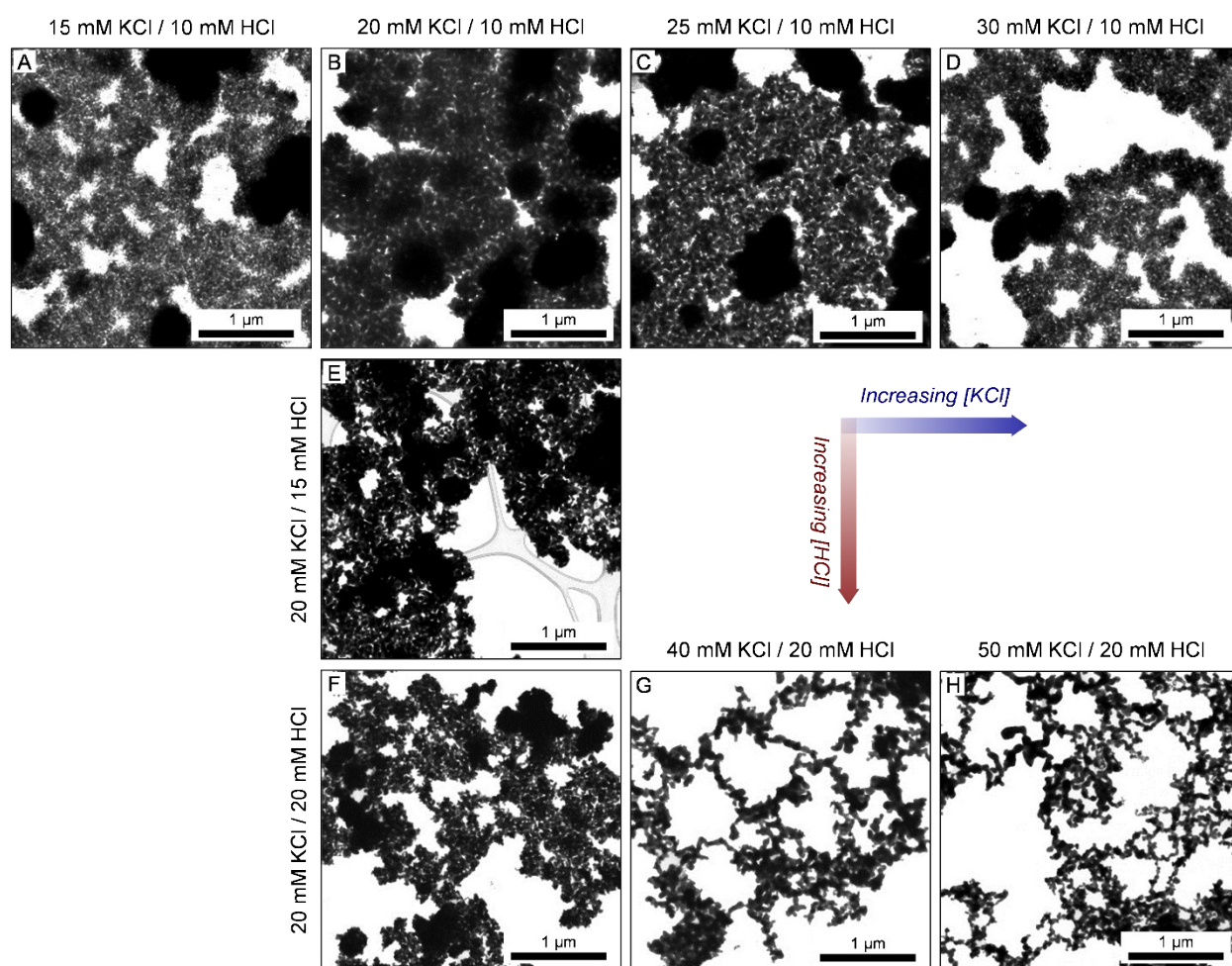


Figure S5. TEM images showing changes of cNPGF in microstructure following changes in both KCl and HCl concentrations. Images are all taken with identical magnification, for size comparison.

