Locally pH controlled and directed growth of supramolecular gel microshapes using electrocatalytic nanoparticles

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1. Materials:

Sodium Nitrate ($NaNO_3$) (98.5%, Sigma Aldrich), Sodium Chloride (NaCl) (99%, Sigma Aldrich), Potassium Hexachloroplatinate (K_2PtCl_6) (99.9%, Sigma Aldrich) , Sodium Tetrafluoroborate ($NaBF_4$) (97%, Sigma Aldrich), Nitric Acid (HNO_3) (60%, Sigma Aldrich), Hydrochloric Acid (HCl) (1M, Sigma Aldrich)) , Sodium Hydroxide (NaOH) (99%,Pellets, Sigma Aldrich), Dibenzoyl-L-Cystine (DBC) (98%, Sigma Aldrich), Tetramethylammonium Chloride (TMA-Cl) (98%, Sigma Aldrich), Potassium Tetrakis(4-chlorophenylborate) (97%, Sigma Aldrich) (K^-TPBCl), Bis(triphenylphosphoranylidene)ammonium Chloride (BTPPA-Cl) (97%, Sigma Aldrich), Chlorotrimethylsilane (99%, Sigma Aldrich) , 1,2-Dichloroethane (1,2-DCE) (Solvent grade, VWR International), Ethanol (Solvent grade, Biosolve), Methanol (Solvent grade, VWR International) and Acetone (Solvent grade, Biosolve) were obtained from commercial suppliers. Salts Na_2-DBC, BTPPA-TPBCl, and $(BTPPA)_2PtCl_6$ were synthesized according to protocols described below.

1.1 Na_2-DBC protocol of preparation

Sodium salt of the gelator (DBC) was prepared by titrating acidified gelator against 0.1 M NaOH (1:2 molar ratio). The solution contained neutralized and non-neutralized gelator was passed through an Acrodisc syringe filter (0.2 µm, PTFE membrane) to remove any possible impurities and non-neutralized gelator which was present as white precipitate in the solution. The resulting clear solution was checked for turbidity and freeze dried under vacuum to yield a white flaky powder which was used for further experiments.

1.2 BTPPA-TPBCl protocol of preparation

BTPPA-TPBCl was used as the organic phase (1,2-dichloroethane) supporting electrolyte and was prepared by simple metathesis reaction reported elsewhere.[1] In brief, 0.6 g of BTPPA-Cl dissolved in 25 mL of water:methanol (1:2 v:v) was added dropwise to a vigorously stirred solution of 0.5 g of K-TPBCl dissolved in water:methanol mixture (1:2 v:v). Resulting white precipitate was than filtered under vacuum and washed with 100 mL of water:methanol (1:2 v:v) mixture. Next, white precipitate was recrystallized from acetone giving large and transparent crystals. After washing with 50 mL of water:acetone (1:1 v:v) mixture it was dried under vacuum and used in experiments.

1.3 $(BTPPA)_2PtCl_6$ protocol of preparation

$(BTPPA)_2PtCl_6$ was used as the organic phase soluble salt of the Pt NPs precursor $PtCl_6^{2-}$. Its preparation is similar to already described BTPPA-TPBCl. The only difference is the ratio between BTPPA-Cl to K_2PtCl_6 equal to 1.1 g to 1.9 g, respectively. The resulting salt had an appearance of orange flakes very well soluble in the 1,2-DCE.

2. Electrochemical experiments

The electrochemical experiments described in the main text of this work and in the supporting information were performed in different electrochemical configurations using few types of custom made electrochemical cells. All electrochemical experiments were performed using Potentiostat/Galvanostat Autolab 302N or portable potentiostat EmStat3+ from PalmSens that were controlled with the Nova 1.10 or PSTrace software respectively.

