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Electrosynthesis of gold nanoparticles mediated by methylviologen using a gold anode in single compartment cell

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Experimental

The study was performed using cyclic voltammetry (CV), preparative electrolysis, dynamic light scattering (DLS), scanning electron microscopy (SEM), high resolution transmission electron microscopy and UV and visible spectroscopy.

Cyclic voltammograms (CV curves) were recorded using a P-30J potentiostat (without IR compensation) in an argon atmosphere at potential scan rates from 10 to 200 mV/s in an H_2O/0.1 M NaCl medium. A glass-carbon (GC) disc electrode (dia. 2.0 mm) soldered into glass was used as the working electrode. Prior to each measurement, the electrode was mechanically polished. Platinum wire was used as the auxiliary electrode. Potentials were measured and reported *versus* an aqueous saturated calomel electrode (SCE) connected to the solution being studied through a bridge containing the supporting electrolyte and having a potential of -0.57 V relative to E_0' $Fc^{+/0}$ (internal standard). The temperature was 295 K. The diffusion nature of peak currents i_p was confirmed by the theoretical shape of the voltammograms and the linear i_p - $\nu^{1/2}$ plot with the potential sweep rate ν varied in the range from 10 to 200 mV/s.

The pH of the solutions was adjusted to the required values by titration with 0.1 M HCl solution.

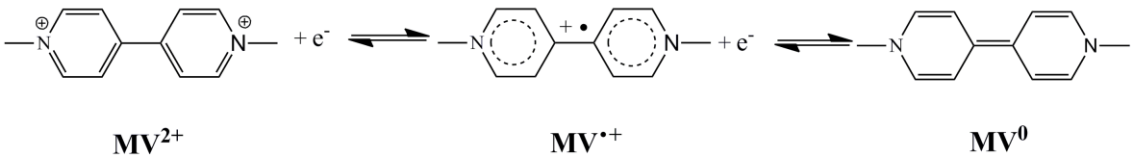
Preparative electrolysis was carried out in an three-electrode undivided glass cell in potentiostatic (Nos. 1, 3, 4) and galvanostatic (No. 2) modes, in argon atmosphere at room temperature (T = 295 K), using a P-30J potentiostat. The solution was stirred with a magnetic stirrer during the electrolysis. A gold plate (S = 2.4 cm^2) was used as the working electrode. A carbon glass plate was used as the auxiliary electrode. A saturated calomel electrode (SCE) connected to the working solution through a bridge with the supporting electrolyte was used as the reference electrode. The working solution for the electrolysis (15 ml) was prepared by dissolving $MV^{2+}\cdot 2Cl^-$ (9.4 mg, *C* = 2.0 mM), NaCl as the supporting electrolyte (87.8 mg, *C* = 0.1 M) and PVP (124.9 mg, *C* = mM) in H_2O.

DLS measurements were performed using a Zetasizer Nano tool from Malvern Instruments. The measured autocorrelation functions were analyzed using Malvern DTS software.

UV and visible spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer.

Commercial reagents: NaCl, $MV^{2+}\cdot 2Cl^{-}$ and poly(N-vinylpyrrolidone) (PVP, 40 000 D) were used without additional purification. Double distilled water was used.

Schemes and Figures



MV^{2+} $MV^{\bullet+}$ MV^{0}

Scheme S1 Two-stage reversible electroreduction of methylviologen.

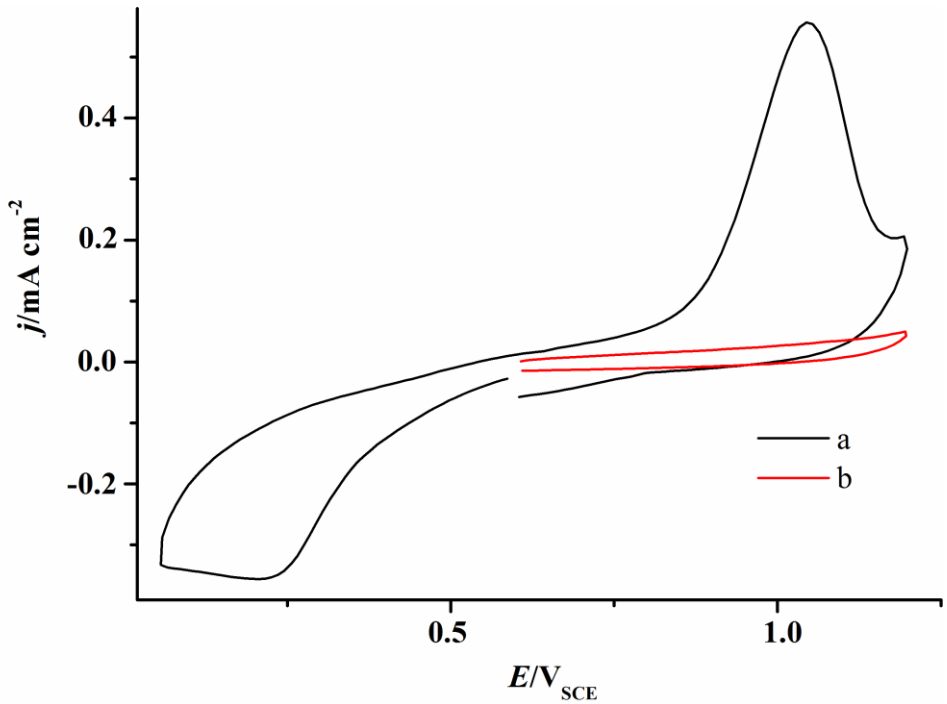


Figure S1 CV curves of 1.5 mM AuCl + 75 mM PVP in the cathodic (a) and anodic (b) region. GC, H_2O/0.1 M NaCl, ν = 100 mV/s.

