Supplementary Information

Why do Some Metal Ions Spontaneously Form Nanoparticles in Water Microdroplets: Disentangling the Contributions of the Air–Water Interface and Bulk Redox Chemistry

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Section S1: Water microdroplet generation via sprays

We adapted the experimental setup built by Gallo et al.[1] to produce water microdroplets. In a coaxial system, water was injected through an inner tube with a 100-µm diameter using a syringe pump (PHD Ultra, Harvard Apparatus). Dry N_2(g) was pushed through the outer tube with a 430-µm diameter. Additionally, HPLC-grade water was used to make salt solutions, and a glass cell (equipped with a tiny opening to prevent pressure build-up) was employed to collect microdroplets while minimizing ambient contamination. The water flow rate was 25 µL/min, whereas the gas (N_2) pressure was 100 psi.

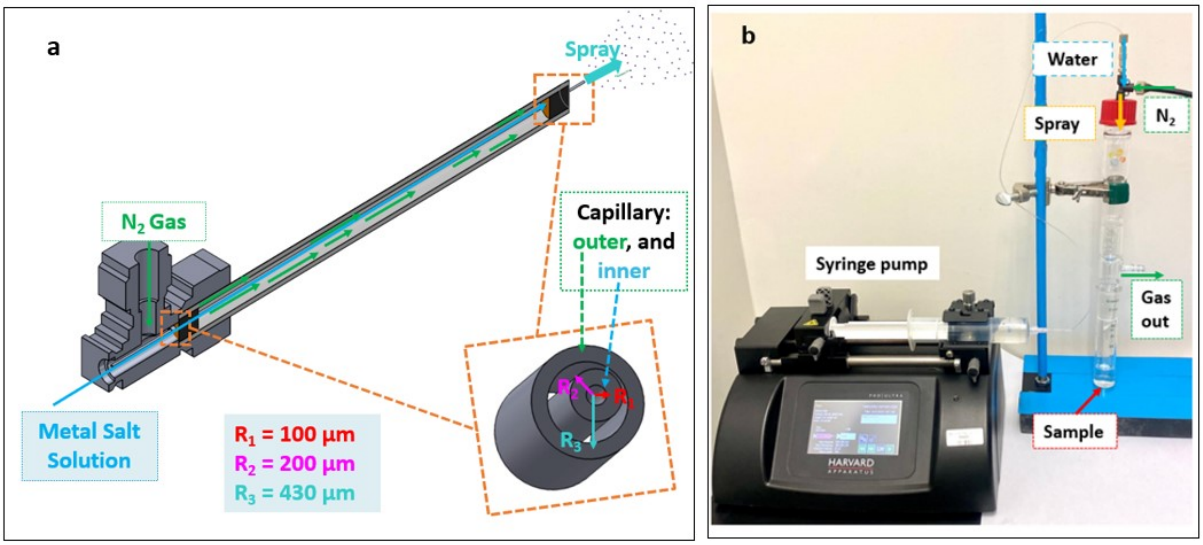

Fig. S1: **a)** Schematics of pneumatic spray setup. **b)** Photograph of spray setup connected to a removable glass flask for sample collection, comprising two coaxial capillary tubes. Liquid flows through the inner tube, whereas nitrogen gas flows through the outer annulus. Metal salt solution samples were injected via a syringe pump, and a high-pressure cylinder supplied N_2 gas. Sprayed microdroplets were collected in a clean glass flask until a sufficient analyte volume was collected.[2]

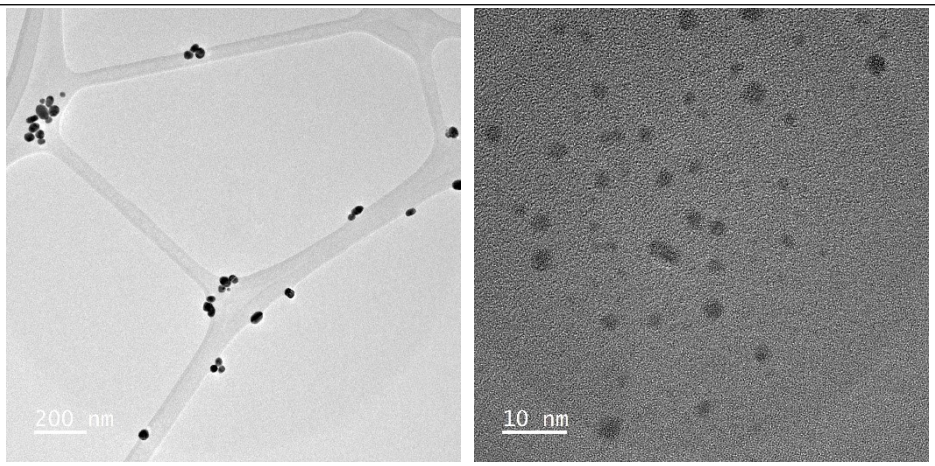

Fig. S2 TEM imaging of microdroplets samples formed by spraying 100 μM $HAuCl_4$ solution, collected and drop cast, shows the presence of AuNPs.