2.1 Pt NPs deposition in three electrode configuration

The Pt NPs deposition over Fluorine-doped tin oxide (FTO) was performed in a three electrode configuration using dedicated Teflon cell shown in **Fig. SI1-A**. The FTO served as the working electrode, Ag/AgCl was used as the reference electrode whereas 5 cm long Pt wire served as the counter electrode. The cell itself allowed the position of a FTO electrode between o-ring terminated cell and a plate that was attached to the cell body via two screws. The electroactive surface area was defined by o-ring with a diameter equal to 5 mm. Chronoamperometry at *E* = – 1.5 V was used for the electrochemical deposition of Pt NPs from 1 mM K_2PtCl_6 in 250 mM $NaNO_3$. Further characterization of Pt NPs was performed with cyclic voltammetry at scan rate equal to 50 $mV \cdot s^{-1}$ in 250 mM $NaNO_3$.

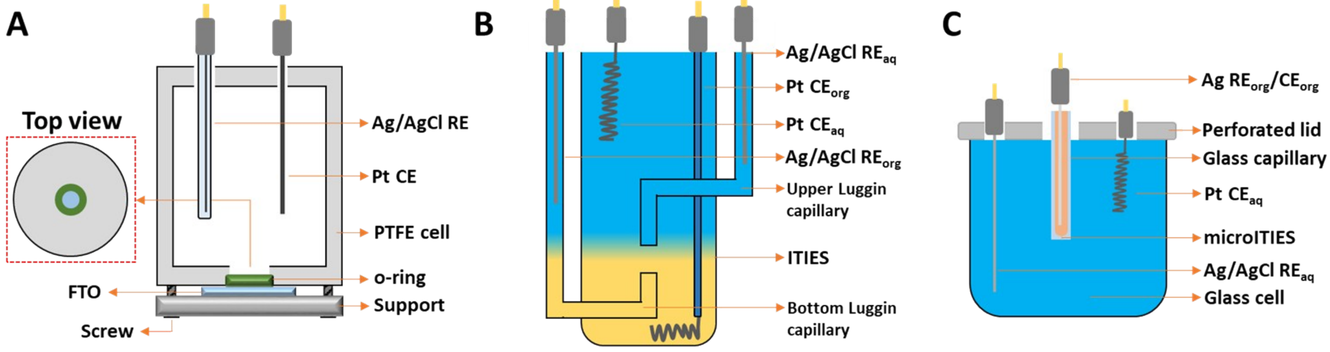


Figure S1. Different electrochemical cells used in this work. **A** – is the cell used to modify FTO electrode with the Pt NPs; **B** – is the "cactus like" cell to study interfacial behavior of $BTPPA_2PtCl_6$ at macroscopic liquid – liquid interface and **C** is the cell used to characterize micropipettes that were used to support micro-liquid-liquid interface. The abbreviations used stand for: **PTFE** – polytetrafluoroethylene, **RE** – reference electrode, **CE** – counter electrode, **aq** – the aqueous phase, **org** – the organic phase and **ITIES** – the interface between two immiscible electrolyte solutions.

2.2 Macroscopic electrified liquid – liquid interface

Experiments at the macroscopic liquid – liquid interface were performed in four electrode configuration in the "Cactus like" glass cell with two Luggin capillaries **(see Fig SI1-B).** The geometrical diameter of a liquid – liquid interface placed in this cell was equal to 0.65 cm. The counter electrodes were made out of Pt spiral wires. The organic phase counter electrode was additionally sealed in glass to prevent the contact with the aqueous phase. Both, the organic and the aqueous phase reference electrodes were made out of Ag/AgCl wires. During experiments, the organic phase reference electrode was immersed into the solution of 10 mM NaCl, 10 mM BTPPA-Cl that was contacted to the organic phase in the bottom Luggin capillary. Typical composition of a cell can be denoted with a following scheme:

$$(aq)\ Ag\left|AgCl\right|10\ mM\ NaCl\left\|\begin{matrix}10\ mM\ BTPPA-TPBCl\\ x\ \mu M/mM\ BTPPA_2PtCl_6\end{matrix}\right|\begin{matrix}10\ mM\ NaCl\\ 10\ mM\ BTPPA-Cl\end{matrix}\left|AgCl\right|Ag\ (org)$$

Scheme 1. Electrochemical cell used at macroscopic liquid – liquid interface. Double line indicates liquid – liquid interface under investigation.

