

## Electronic Supplementary Information

### Rapid synthesis of supported single metal nanoparticles and effective removal of stabilizing ligands

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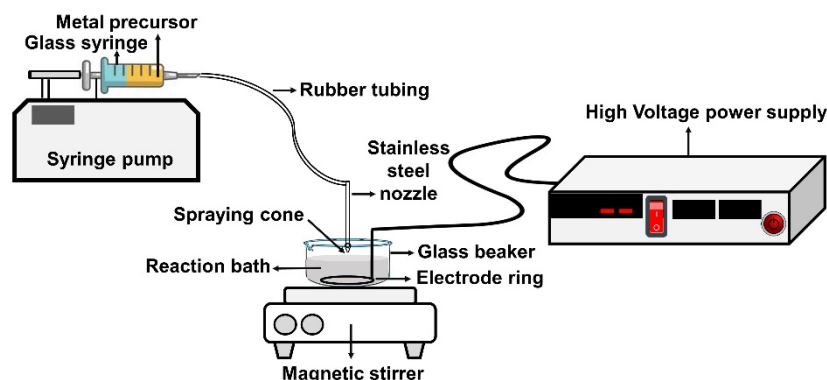
<sup>†</sup> Both authors contributed equally

#### S1. Experimental section

**S1.1 Chemicals.** Silver nitrate ( $\text{AgNO}_3$ , 99.99% pure), gold trichloride acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.99% pure), dodecylamine (98% pure), formaldehyde (37% in water), isopropanol (anhydrous, 99.5% pure), and cyclohexane (99% pure), were purchased from Sigma Aldrich. Nozzles for electro spraying (0.007, 0.020, 0.030, 0.046 inch internal diameter) were purchased from Gilson Scientific. Chemical resistant tubing is purchased from Tygon (L60, 1/16 inch internal diameter). A coiled electrode ring (soldering alloy-Sn:Cu = 99.3:0.7) is purchased from Stannol. Graphene nanoplatelets (5  $\mu\text{m}$ , xGNP) and Vulcan carbon XC-72 were purchased from Sigma Aldrich and Cabot, respectively.

TS-1 was synthesized in-house, using a procedure reported in the literature.<sup>1</sup>

#### S1.2 Electro spraying setup.



**Figure S 1.** Experimental set-up used for the synthesis of metal nanoparticles via electro spraying.

### **S1.3 Evaporation and calcination.**

10 mg of the chosen support is added to the produced metal nanoparticle solution (2 mL), which is vigorously stirred for 2 h at room temperature to ensure that metal nanoparticles are adsorbed on the support. Then, a rotary evaporator (Buchi R-210 Rotavapor System) is utilized to dry the liquid solution (operating conditions: 60 °C, 200 mbar, 100 rpm).

All in-house synthesized supported metal nanoparticles are subjected to heating in a furnace (Carbolite Gero) under air at 350 °C for 3 h (1 °C min<sup>-1</sup> heating rate).

### **S1.4 Characterization.**

*Ultraviolet-visible spectroscopy (UV-vis).* Absorption spectra are measured using a Cary 4000 UV-vis spectrophotometer. Samples of metal precursor solutions are contained in quartz cuvettes (1 mL). A quartz cuvette is used as a sample holder for the synthesized metal precursor solutions. Data are corrected using the same solvent in the solution (cyclohexane) for background absorption.

*Transmission electron microscopy (TEM).* High-resolution TEM images are performed with a JEOL 2100 instrument operating at 200 kV. Samples are prepared by sonicating dilute dispersions in ethanol for 10 min, drop-casting these dispersions onto holey carbon-coated copper grids (EM resolutions), and drying them in air at room temperature prior to the TEM measurement. ImageJ software is used for the analysis of particle size.

*Thermogravimetric analysis (TGA).* TGA measurements are performed via a Mettler Toledo (TGA/DSC 3+) thermogravimetric analyzer. The samples are analyzed at a heating rate of 10°C min<sup>-1</sup> under air from room temperature until 800°C and maintained at 800°C for 2 h.

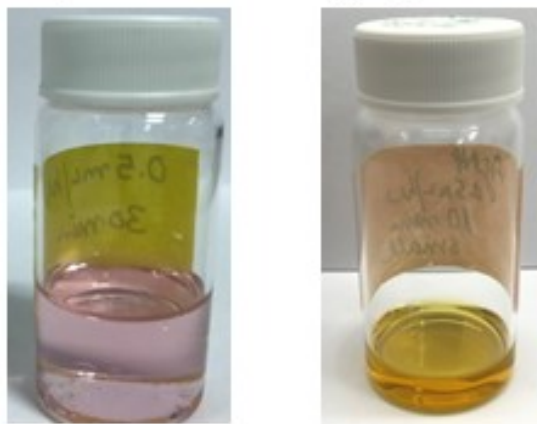
*Fourier transform infrared spectroscopy (FTIR).* FTIR spectrum is obtained via a Vertex 70 Bruker spectrometer between 400 and 4000 cm<sup>-1</sup> inverse wavelengths. The spectrometer is equipped with a Pike MIRacle™ Ge ATR crystal. The powder is directly deposited on the Ge crystal. Each spectrum is obtained by averaging 64 scans at 4 cm<sup>-1</sup> resolution.