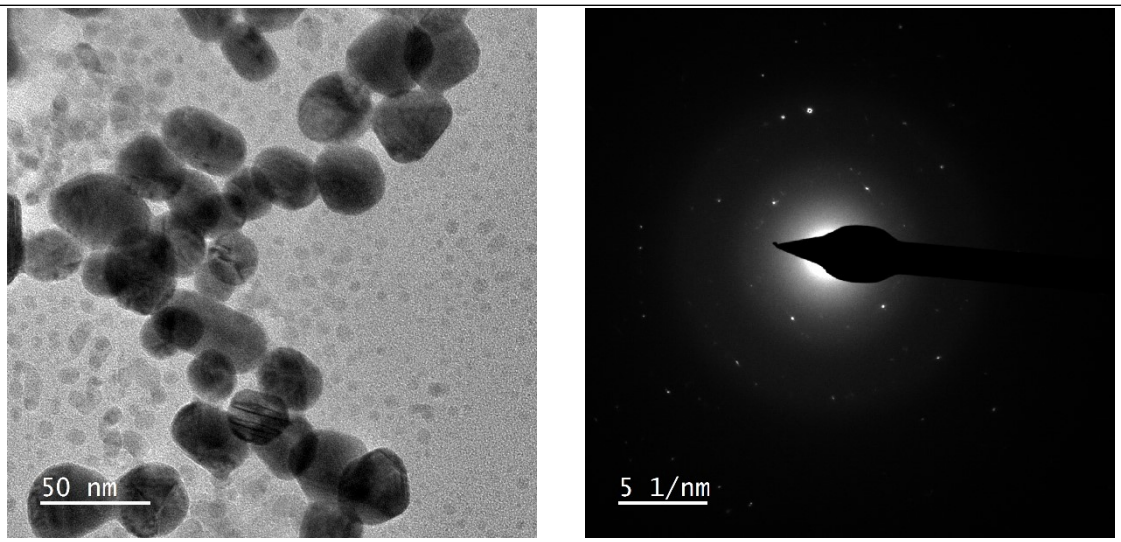

Fig. S3 TEM imaging of bulk aqueous 100 μM $HAuCl_4$ solution: Micrograph showing the presence of nanoparticles of different sizes and diffraction pattern showing the formation of Au(0).

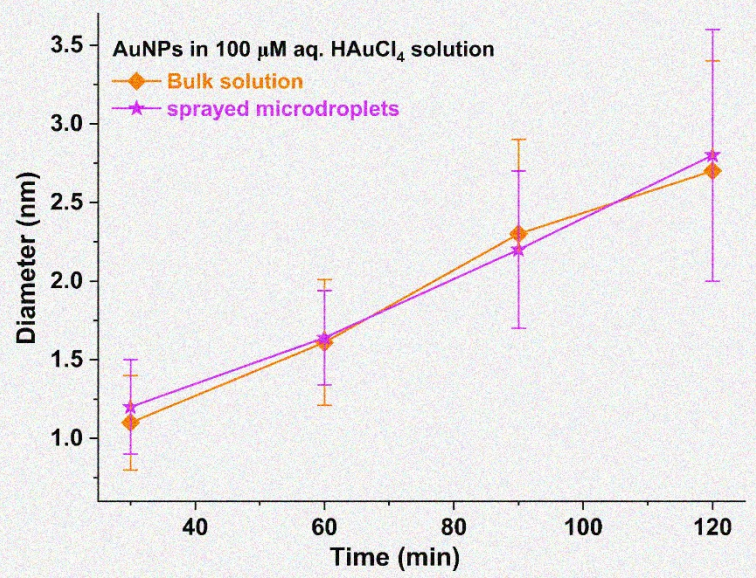

Fig. S4 DLS measurements of the sizes of nanoparticles formed in bulk solutions and sprays. Typical sample's age, i.e., the time on the x-axis, depends on sample preparation (~5 mins), the water flow rate during spraying (viz., 25, 50, 75, and 100 µL/min), and subsequent DLS measurements. Since the particles size distributions are indistinguishable between bulk solutions and sprays, the effects of microdroplet geometry or the air–water interface seem to be negligible on NP formation.