Ion transfer voltammetry was used to characterize the interfacial behavior of $BTPPA_2PtCl_6$ dissolved in the organic phase. The forward polarization was from more positive to less positive potential values. The scan rate was equal to 10 $mV \cdot s^{-1}$.

2.3 Miniaturized electrified liquid – liquid interface

Miniaturization was achieved with the help of metal templated glass-micro-capillaries.[2,3] In brief, the gold µ-wire with diameter equal to 25 µm was sealed in a glass capillary (ID: 1.6 mm and OD: 2.0 mm) upon heating in Bunsen burner flame. Attention has to be taken to entrap only part of the wire. Next, gradual polishing with fine polish paper allowed the removal of glass excess until µ-wire is exposed (**see Figure S2**). Following that, gold µ-wire was dissolved in aqua-regia (3:1 $HCl:HNO_3$) and the capillary has been washed few times with miliQ water (see empty pore in the inset of **Figure S2**). In order to assure that only the organic phase will be present inside the pore during the experiments, the internal walls of the pore were modified with trimethylsilyl groups via chemical vapor deposition of chlorotrimethylsilane.

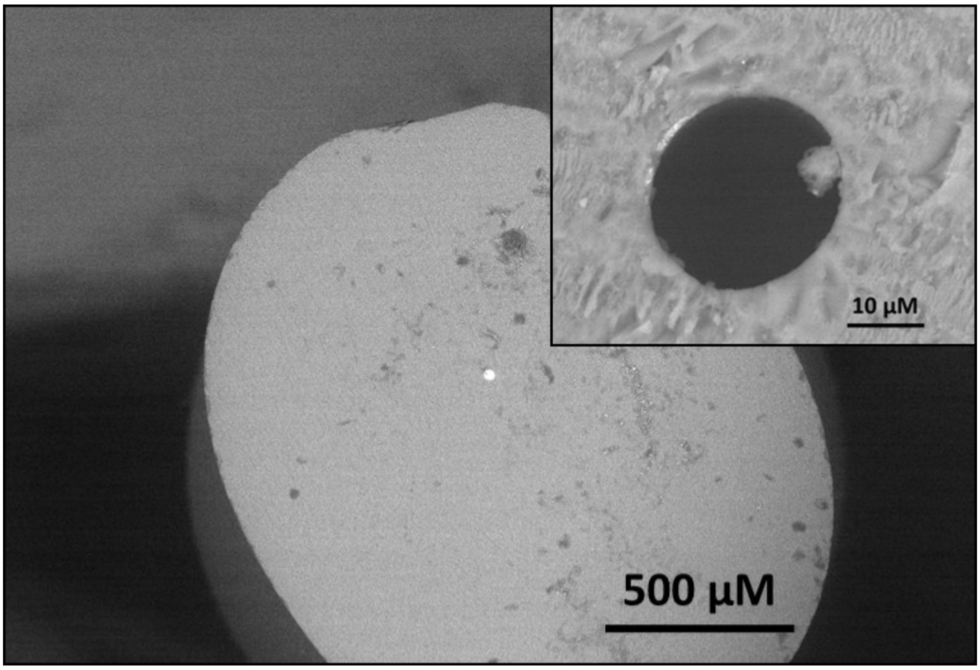


Figure S2. SEM image of the gold µ-wire (25 µm in diameter) embedded in glass after polishing. Insert shows the µ-pore formed after gold wire dissolution in *aqua regia*.