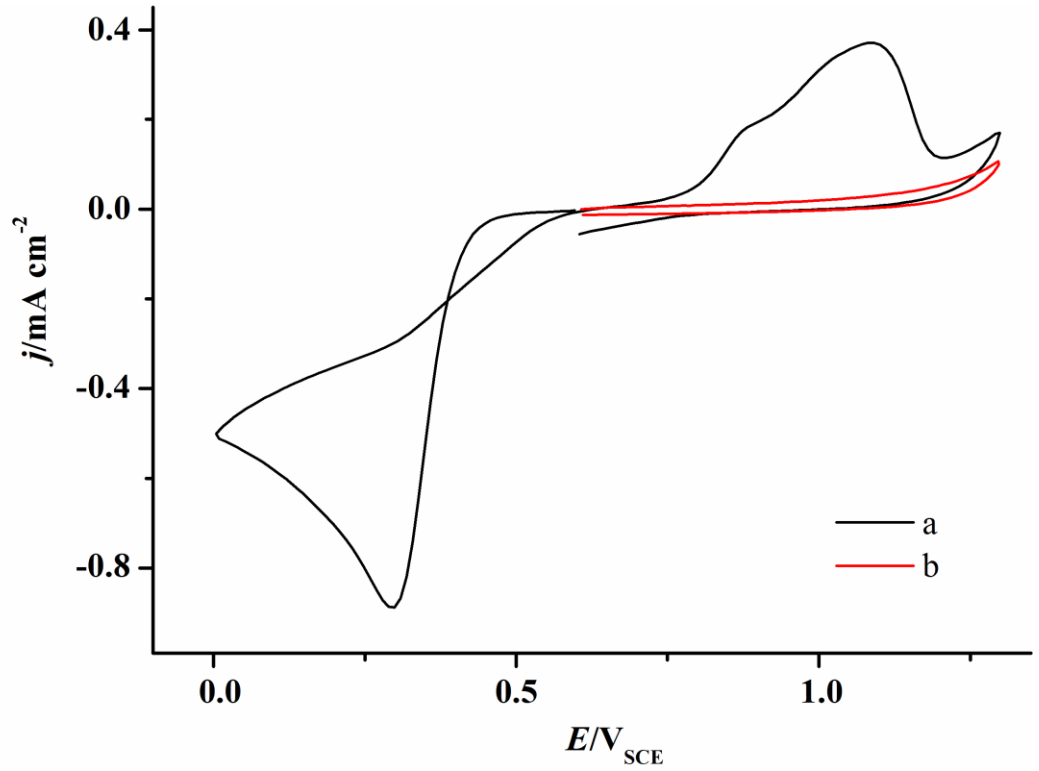


Figure S2 CV curves of 1.5 mM $H[AuCl_4]$ in the cathodic (a) and anodic (b) region. GC, H_2O/0.1 M NaCl, ν = 100 mV/s.