*X-ray photoelectron spectroscopy (XPS).* The powder samples of uncalcined and calcined supported metal nanoparticles are dried in vacuum at 60°C overnight, prior to XPS measurements. A survey scan between 0 and 1200 eV is performed for each sample. Then, high-resolution scans (100 per element) for carbon and nitrogen are conducted with 20 eV pass energy. CasaXPS software is used for data processing.

**S1.5 Electrochemical measurements.** All electrochemical measurements are performed in an electrochemical cell with three compartments in 0.1 M KOH at room temperature. A RHE is used as the reference electrode, and a platinum mesh as the counter electrode. A glassy carbon disk is used as the working electrode. The supported metal nanoparticles are dispersed in DI water by sonication for 1 h and, then, 30-40 µL of the suspension is deposited with a pipet on the glassy carbon disk. A solution of Nafion (0.1 wt%, 15 µL) is added on top of the catalyst and dried in air. Cyclic voltammograms are recorded in nitrogen, saturated at 50 mV s<sup>-1</sup> scan rate. Linear sweep voltammograms are recorded in oxygen saturated electrolyte at 20 mV s<sup>-1</sup> and 400, 800, 1200, and 1600 rpm rotation speed.

## S2. TEM measurements

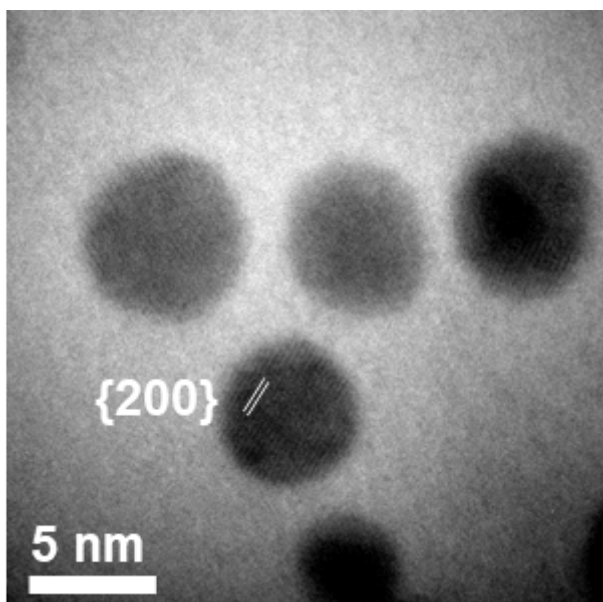
**Au nps solution      Ag nps solution**



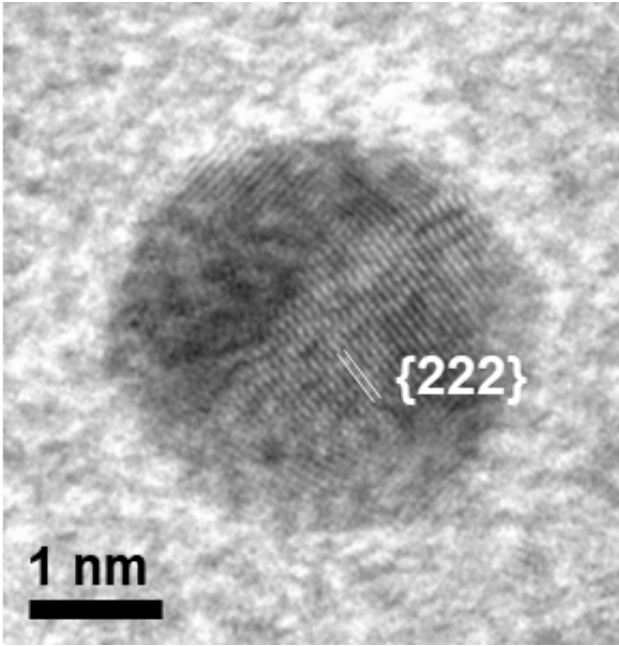
**Figure S 2.** Formation of Au and Ag nanoparticles after the completion of the electro spraying process.

**Table S 1.** Average size and standard deviation of synthesized Ag and Au nanoparticles using different spraying nozzles. Calculation is based on TEM measurements (200 counts).

