Electronic Supplementary Information

Temperature-induced Au nanostructure synthesis in a nonaqueous deep-eutectic solvent for high performance electrocatalysis

by

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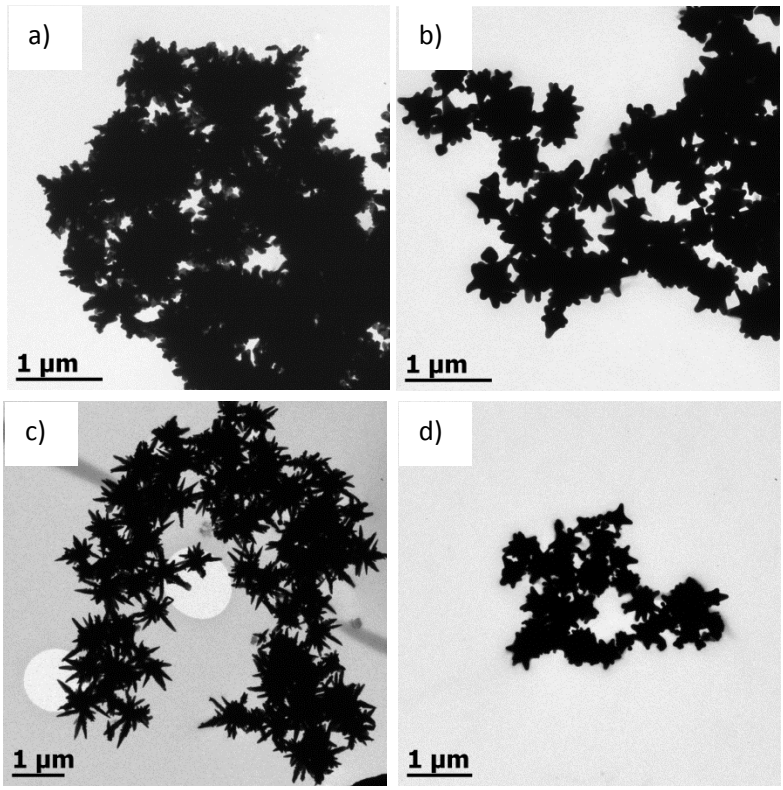

Figure S1. TEM images of the Au nanostructures prepared at different reaction temperature. (a) 30 °C (b) 60 °C (c) 90 °C (d) 120 °C.

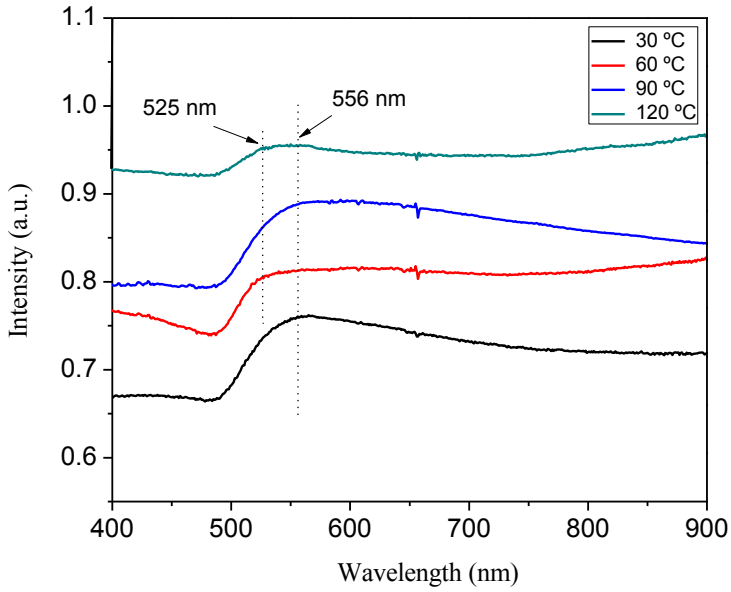

Figure S2 UV-vis analysis of Au nanostructures prepared at different temperatures.