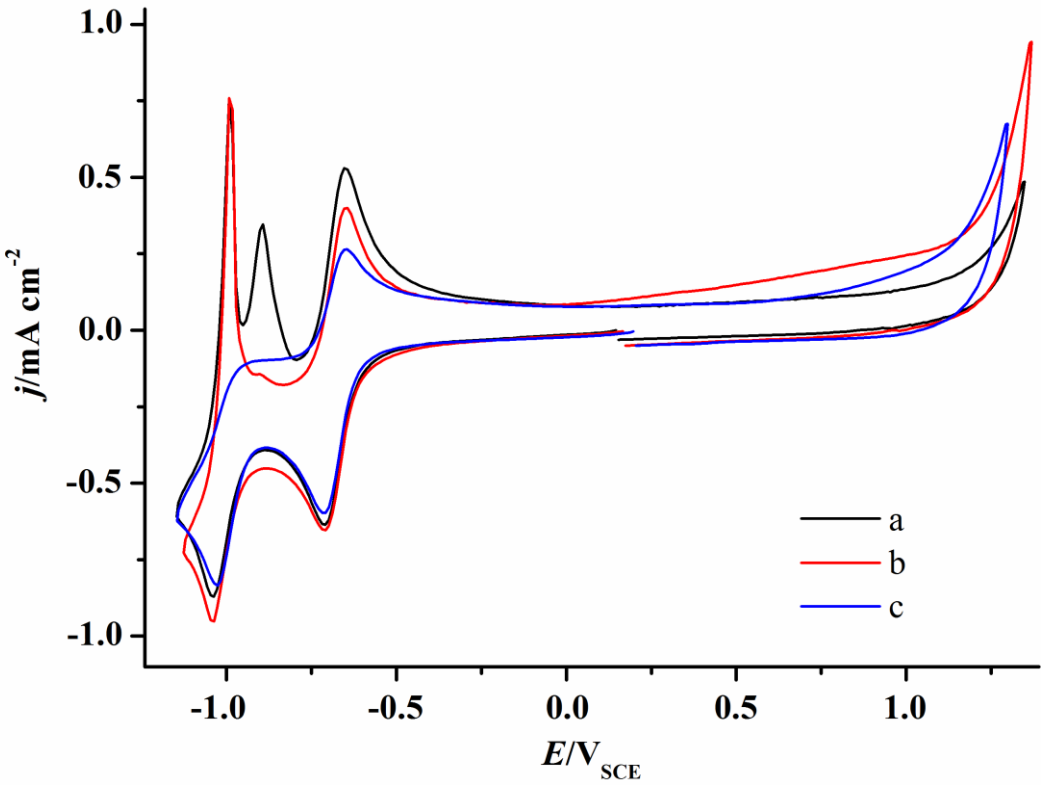


Figure S3 CV curves of 2.0 mM MV^{2+} (a) and the 2.0 mM MV^{2+} + 75 mM PVP system at pH 5.0 (b) and 3.0 (c) electrolysis No. 1. ν = 100 mV/s.

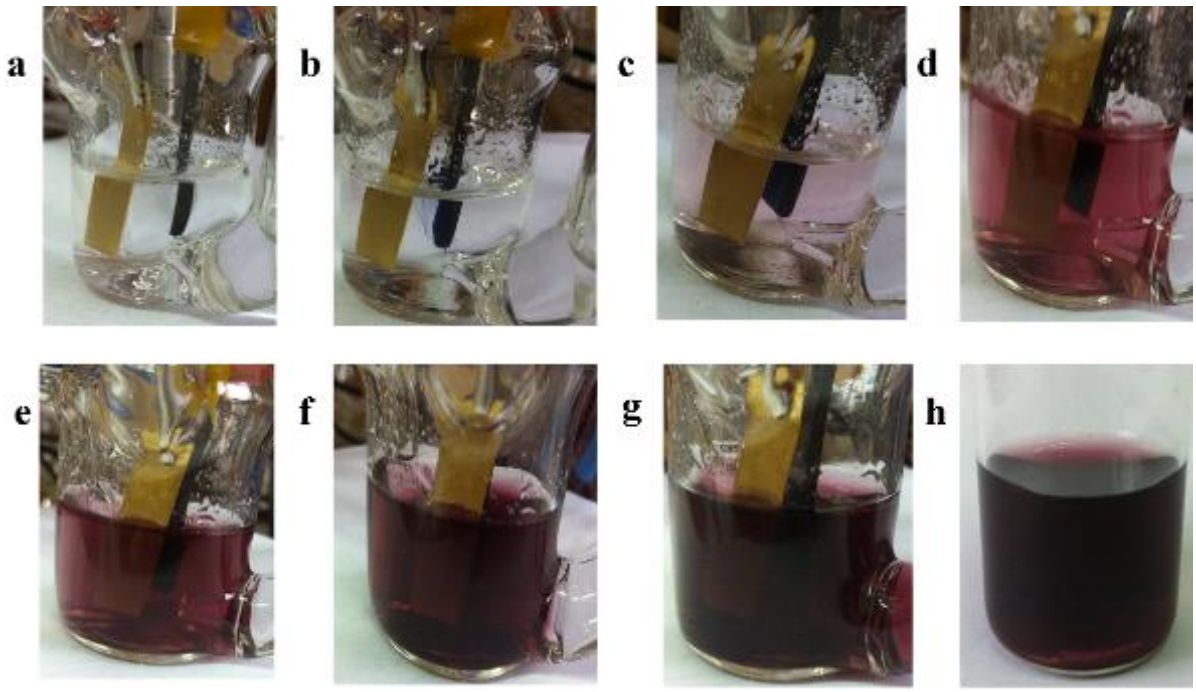


Figure S4 Photos of the solution during electrolysis No. 1: **a** – starting solution, **b** – in the first seconds of electrolysis, **c** - 90 s after the start of electrolysis (Q = ~ 0.1 F), **d** – 0.25 F, **e** – 0.50 F, **f** – 0.75 F, **g** and **h** – after the end of electrolysis (1.0 F).