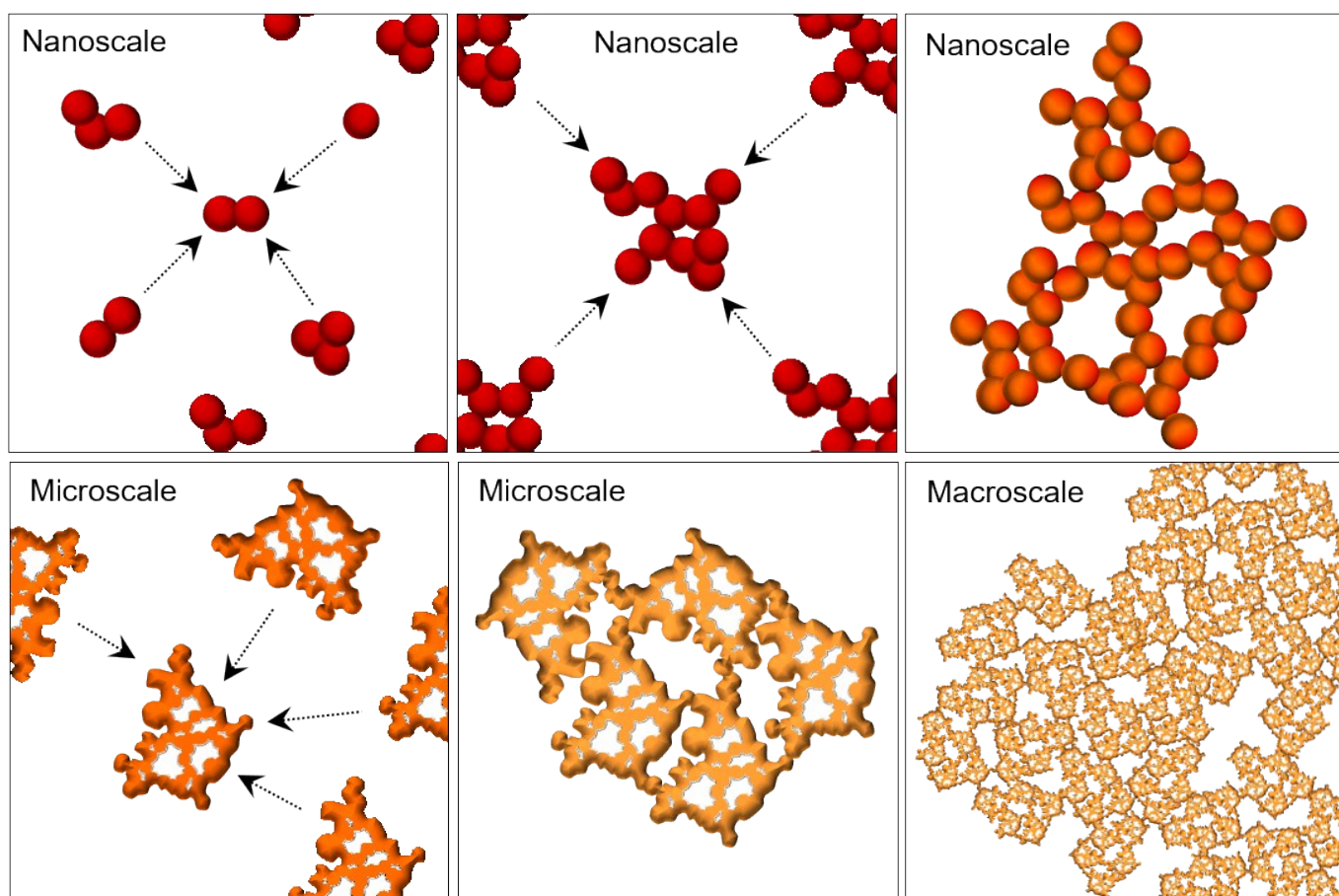


Figure S6. Scheme of cNPGF formation and features evolution from nanoscale to macroscale.

The cNPGF structure has similar nano- and microstructure features (Figures 1B and 1C). This originates from the nature of Au NPs aggregation during the entire cNPGF formation. The cNPGF assembles at the air-liquid interface. The predominantly spherical Au NPs undergo interfacial sorption. When at the interface, Au NP moves in two dimensions and sinters to individual Au NP or cluster of NPs. Due to surface tension forces, synthesis solution evaporation and size of NPs, the sintered nanoscale structure contains fine pores (nm range). As the cNPGF synthesis continues, the nanoscale structures continuously expand by sintering to other nanoscale units. By sintering into larger 2D networks, the microscale features are formed. Due to the nature of material sintering, the nanoscale features are reproduced and maintained within the newly formed microscale structure, resulting in similar morphology observed at two different scales, Figure S6.