Four electrode configuration was used to polarized miniaturized liquid – liquid interface. The organic phase was placed inside the capillary and then silver wire working as the organic phase counter and pseudo-reference electrode was inserted (see **Figure S1C**). The capillary together with the connection was placed in the aqueous phase through a hole in a lid of a glass cell. The Ag/AgCl and spiral Pt wire were used as the aqueous phase reference and counter electrodes respectively. The electrochemical cell can be described using scheme 2:

$$(aq)\ Ag\left|AgCl\right|\begin{matrix}10\ mM & NaCl\\ x\mu M & TMA-Cl\end{matrix}\left|\right|\begin{matrix}10\ mM\ BTPPA-TPBCl\\ in\ 1,2-DCE\end{matrix}|Ag\ (org)$$

Scheme 2. Electrochemical cell used at miniaturized liquid – liquid interface. Double line indicates liquid – liquid interface under investigation.

The micro-capillaries used for local Pt NPs deposition were first characterized using ion transfer voltammetry as shown in **Figure S3**. The blank voltammogram (**Figure S3A**) was recorded in the cell described in scheme 2 for x = 0. Here, the forward polarization was from less positive to more positive potential values (scan rate 10 $mV\cdot s^{-1}$). In this graph, the potential window is limited on both sides by the transfer of the aqueous phase background electrolyte ions. Positive and negative currents on the more positive potential site arise from the Na^+ transfer to the organic phase and back to aqueous phase, respectively. The interfacial transfer of Cl^- is limiting the negative side of the potential window. Here, the negative and the positive currents are due to Cl^- transfer to the organic and back to the aqueous phase, respectively. After adding TMA-Cl to the aqueous phase (Scheme 2, x = 40 µM) we recorded voltammogram shown in **Figure S3B**. The voltammetric response is asymmetric, this is sigmodal wave on the forward scan and peak shaped signal on the reversed scan, and is in agreement with the asymmetric diffusion layer profiles established on both sides of the liquid – liquid interface (see insets of **Figure S3B**).