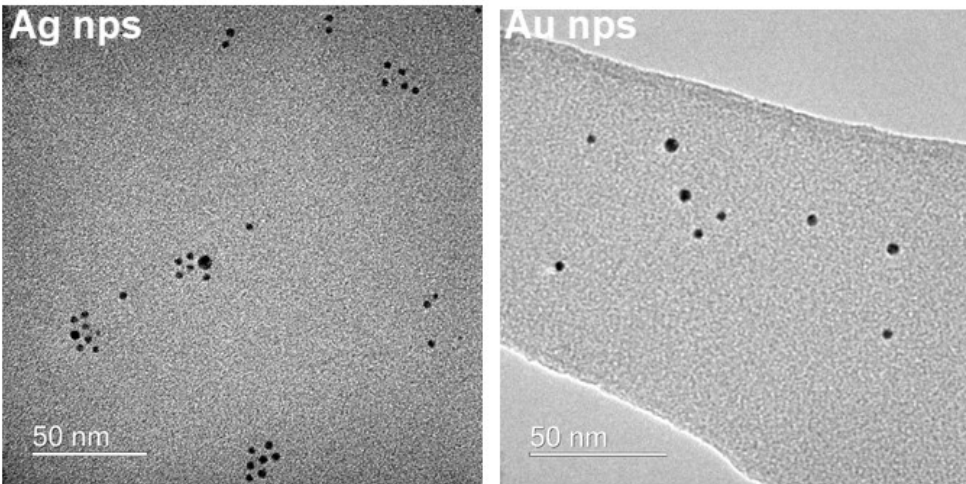
Nozzle diameter (inch)	Ag nanoparticles (nm)	Au nanoparticles (nm)
0.007	$1.8 \pm 0.2$	$4.5 \pm 0.4$
0.020	$4.1 \pm 0.4$	$4.8 \pm 0.3$
0.030	$4.6 \pm 0.5$	$6.9 \pm 0.5$
0.046	$9.4 \pm 0.7$	$8.5 \pm 0.6$



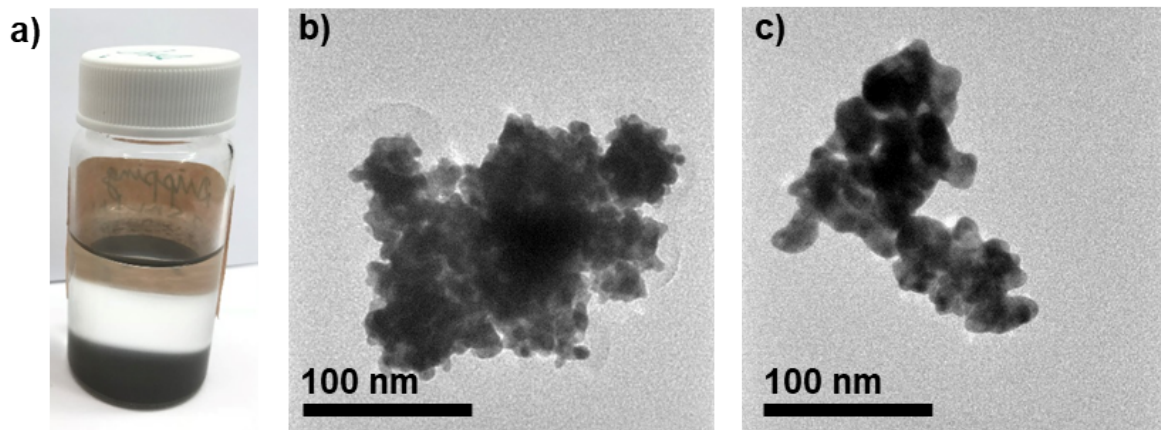
**Figure S 3.** High-resolution TEM of synthesized Au nanoparticles.