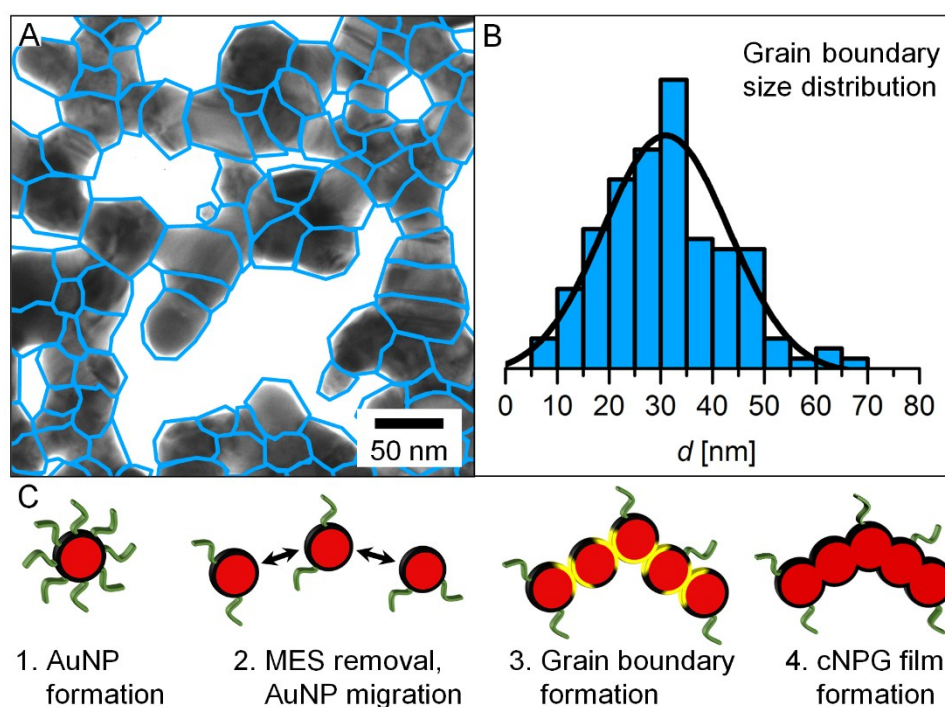


Figure S7. (A) TEM image of cNPGF film with highlighted AuNP boundaries (blue). (B) A AuNP grain boundary size distribution histogram. (C) Scheme of a ligament attachment of individual AuNPs into cNPGF films.

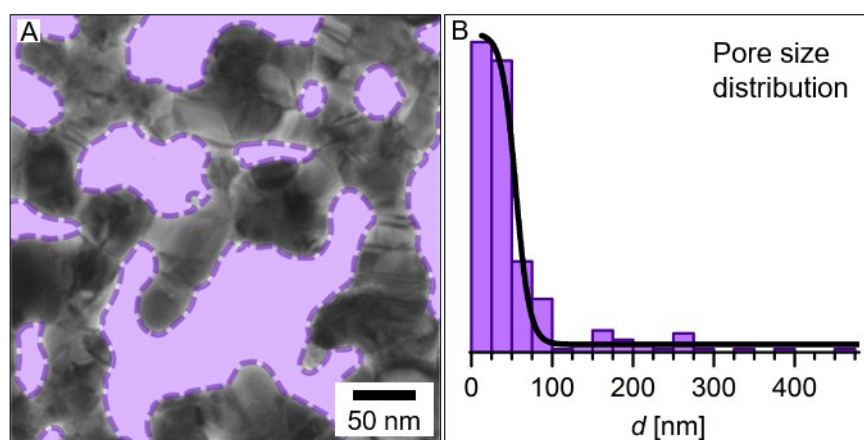


Figure S8. (A) TEM image of cNPGF with highlighted pores (purple) and (B) the corresponding pore size distribution histogram.

Table S1. The summary of cNPG synthesis parameters, chemical concentrations and experimental observations.

Type of additive	Concentration range [mM]	Observed effect
KCl	10-50	Increased amount of film formation, and increased ligament thickness
HCl	10-20	Larger macropore-to-mesopore ratio
KH ₂ PO ₄ /K ₂ HPO ₄ (pH 8.0)	5-25	Suppression of film formation
KClO ₄	10-25	Suppression of film formation