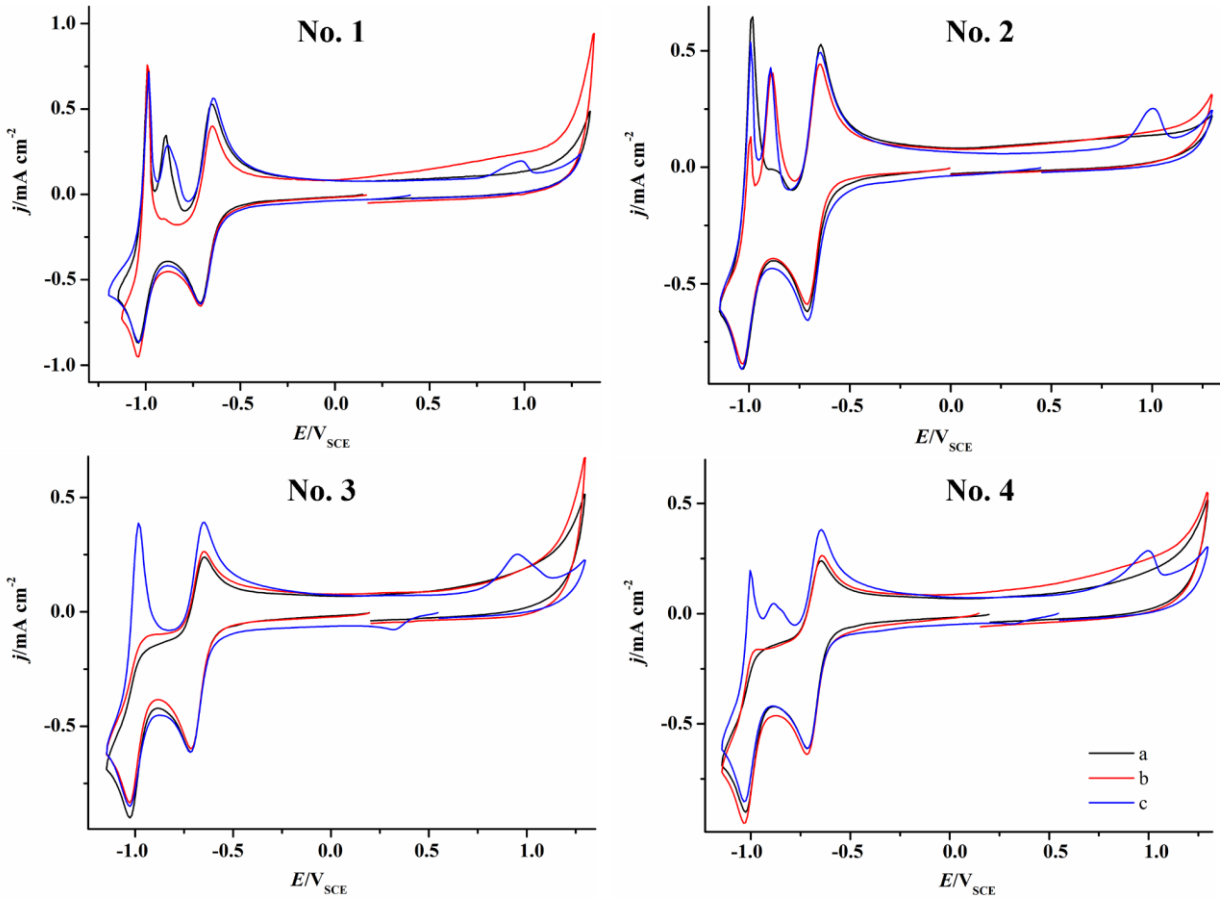


Figure S5 CV curves of 2.0 mM MV^{2+} (a) and the 2.0 mM MV^{2+} + 75 mM PVP system before (b) and after (c) electrolyses No. 1 - 4 (Q = 1.0 F) using a soluble gold anode. GC, H_2O/0.1 M NaCl, ν = 100 mV/s.