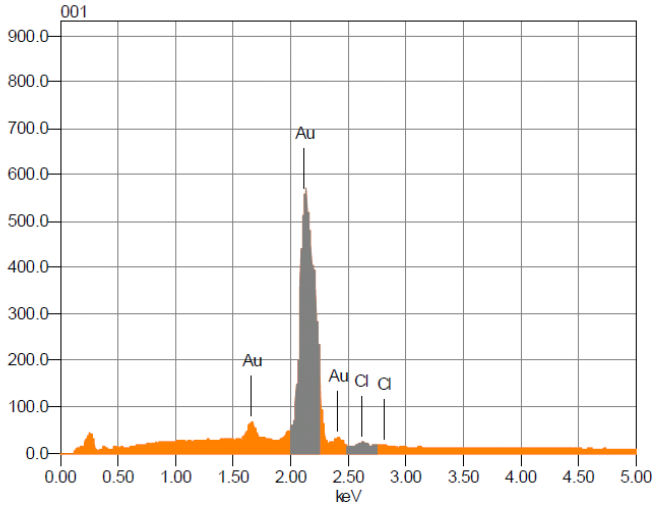

Figure S3. Representative energy dispersive X-ray spectroscopy (EDX) of as-prepared AuNSs.

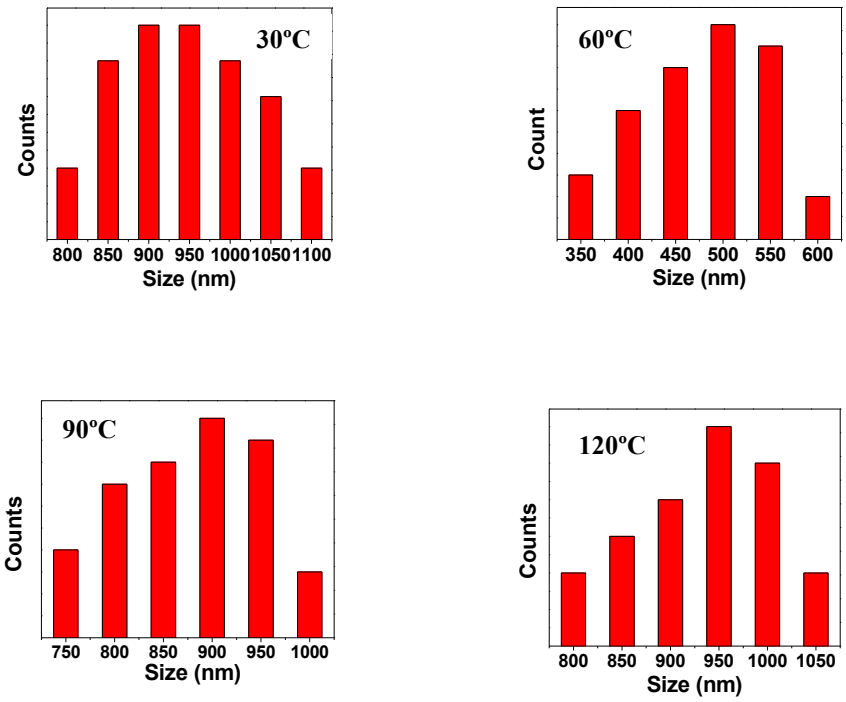

Figure S4. Size distribution of AuNSs prepared at different reaction temperatures.

To understand the mechanism of AuNSs growth, we examined the reaction products at 90 ^{o}C for shorter reaction times: 2, 3, 5, 8, 12 and 15 minutes (ESI Figure S5). The TEM images of the reaction products obtained in 2 min after addition of DES containing AA show formation of polydisperse Au nanoparticles with an average size of 5 nm. After 3 and 5 minutes of reaction, the NPs aggregate and formed twined nanocrystals slightly larger with an average size of 8 nm. After 8 min, the aggregated twined AuNPs were formed into small five-fold {111} twinned AuNSs. When the reaction time was further increased to 12 minutes, the small five-fold AuNPs were transformed into branched structure (i.e. growth of facets {110} over the planes {331}). Finally, at about 15 minutes the formation of more branched AuNSs were formed due to controlled nucleation and self-assembly process.