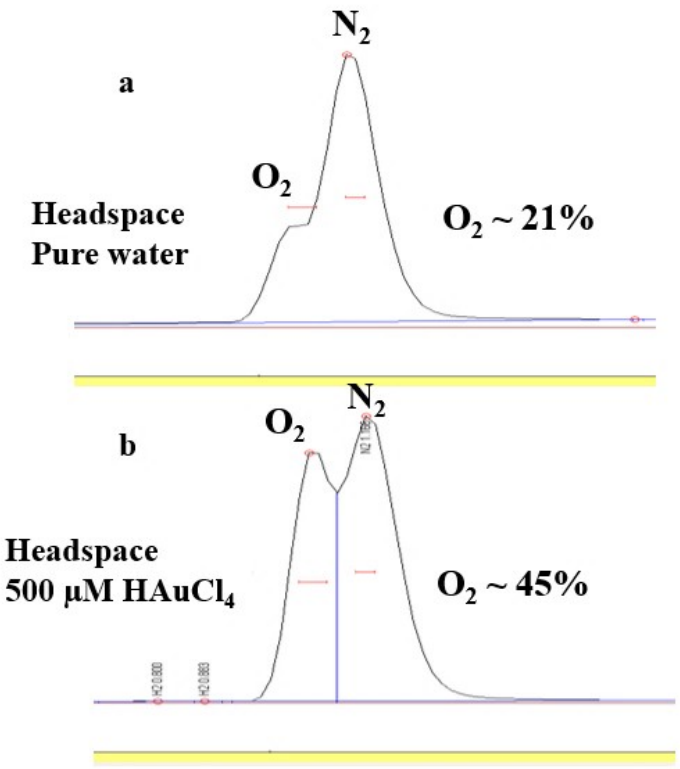

Fig. S5: Gas chromatography results show oxygen gas evolution from the $HAuCl_4$ aqueous solution. **a** showing the presence of around 21% oxygen in the headspace of pure water (DI used for making solutions). **b** shows the presence of around 45% oxygen in the headspace of 500 µM $HAuCl_4$ solution after the age of around 24 h. This reveals that the $HAuCl_4$ solution evolves oxygen gas.