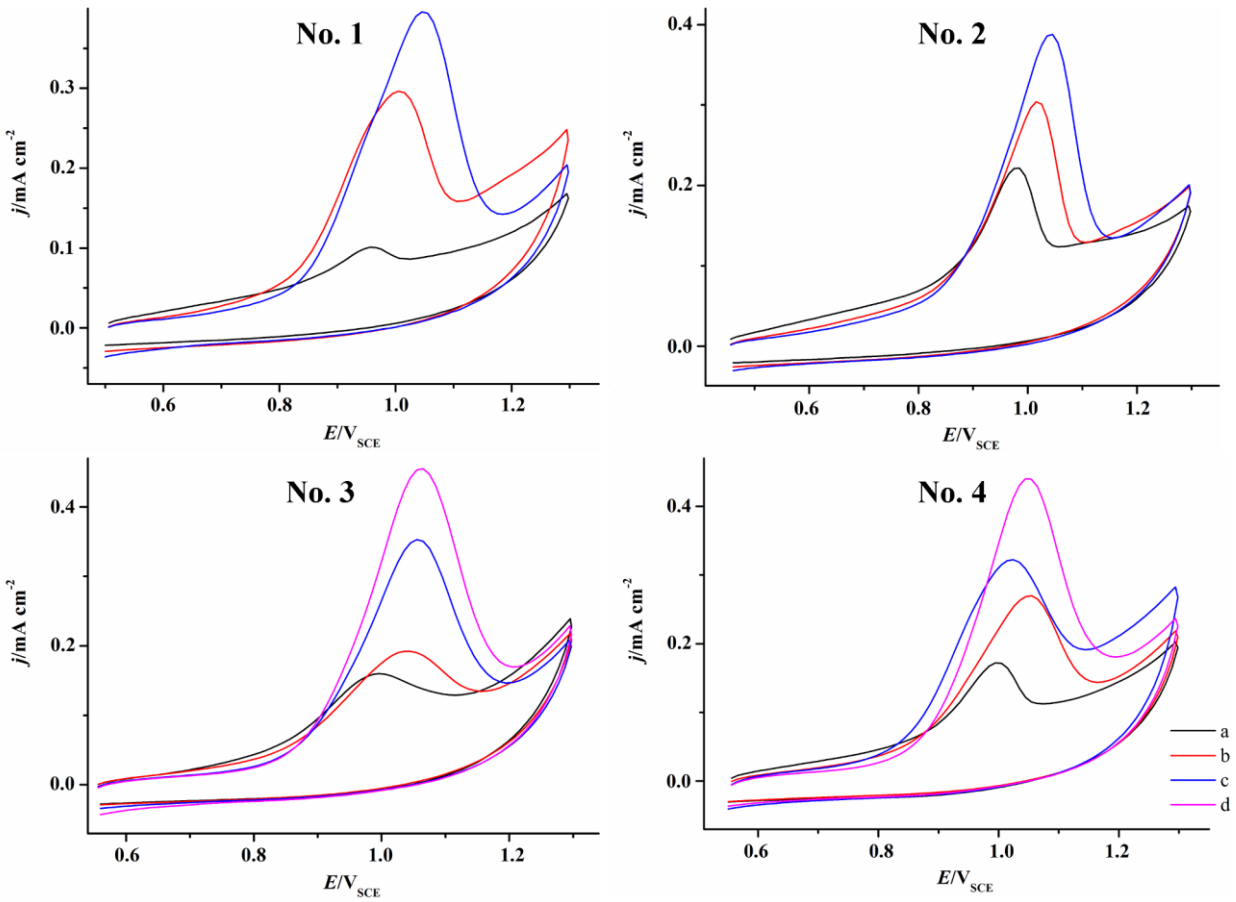


Figure S6 CV curves of solutions after electrolyses No. 1-4 at various electrode exposure times in the solution without stirring and without applying a potential, min: 0 (a), 1 (b), 3 (c), 5 (d). H_2O/0.1 M NaCl, ν = 100 mV/s. (In electrolyses No. 3 and 4, pH = 3.0).