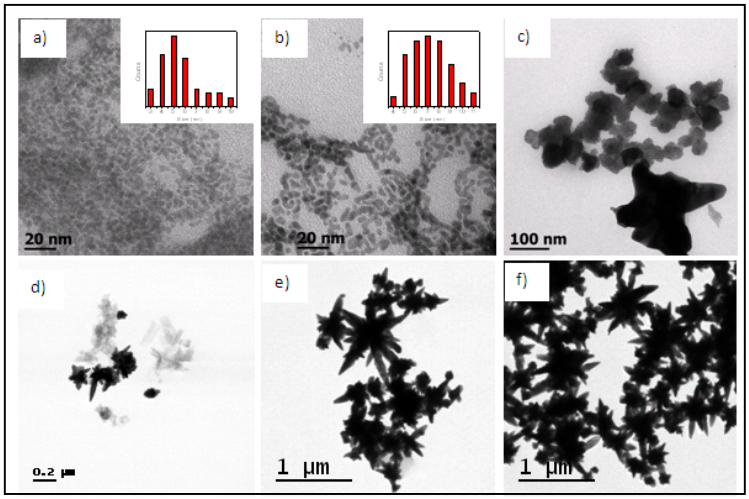

Figure S5. TEM images of AuNSs for different reaction times at 90 °C. a-f) 2, 3, 5, 8, 12 and 15 minutes, respectively.

In addition, the nucleation and self-assembly of AuNSs was further confirmed by UV-Vis and X-ray diffraction (XRD) analysis at different reaction times (2-30 min, 90 oC). The normalized UV-Vis spectra of pure DES containing HAuCl4•4H2O solution do not show any surface plasmon resonance (SPR) absorption peaks before the reaction started. Conversely, with the different reaction times (2, 5, 8, 15, 30 min) two pronounced SPR characteristic peaks at 343 nm and 530 nm, corresponding to the transverse and longitudinal SPR band of the anisotropic AgNSs appeared. (ESI Figure S6a). It should be noted that the intensity linearly increases and the L-SPR band position at 530 is red-shifted with the reaction times, suggesting the evolution of AuNSs via nucleation and self-assembly into higher size of the AuNSs. The observed results are consistent with the previous report (Zhang et al. RSC Adv., 2014, 4, 36757–36764). In addition, the color of the solution changes with increasing of reaction time. (ESI inset of Figure S6a). The XRD pattern (ESI Figure S6b) shows a gradual increase of the intensities of the peaks with the reaction times from 2-30 min, suggesting an increase of the crystal size at longer reaction time (completion of reaction and self-assembly process). Similar observation was reported for PbS microstructures in DES with different reaction times (Fernández et al. ACS nano, 2012, 6, 3800-3812). These results are consistent also with TEM observations.

a) **b)**

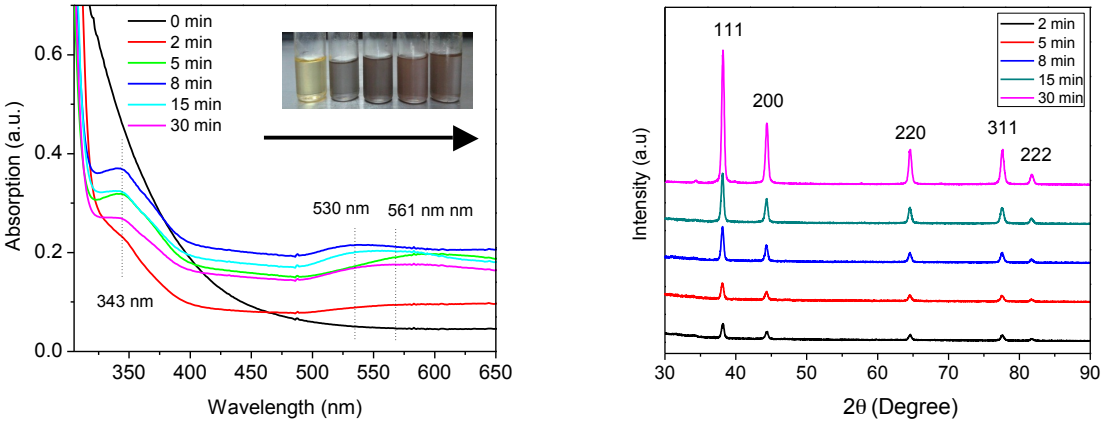

Figure S6. a) Normalized UV-vis absorption spectra of the as-prepared DES containing AuNSs (reaction temperature 90 °C) recorded at different reaction times. Inset: photograph images of AuNSs at different reaction times. b) XRD patterns of the AuNSs obtained at different reaction times.