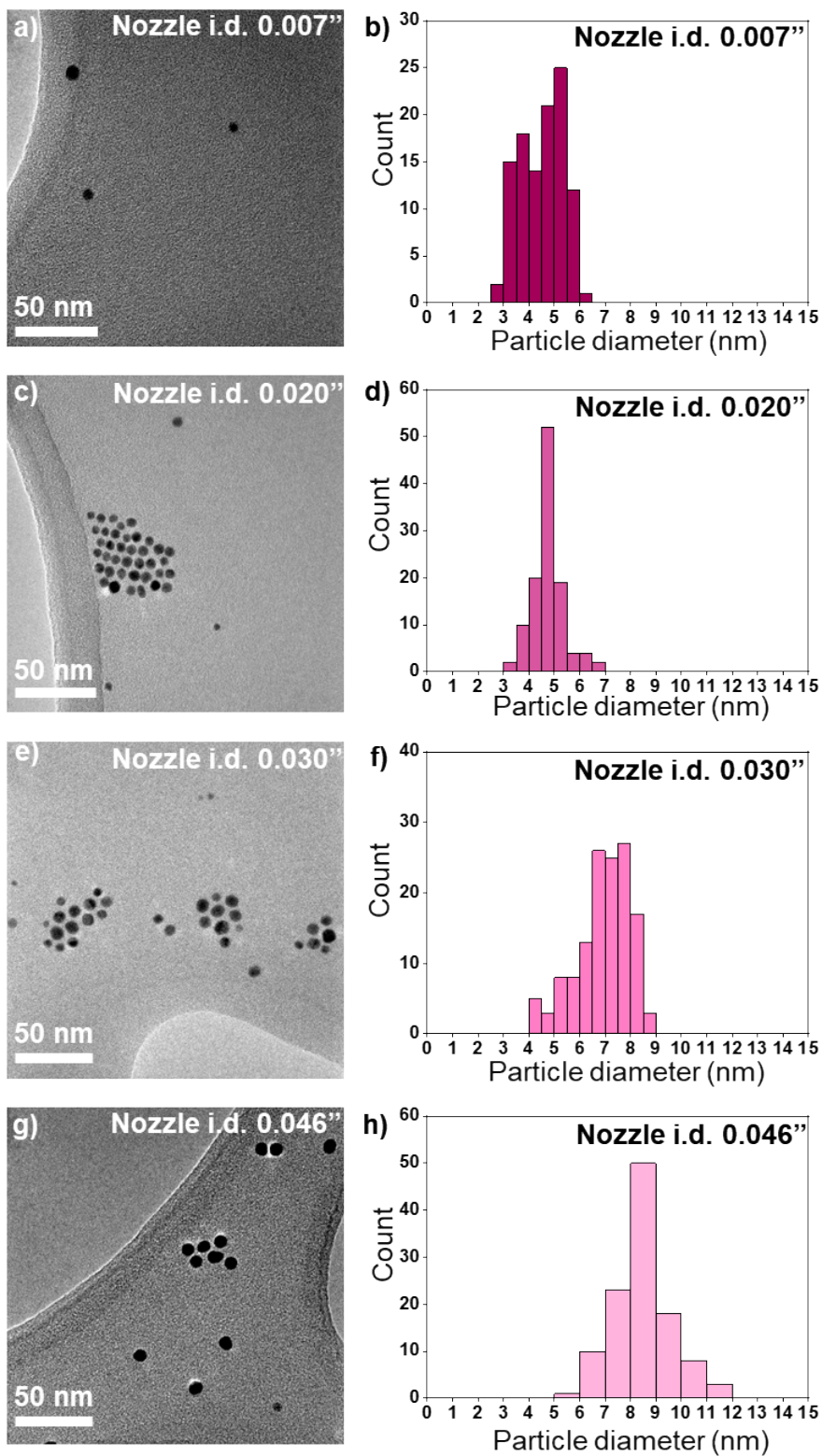
**Figure S 4.** High-resolution TEM of synthesized Ag nanoparticles.



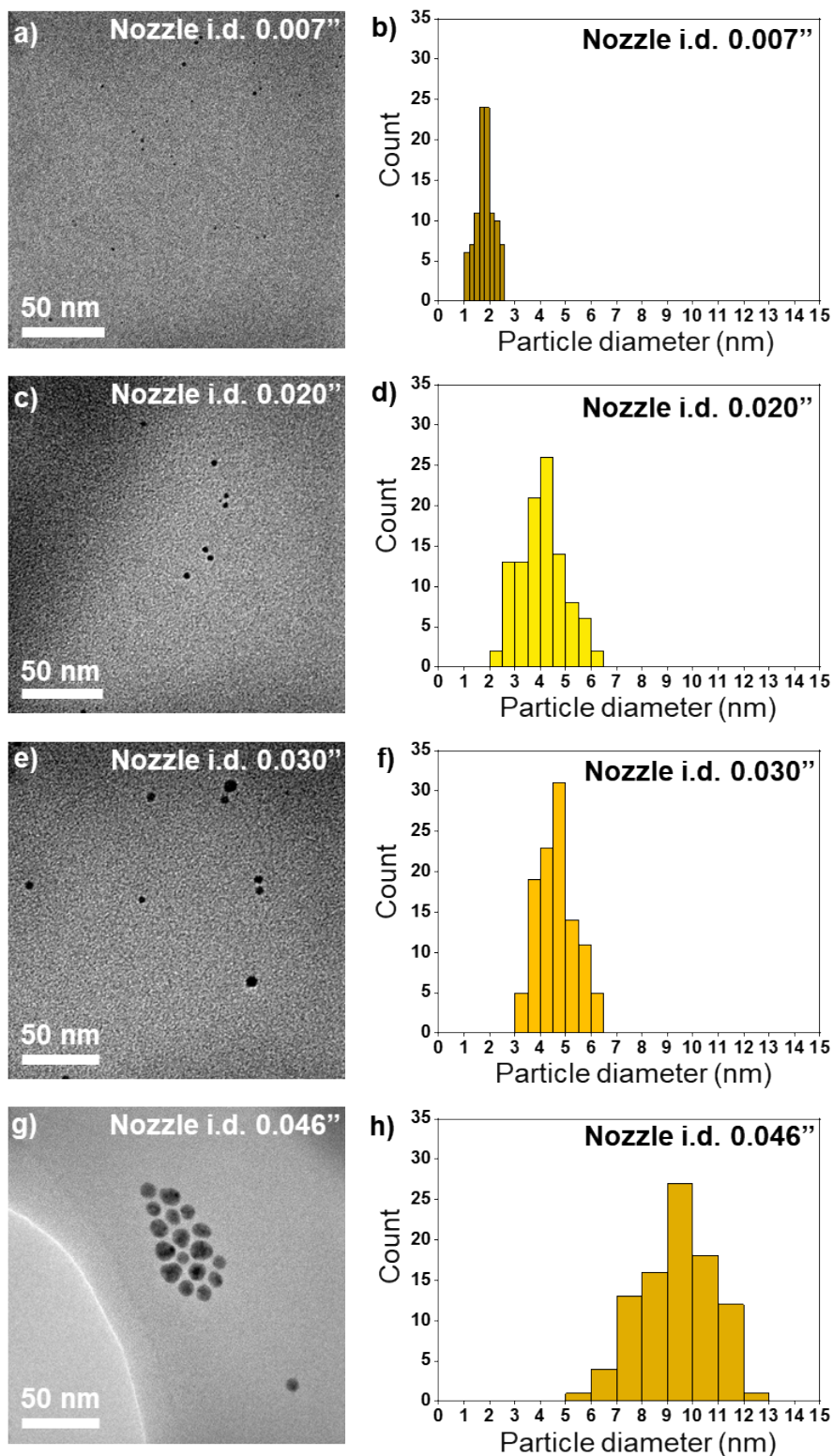
**Figure S 5.** TEM images of synthesized Ag and Au nanoparticle solutions after prolonged storage (8 months).