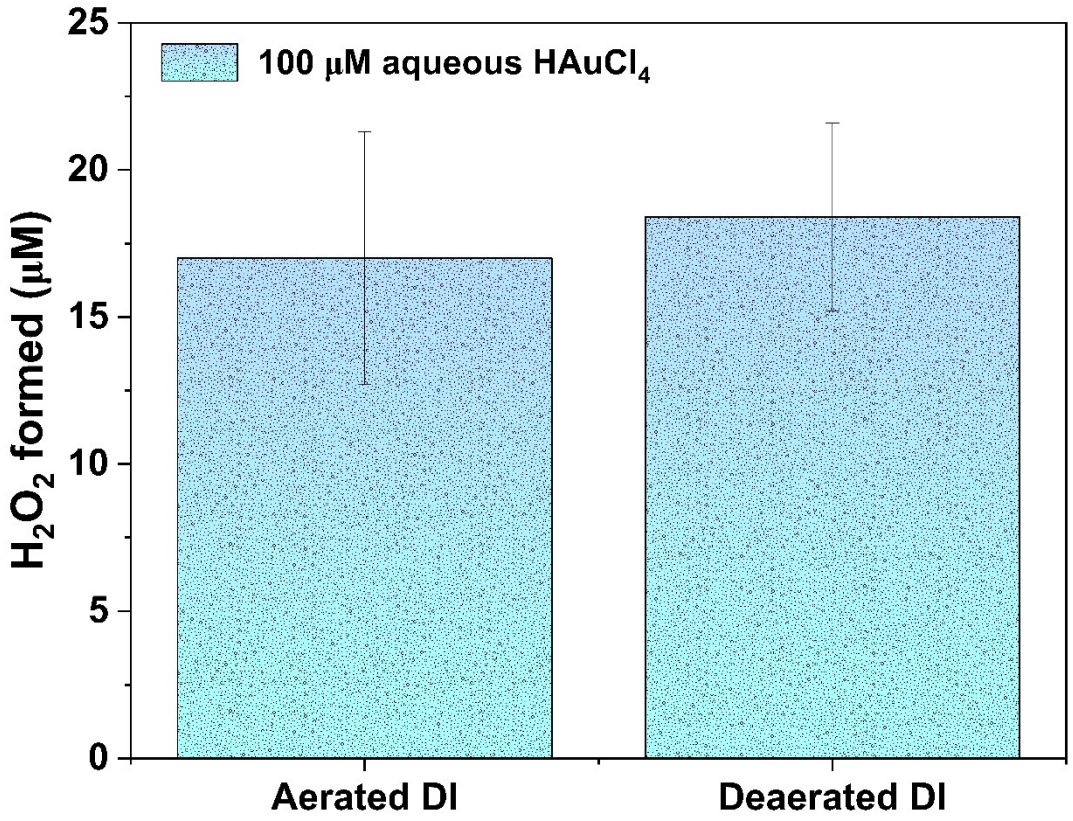

Fig. S6 Effect of water deaeration on H_2O_2 formation by Au^{3+} cations in water. These results reveal that deaeration has no significant effect on the H_2O_2 formation. Note that these measurements were conducted in the absence of light.

In order to investigate whether the presence of H_2O_2 in the gold salt solutions resulted from an oxygen reduction reaction or light exposure, the measurements were carried out under conditions where dissolved oxygen was removed from the water and in the absence of light. The findings indicated that the H_2O_2 present in the gold salt solution did not originate from an oxygen reduction reaction, nor was it induced by light.