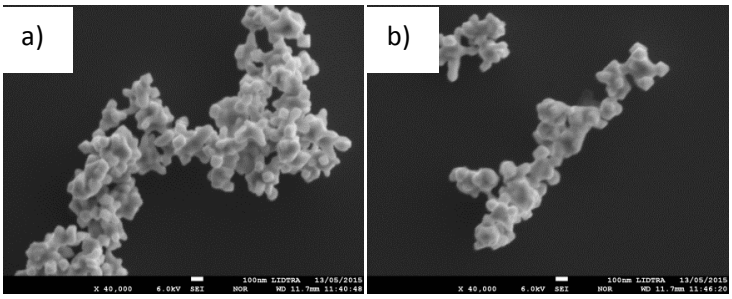

Figure S7. SEM images of the AuNSs synthesized at high temperature (150 °C)

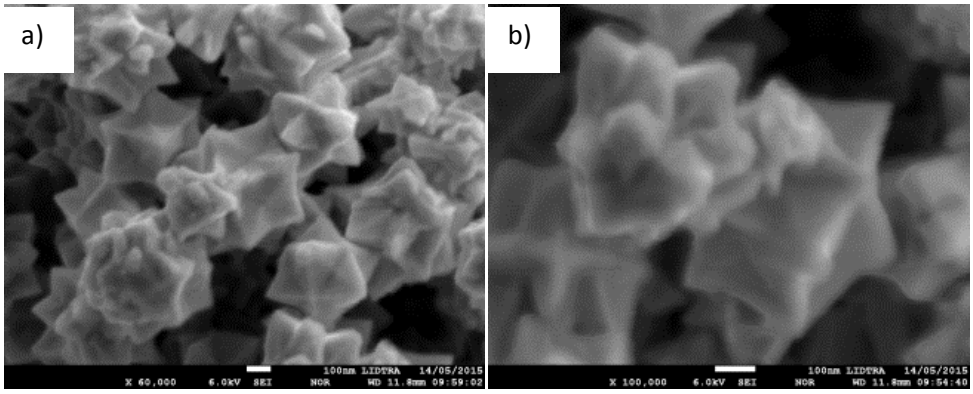

Figure S8. SEM images of the AuNSs synthesized in the 1:1 ratio of ChCl: Urea based DES at 60 °C.

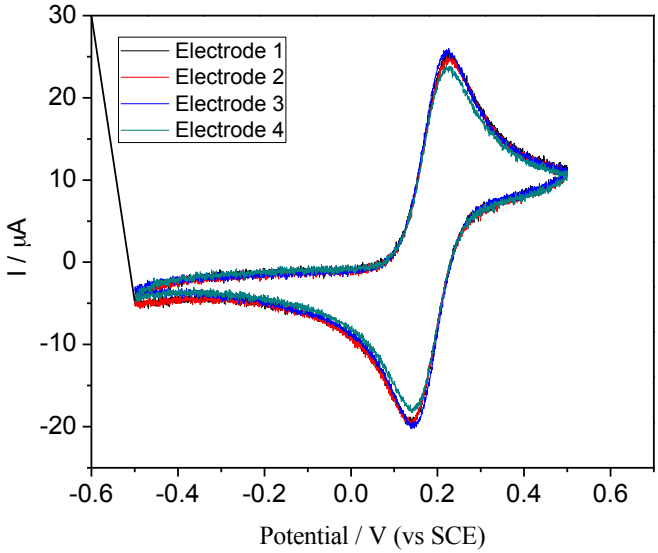

Figure S9. Cyclic voltammograms recorded at four different naked GC electrode before modified with the AuNSs.All measurements were performed in 1 M KCl solution containing 2 mM of $K_3Fe(CN)_6$. Scan rate v = 50 mV s^{-1}.

Table S1. Calculated electrochemical active surface areas for different AuNSs modified electrodes.

Temperature of reaction	Observed morphologyof Au Nanostructures	Electrochemically active surface area (cm^2)
30ºC	Au flower	0.2853
60ºC	Au urchins	0.3475
90ºC	Au star	0.5414
120ºC	Au branched structure	0.356