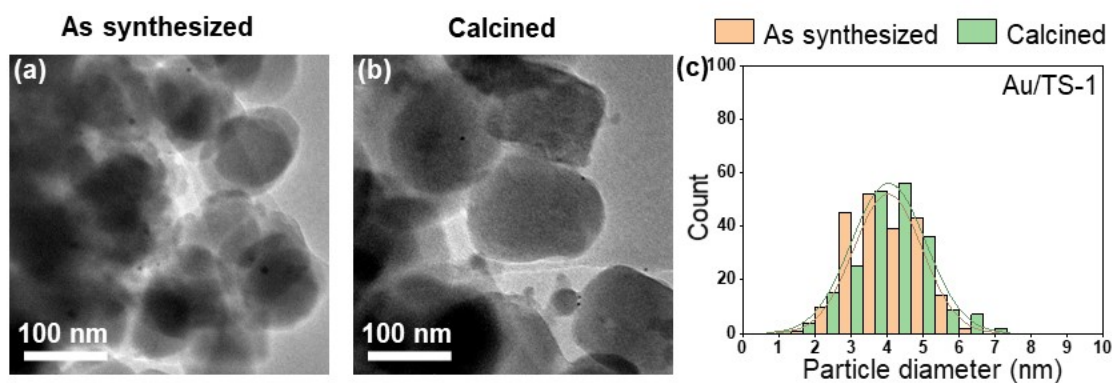
**Figure S 6.** Clusters of agglomerated metal nanoparticles are produced via dripping mode (i.e., 0 V applied potential): a) Vial showing agglomeration in this sample, b-c) TEM images of agglomerated particles in solution.



**Figure S 7.** TEM images and particle size distribution of Au nanoparticles via electrospaying, using different nozzles, as indicated.



**Figure S 8.** TEM images and particle size distribution of Ag nanoparticles via electrospaying, using different nozzles, as indicated.



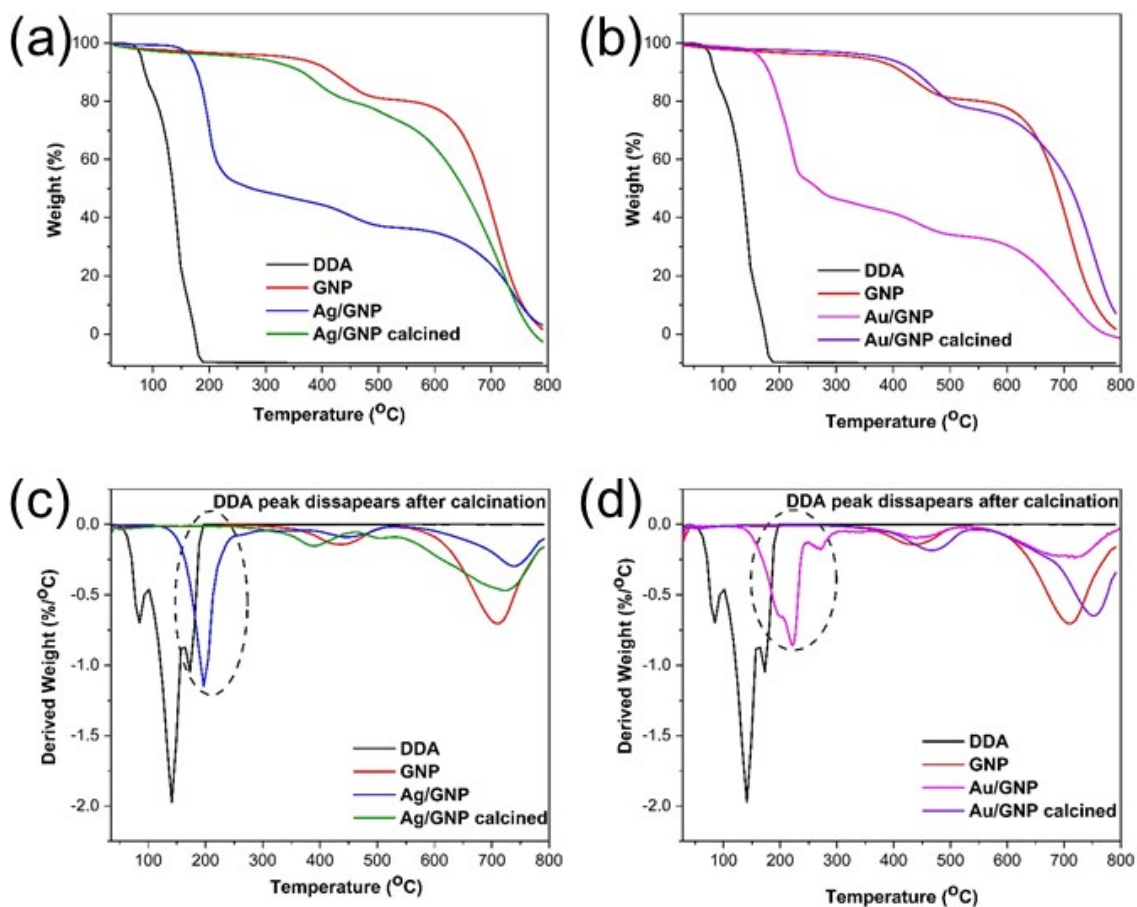
**Figure S 9.** TEM images of (a) as synthesized and (b) post calcination, Au nanoparticles supported on TS-1. (c) Corresponding particle size distributions.