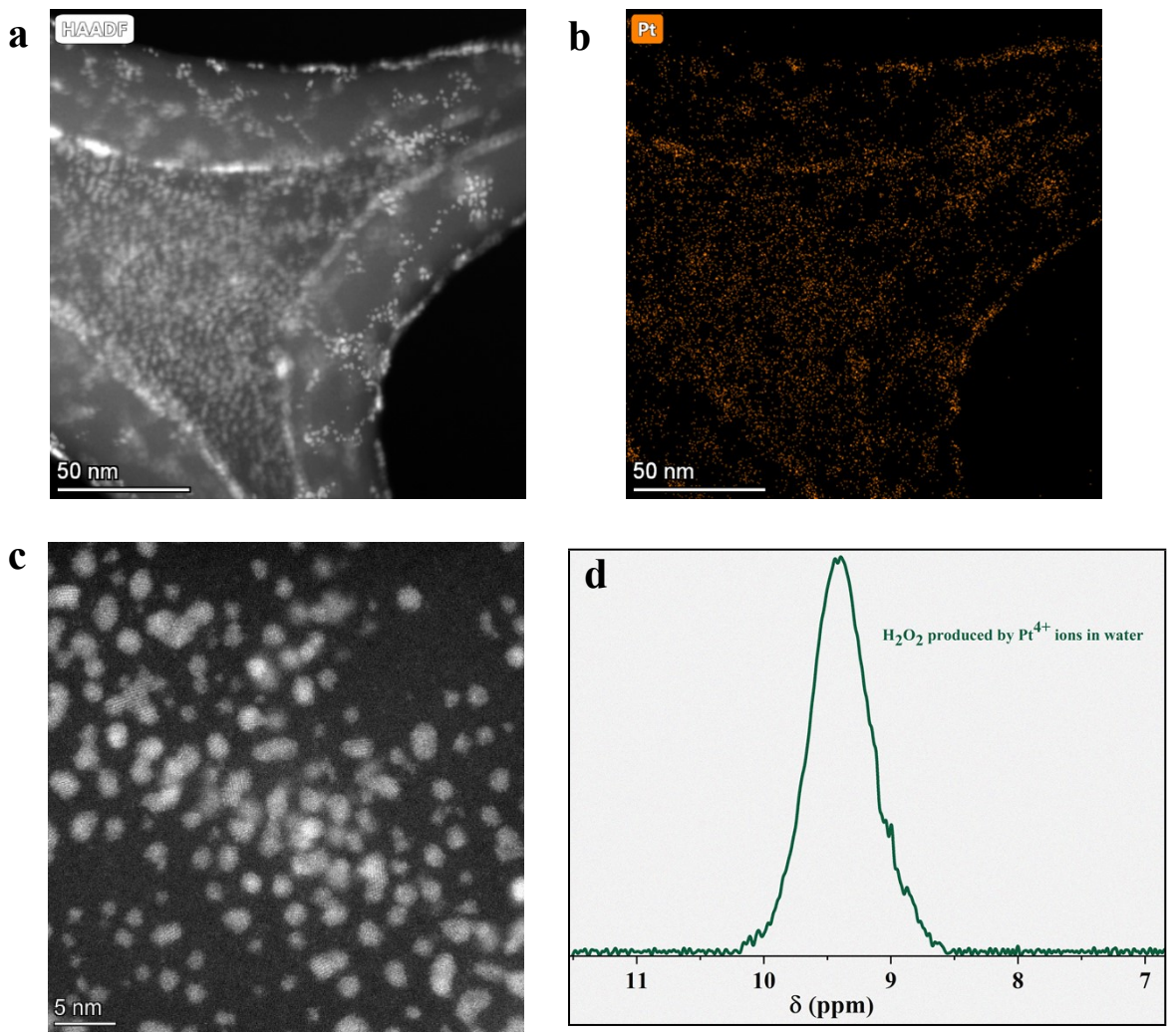

Fig. S7 Characterization of bulk aqueous PtCl4 solution. **a-c** TEM imaging of drop casted bulk $PtCl_4$ solution shows the presence of Pt nanoparticles. **d** NMR spectroscopy results revealing H_2O_2 formation by Pt^{4+} ions in water.

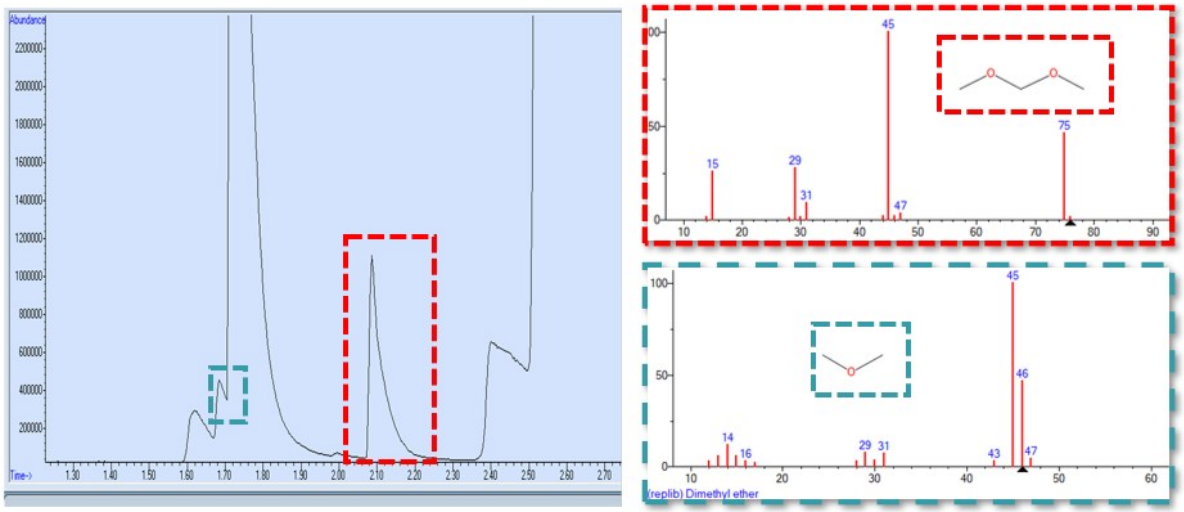

Fig. S8 GC-MS for $HAuCl_4$ salt in methanol. The results reveal the presence of Methylal ($CH_3OCH_2OCH_3$) and Dimethyl ether (CH_3OCH_3)

Table S1 Summary of some key observations in this study

Solvent	**Environment (bulk or microdroplet)**	**Formation of Nanoparticles $M^{n+} + ne^- = M$ (s)**	**Metal ions which form H_2O_2**	**Kinetics of Formation of Nanoparticles $M^{n+} + ne^- = M$ (s)**
Water	Bulk	Au and Pt nanoparticles	Au^{3+}, Pt^{4+}, Fe^{3+}	Fast
	Microdroplet			
Methanol	Bulk	Au and Pt nanoparticles	Au^{3+}, Pt^{4+}, Fe^{3+}	Fast
Ethanol	Bulk	Au and Pt nanoparticles	Au^{3+}, Pt^{4+}, Fe^{3+}	Fast
Acetonitrile	Bulk	Negligible NPs formation	No H_2O_2	Sluggish

Table S2:

Standard electrochemical series with the standard reduction potentials:

Standard Reduction Half-Reaction	**Standard Reduction Potential E° (volts)**
$Au^{+} + e^{-} \rightleftharpoons Au(s)$	1.83
$Au^{3+} + 3e^{-} \rightleftharpoons Au(s)$	1.52
$Au^{3+} + 2e^{-} \rightleftharpoons Au^{+}$	1.36
$AuCl_4^{-} + 3e^{-} \rightleftharpoons Au(s) + 4Cl^{-}$	1.002
$AuCl_4^{-} + 2e^{-} \rightleftharpoons AuCl_2^{-} + 2Cl^{-}$	0.926
$Pt^{2+} + 2e^{-} \rightleftharpoons Pt(s)$	1.2
$PtCl_2 + 2e^{-} \rightleftharpoons Pt(s) + 4Cl^{-}$	0.78
$PtCl_4 + 2e^{-} \rightleftharpoons PtCl_2 + 2Cl^{-}$	0.75
$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	0.771
$H_2O_2 + H^{+} + e^{-} \rightleftharpoons HO^{*} + H_2O$	**0.710**
$O_2(g) + 2H^{+} + 2e^{-} \rightleftharpoons H_2O_2$	0.695
$O_2(g) + 2H_2O(l) + 4e^{-} \rightleftharpoons 4OH^{-}$	**0.401**
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	0.34
$Fe^{3+} + 3e^{-} \rightleftharpoons Fe(s)$	-0.037
$Ti^{2+} + 2e^{-} \rightleftharpoons Ti(s)$	-0.163
$Ti^{3+} + e^{-} \rightleftharpoons Ti^{2+}$	-0.37
$Fe^{2+} + 2e^{-} \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	-0.76
$Al^{3+} + 3e^{-} \rightleftharpoons Al(s)$	-1.706
$Mg^{2+} + 2e^{-} \rightleftharpoons Mg(s)$	-2.356

Section S2: Confirmation of H_2O_2 peak position

To confirm that the obtained peak positioned at a chemical shift around 9.4 ppm in gold ion solution (0.3M $HAuCl_4$ in water) corresponds to the H_2O_2 only (Fig. S9), the peak was compared to one obtained for the same gold ion concentration (0.3M $HAuCl_4$) with the addition of 200µM H_2O_2 (i.e., 0.3M $HAuCl_4$ + 200 µM H_2O_2) and the new peak was found at the same position/chemical shift with relatively more intensity and no other additional peak/s was found in the spectra. This confirms that the peak at around 9.4 ppm corresponds to H_2O_2 only.

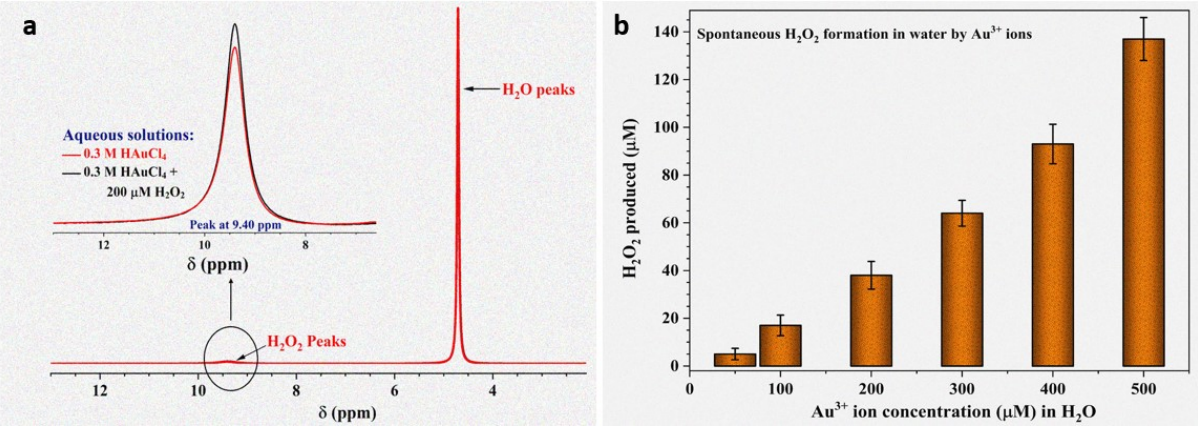

Fig. S9 NMR Spectra confirms the peak position of H_2O_2 in water produced by Au^{3+}ions.

Fig. S10 shows the data obtained for the same concentration of gold ion (Au^{3+}) in water and acetonitrile, which confirmed the formation of H_2O_2 in water and not in acetonitrile.