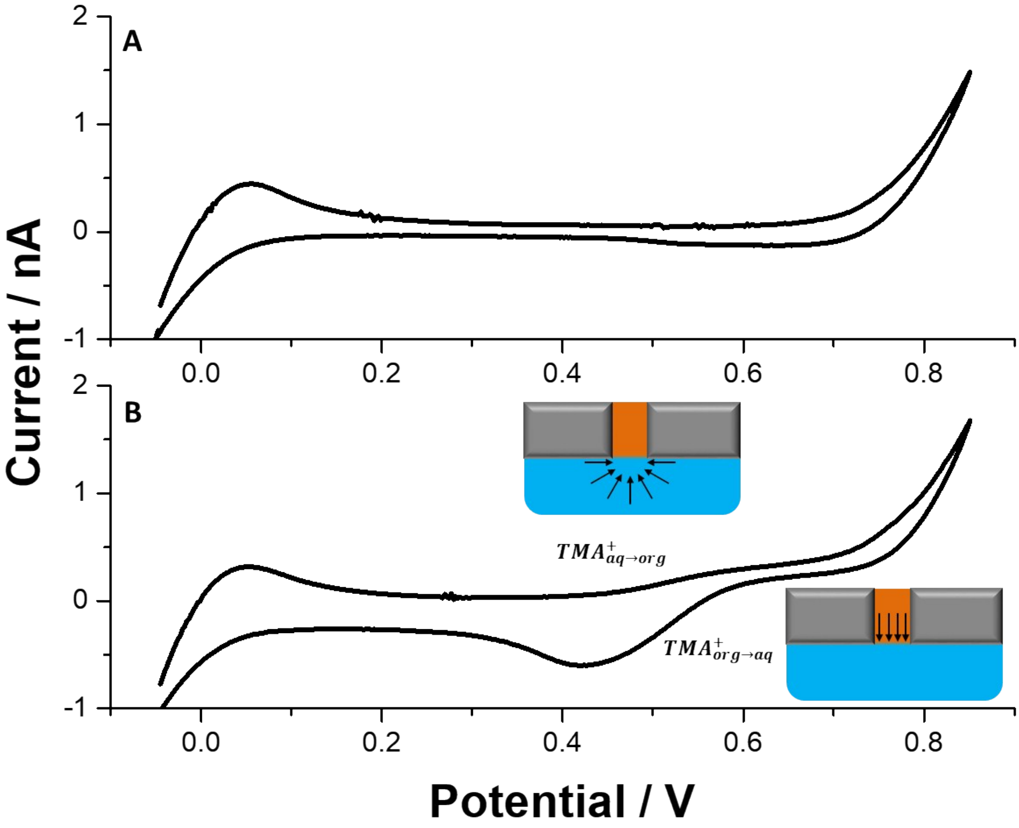


Figure S3. Ion transfer voltammograms recorded at the micro-pore supported interface between 10 mM NaCl and 10 mM $BTPPA^+TPBCl^-$ in the absence (A) and in the presence (B) of 40 µM TMA^+Cl^-. The current of the forward wave (0.25 nA) correspond to pore radii equal to 12 µm (24 µm in diameter).

The transfer of ions from the aqueous to the organic side of the interface is analogical to the mass transfer of an analyte towards micro-disc electrode, and hence, can be described with the Saito expression:

$$I_{ss} = 4nFDCr \qquad \text{(eq. 1)}$$

where I_{ss} is the faradaic current (steady state current), n is the molecular charge, r is radius of a capillary, D is the TMA^+ diffusion coefficient ($13.8 \cdot 10^{-6}$ $cm \cdot s^{-2}$)[4] and C is the concentration of an analyte. Simple rearrangement of the eq. 1 allows for the good capillary dimensionality estimation. The calculated diameter of capillary used to record the voltammgoram from Fig. SI3-B is equal to 24.0 μm and is almost identical with the diameter measured from the SEM image (24.1 μm) available in **Figure S2**.

2.4 Pt NPs deposition at three phase junction

In all experiments involving three phase junction configuration, the working electrode (FTO) was contacted with the 1 mM $BTPPA_2PtCl_6$ dissolved in 1.2-DCE and 100 mM $NaBF_4$ dissolved in miliQ water. FTO was traversed the planar liquid – liquid interface or a 5 μL droplet was cast on top of it. The Ag/AgCl reference electrode and the Pt counter electrode were always placed in the aqueous phase. The corresponding schemes are available in Fig. 3-A and -B in the text of main manuscript. Pt NPs deposition was performed using chronoamperometry at $E = -1.5$ V.

2.5 Pt NPs deposition with planar liquid – liquid interface

The microcapillary described in section 2.3 was filled with the organic phase being 1 mM solution of $BTPPA_2PtCl_6$ in 1.2-DCE. Next, with the help of the step motor this capillary was approached to the FTO support (the approached was stopped when an edge of the capillary contacted the FTO electrode). The solution of 10 mM $NaBF_4$ in 250 mM $NaNO_3$ was added. The $E = -1.5$ V was applied to the FTO and hold for 30 minutes. The reference and the counter electrodes were Ag/AgCl and Pt wire respectively.

2.6 Electrochemically assisted hydrogel deposition

In all cases, the electrochemically assisted hydrogel deposition was conducted on the FTO electrode decorated with Pt NPs used as the working electrode. Ag/AgCl and Pt served as the reference and counter electrode respectively. The working electrode was polarized towards anodic potential values during linear sweep voltammetry scan. The starting potential was set to 0 V and the stop potential was set to 3.0 V. The hydrogel formation was monitored with optical polarization microscopy and the experiment was stopped when the hydrogel framework was disrupted by the oxygen bubble(s) formation (usually in the potential range from 2.0 V to 2.5 V). The scan rate was 10 $mV \cdot s^{-1}$.