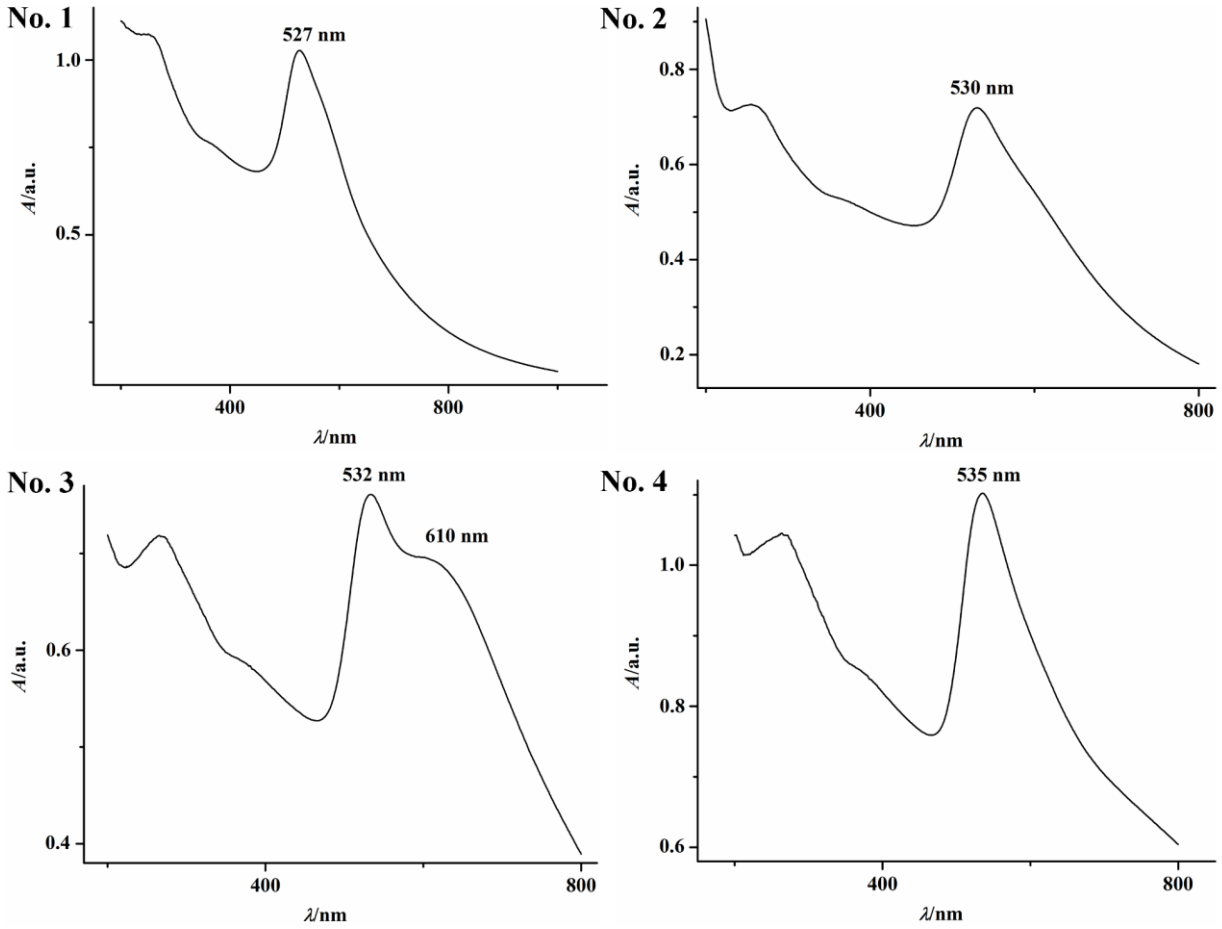


Figure S7 UV spectra of PVP-stabilized Au-NP obtained in electrolyses No. 1 - 4.

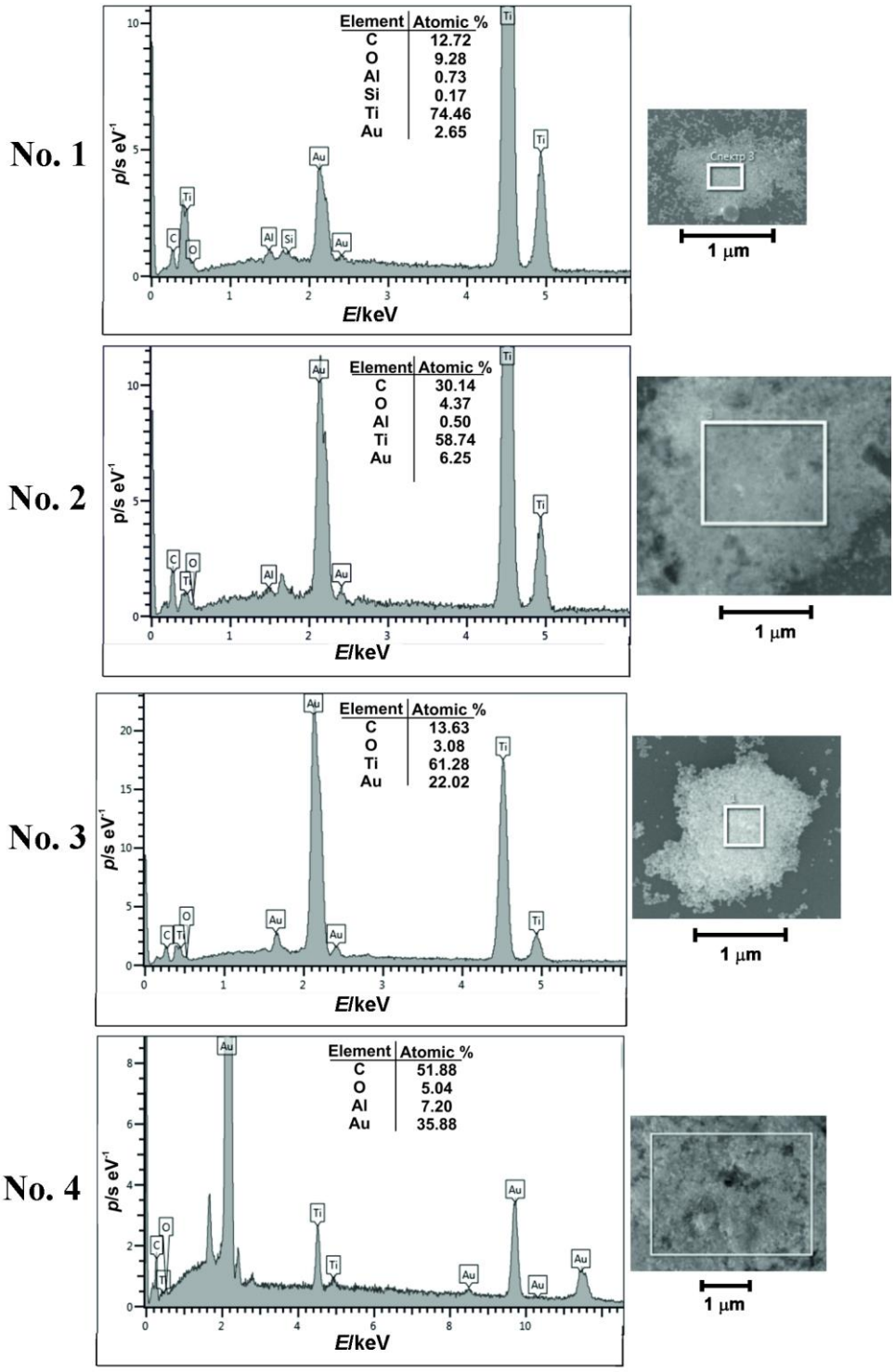


Figure S8 Energy-dispersive spectra of Au-PVP nanoparticles synthesized in electrolyses No. 1 – 4 using a soluble gold anode.