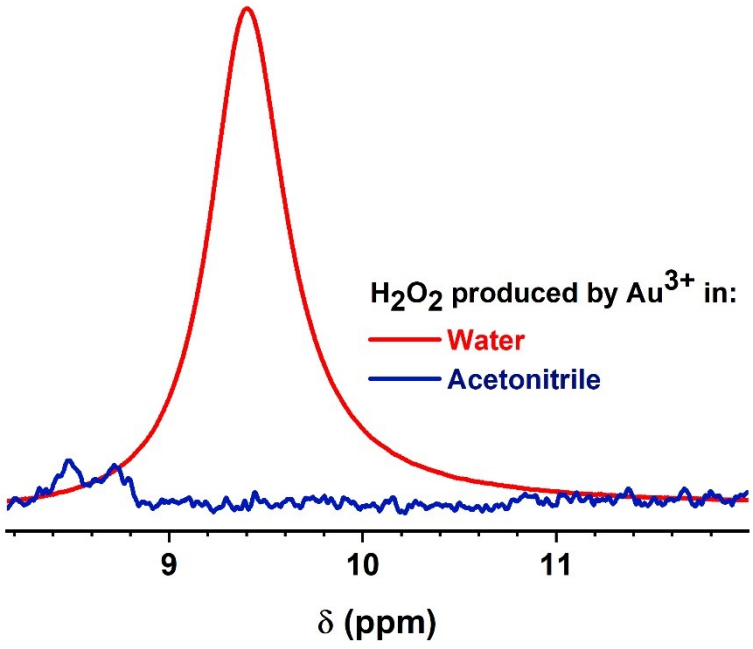

Fig. S10 NMR Spectra showing that Au^{3+} produces H_2O_2 in water and not in acetonitrile.

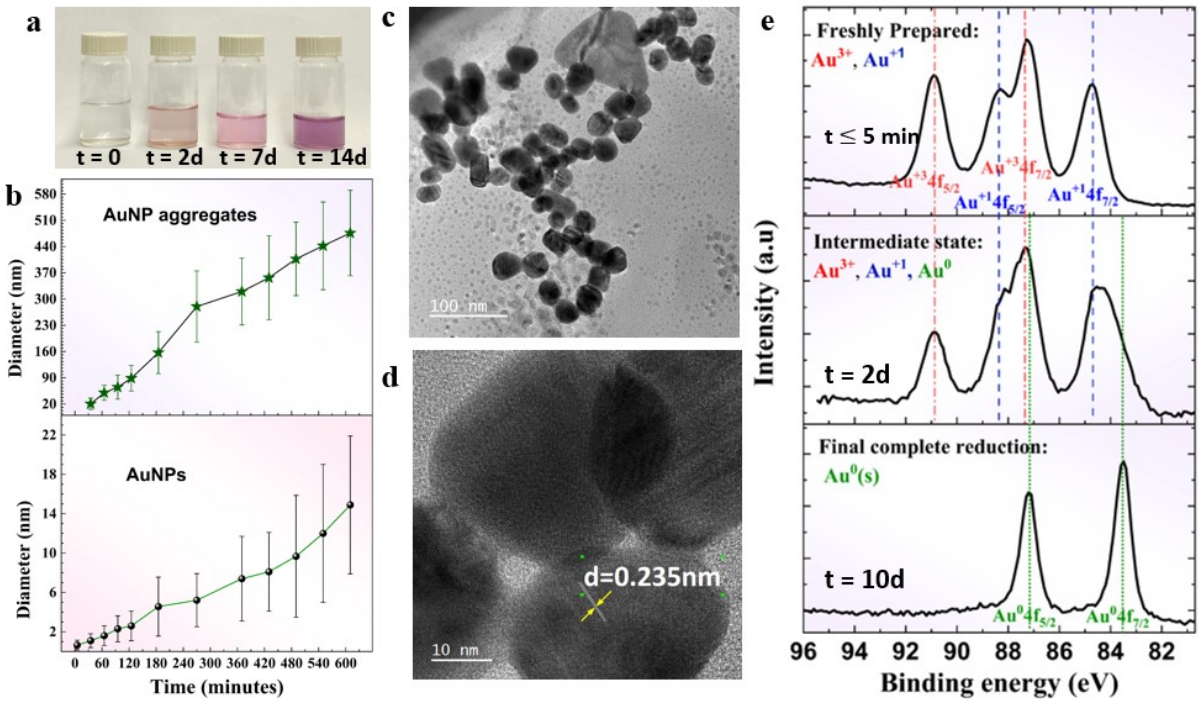

Fig. S11. Spontaneous formation and growth of AuNPs in bulk 100-µM $HAuCl_4$ in water. **a** Bulk solution changing color due to the nucleation and growth of AuNPs. **b** Formation and growth of particles with time, as measured by DLS. **c** TEM micrograph showing the presence of AuNPs of different sizes. **d** TEM imaging showing an interlayer spacing of ~0.235 nm corresponding to the Au(111) atomic plane of metallic gold Au(0). **e** XPS analysis showing the presence of Au^{3+} and Au^{+} in freshly prepared solution, Au^{3+}, Au^{+}, and Au^{0} in 2-day-old solution, and Au^{0} in 10-days-old solution. Complete reduction of gold ions to AuNPs after some time.