**Table S 2.** Average size and standard deviation of synthesized Au supported on TS-1. Calculation is based on TEM measurements (200 counts).

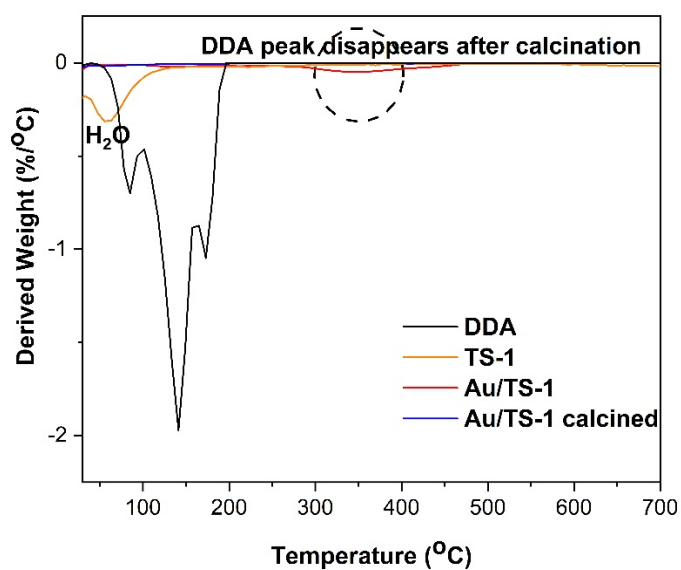
Nozzle diameter (inch)	Au nanoparticles (nm)
0.020	$4.0 \pm 1.0$



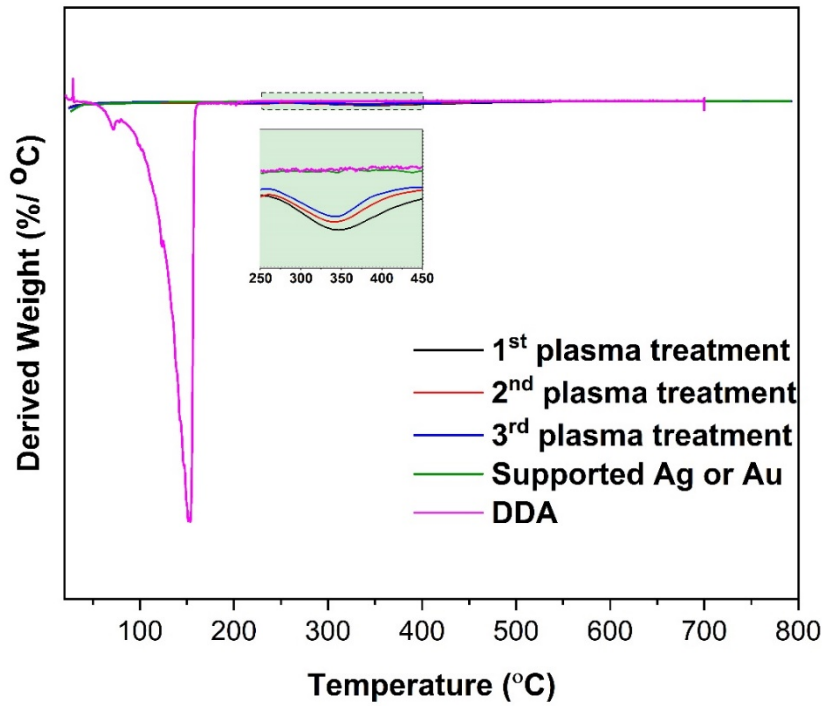
### S3. TGA measurements



**Figure S 10.** TGA spectra of (a) Ag/GNP and (b) Au/GNP, indicating the required annealing temperature for the removal of DDA surfactant, which is confirmed by DTA analysis ((c) and (d)).