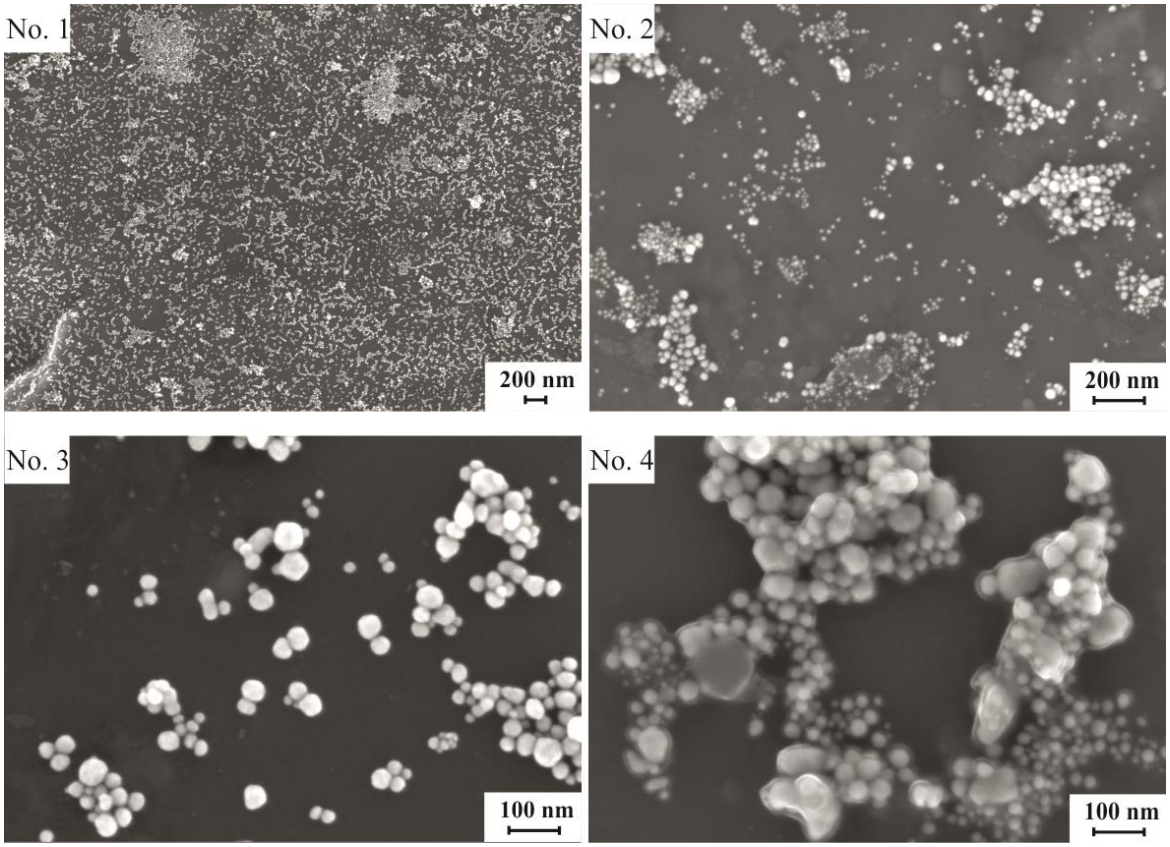


Figure S9 SEM images of Au-PVP nanoparticles synthesized in electrolyses No. 1 – 4.