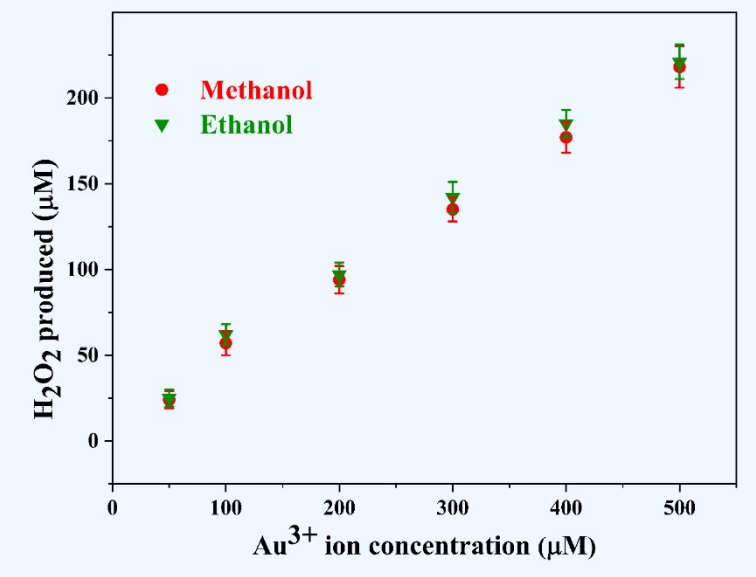

Fig. S12. Spontaneous formation of H_2O_2 by $HAuCl_4$ salt in methanol and ethanol. The results were obtained by the HPAK Assay kit. The results suggest that there is no significant difference in H_2O_2 formation by Au^{3+} ions in methanol and ethanol.

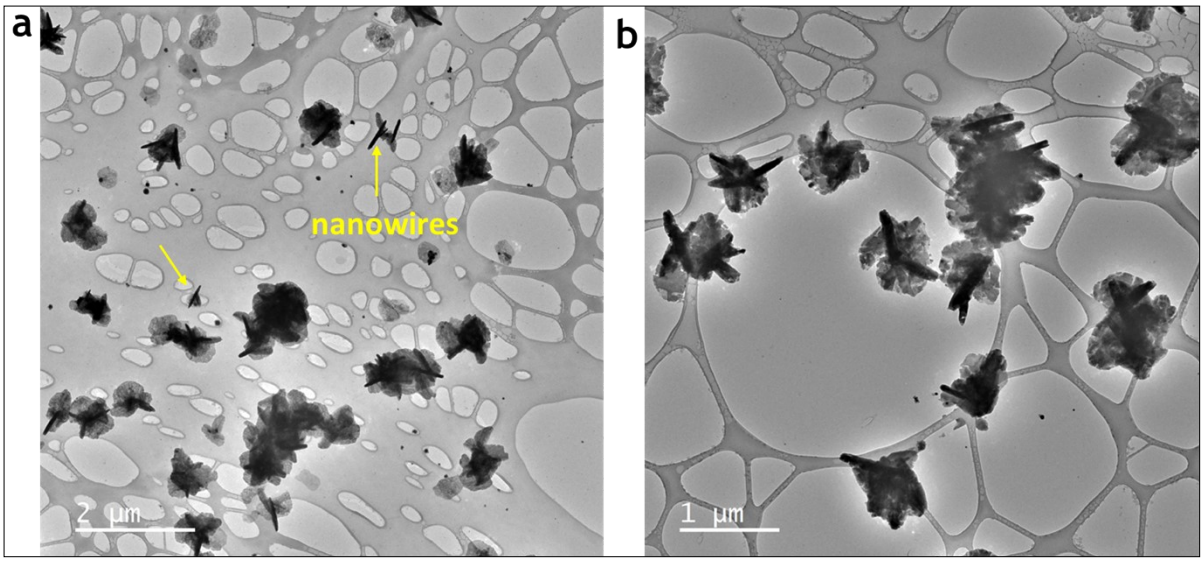

Fig. S13 TEM micrographs of bulk 200 μM $HAuCl_4$ aqueous solution. It clearly shows the presence of gold nanowires.

References:

1. Gallo Jr A*, et al.* On the formation of hydrogen peroxide in water microdroplets. *Chemical Science* **13**, 2574-2583 (2022).
2. Eatoo MA, Mishra H. Busting the myth of spontaneous formation of H2O2 at the air–water interface: contributions of the liquid–solid interface and dissolved oxygen exposed: Chemical *Science* **15**, 3093-3103 (2024).