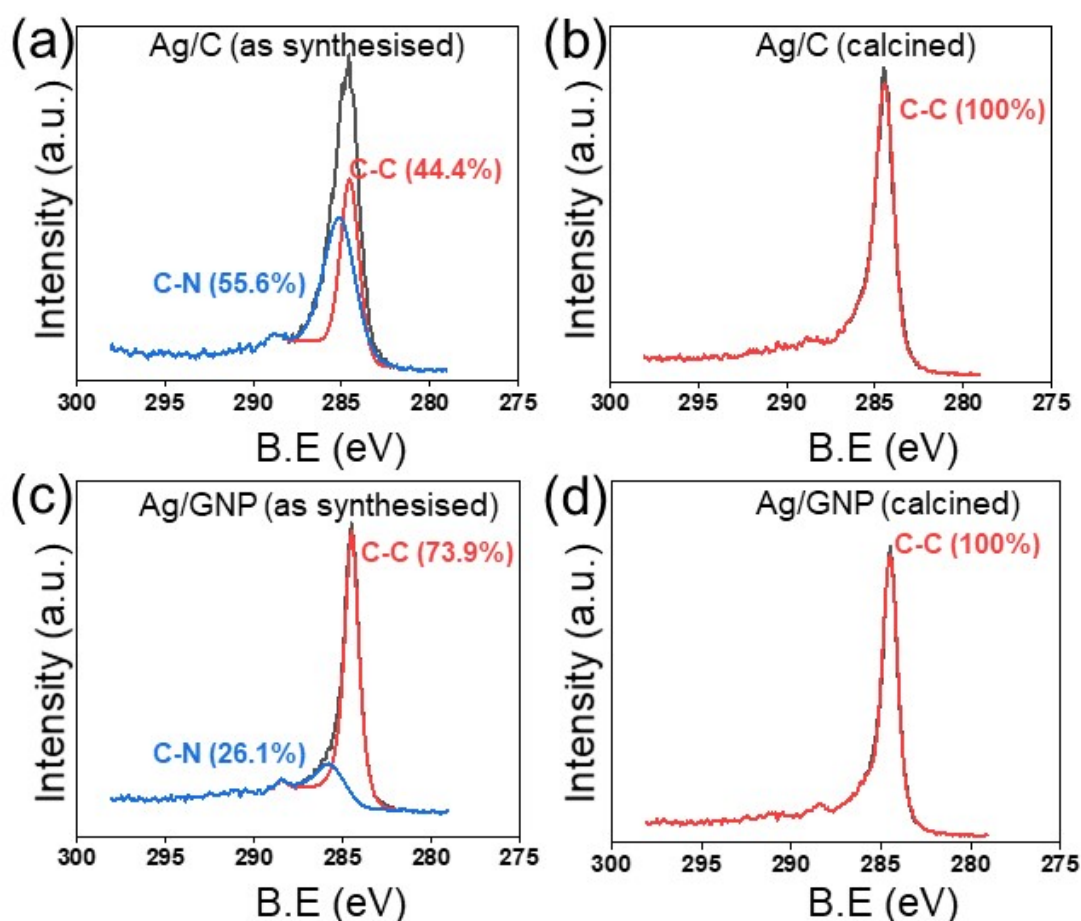


**Figure S 11.** DTA analysis of calcined Au/TS-1 confirms the removal of DDA surfactant. A similar result is obtained for Ag/TS-1.



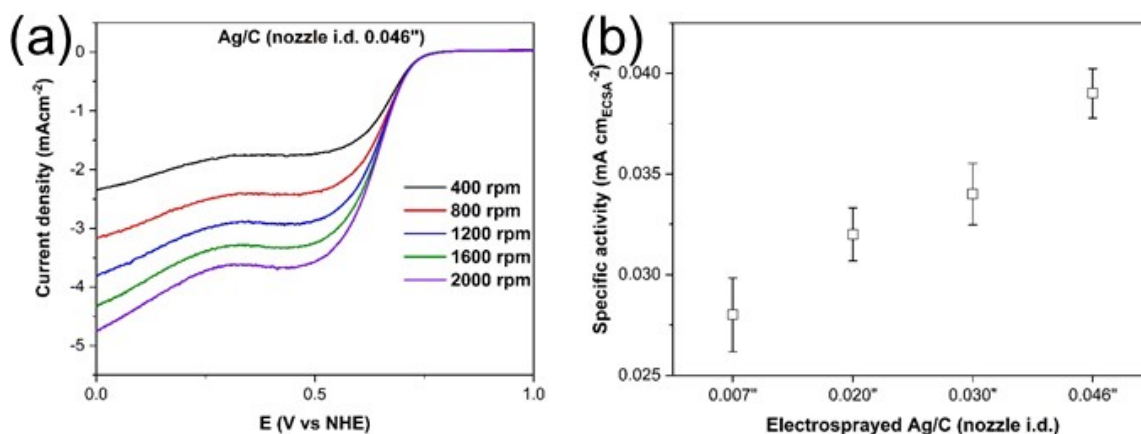
**Figure S 12.** DTA analysis of oxygen plasma-treated Ag or Au on Vulcan carbon, and GNP, showing that the DDA surfactant is not completely removed via this treatment.