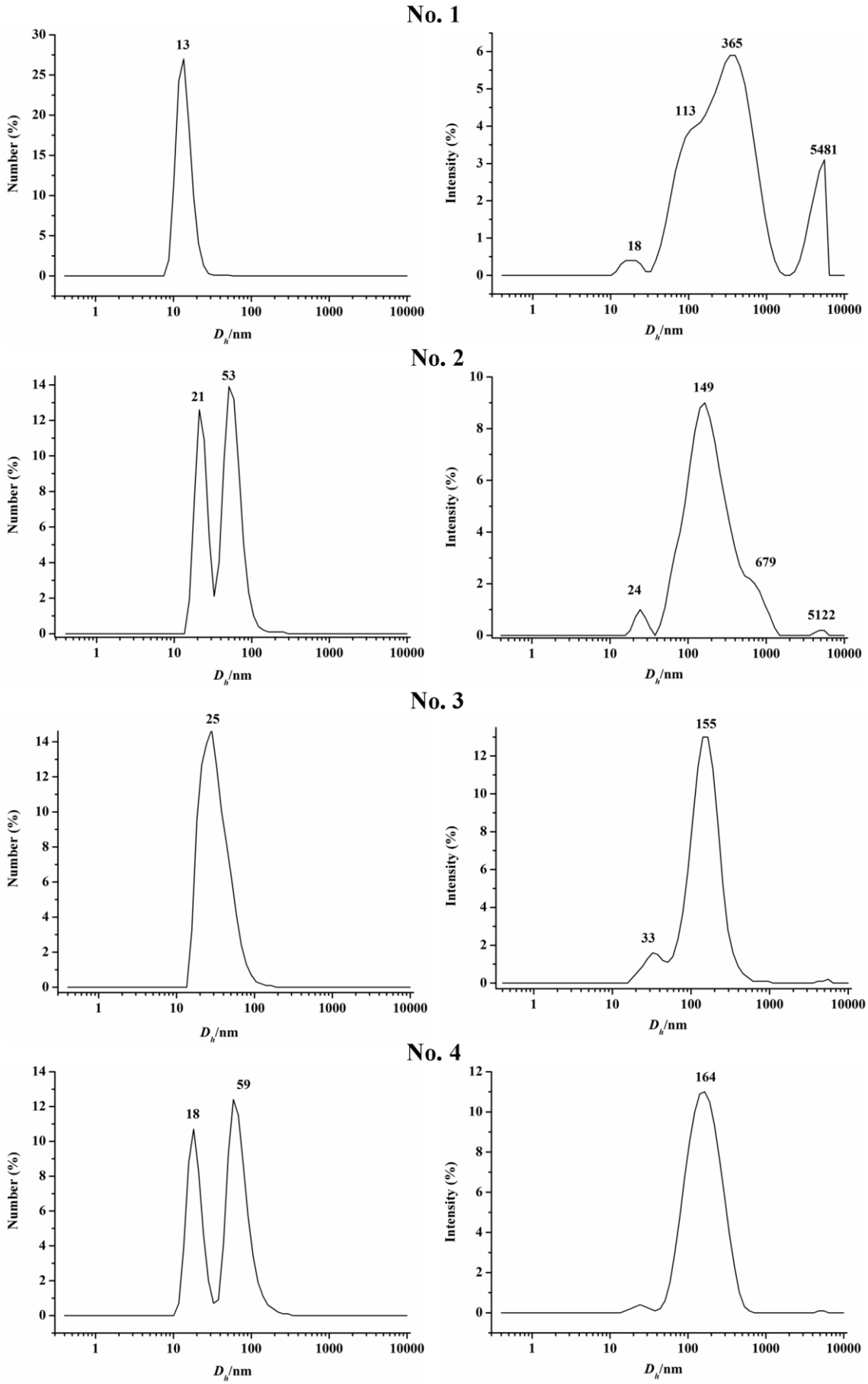


Figure S10 DLS data for Au-PVP nanoparticles synthesized in electrolyses No. 1 – 4. The PdI values were 0.53, 0.43, 0.30 and 0.25, respectively.

Figure S11 Photo of a GC electrode after an electrolysis.

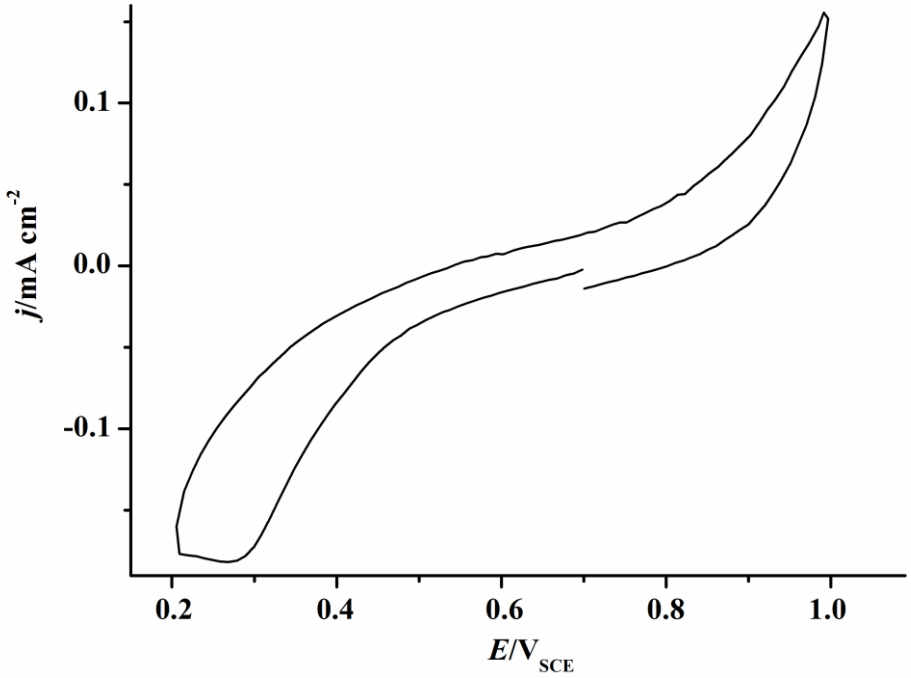


Figure S12 CV curve of the solution after electrolysis No. 9. GC, H_2O/0.1 M NaCl, ν = = 100 mV/s. pH 3.0.