#### S4. XPS measurements



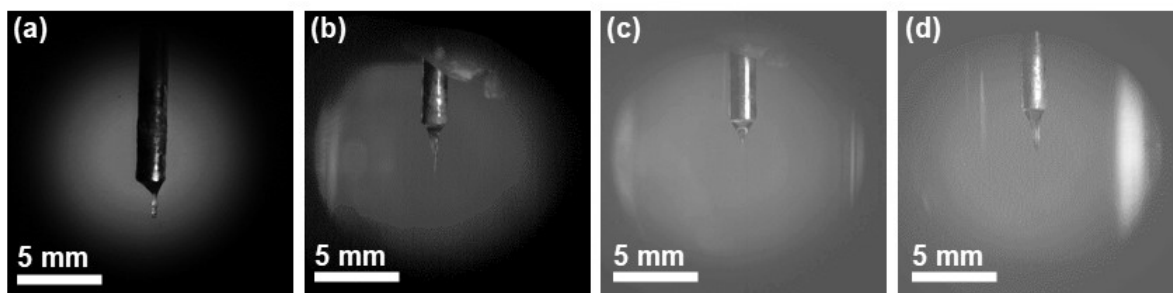
**Figure S 13.** C1s XPS spectra of uncalcined and calcined samples of supported Ag nanoparticles on Vulcan carbon ((a) and (b)), and graphene nanoplatelets ((c) and (d)).

#### S5. Activity



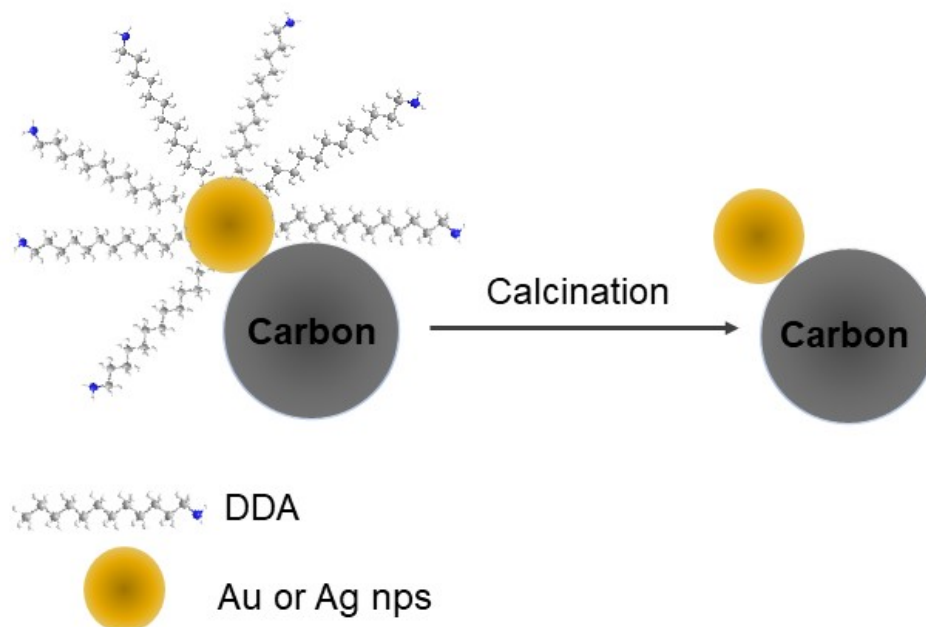
**Figure S 14.** (a) Linear sweep voltammograms (LSV) of Ag nanoparticles supported on Vulcan carbon (spraying nozzle i.d. 0.046"); (b) Specific activity of Ag supported on Vulcan carbon at 0.85 V (vs. RHE), for nanoparticles prepared with different internal diameters of the spraying nozzle.

## S6. High-speed camera measurements: Electrospaying



**Figure S 15.** Images of the Taylor cone recorded during the synthesis using different spraying nozzles; (a) 0.007", (b) 0.020", (c) 0.030", and (d) 0.046".

## S7. Schematic of DDA capped metal nanoparticles onto carbon support and its removal.



**Figure S 16.** Schematic of DDA capped metal nanoparticles onto carbon support and its removal.

## References

1. T.A. Nijhuis, B.J. Huizinga, M. Makkee and J.A. Moulijn, *Industrial & Engineering Chemistry Research*, **1999**, *38*, 884-891.