3. Water – 1,2-dichloroethane partition coefficient and Gibbs free energy of ion transfer calculations

The electrochemistry at the liquid – liquid interface can serve as a simple tool for the partition coefficient calculation, and hence, allows for the evaluation of the molecular hydrophilicity. The potential drop across the polarized liquid – liquid interface can be described with the Nernst like equation for the ion transfer reaction:

$$\Delta_{org}^{aq}\phi = \Delta_{org}^{aq}\phi_i^0 + \frac{2.303RT}{z_iF}log\frac{a_i^{org}}{a_i^{aq}}$$

(eq. 2)

where $\Delta_{org}^{aq}\phi$ is the potential applied from the external power source across the liquid – liquid interface, $\Delta_{org}^{aq}\phi_i^0$ is the standard Galvani potential of ion "I" transfer, z is the chare of the transferring ion, $a_i^{org\ or\ aq}$ is the ion activity in the organic or the aqueous phase whereas R, T and F have their usual meanings. Partition coefficient can be simply defined as:

$$logP_{aq/org}^{i} = log\frac{a_i^{org}}{a_i^{aq}}$$

(eq. 3)

Eq. 2 can be rearranged so that the $logP_{aq/org}^{i}$ can be expressed with $\Delta_{org}^{aq}\phi$ and $\Delta_{org}^{aq}\phi_i^0$:

$$logP_{aq/org}^{i} = \frac{\Delta_{org}^{aq}\phi z_iF}{2.303RT} - \frac{\Delta_{org}^{aq}\phi_i^0 z_iF}{2.303RT}$$

(eq. 4)

Furthermore, one can define the standard value of portion coefficient $(logP_{aq/org}^{i,0})$ with only $\Delta_{org}^{aq}\phi_i^0$:

$$logP_{aq/org}^{0,i} =- \frac{\Delta_{org}^{aq}\phi_i^0 z_iF}{2.303RT}$$

(eq. 5)

The $\Delta_{org}^{aq}\phi_i^0 z_iF$ for BF_4^- was taken from literature, whereas for $PtCl_6^{2-}$ it was calculated using following expression:

$$\Delta_{org}^{aq}\phi_i^0 = \Delta_{org}^{aq}\phi_{1/2}^{ref} - \frac{2.303RT}{z_iF}log\frac{\gamma_i^{org}}{\gamma_i^{aq}} - \frac{2.303RT}{z_iF}\log\left(\frac{D_i^{aq}}{D_i^{org}}\right)^{0.5}$$

(eq. 6)

Where $\Delta_{org}^{aq}\phi_{1/2}^{ref}$ (taken from ion transfer voltammogram) is the half-wave potential, $\gamma_i^{aq\ or\ org}$ and $D_i^{aq\ or\ org}$ are the activity coefficients and diffusion coefficients of ion "i" in the concerned phase, respectively.

Moreover, with the knowledge of $\Delta_{org}^{aq}\phi_i^0$ we can easily calculate the standard Gibbs free energy of the ion transfer reaction:

$$\Delta_{org}^{aq}G_i^0 = zF\Delta_{org}^{aq}\phi_i^0$$

(eq. 7)

Calculated values of $\Delta_{org}^{aq}G_{BF_4^-}^0$ and $\Delta_{org}^{aq}G_{PtCl_6^{2-}}^0$ equal to -19.4 and -29.1 $kJ\cdot mol^{-1}$ respectively.

4. X-ray Photoelectron Spectroscopy (XPS)

XPS characterization was done on Thermofisher Scientific (K-alpha surfaces analysis) instrument using a 400 μm) beam spot. The survey scan is shown in Fig. SI4-A. The majority of the peaks obtained were that for Tin and Oxygen. In the grey spot (Fig. SI4-C) the XPS spectra indicate the presence Pt as shown by the two peaks found around 71 and 74 eV respectively[5] (**Figure S4B**). Additionally, the line scan (Figure S4D) performed from the edge of the grey spot towards the region that was not exposed to H_2PtCl_6 solution during electrochemical deposition show a clear decrease in the Atomic % of Pt as opposed to Sn.

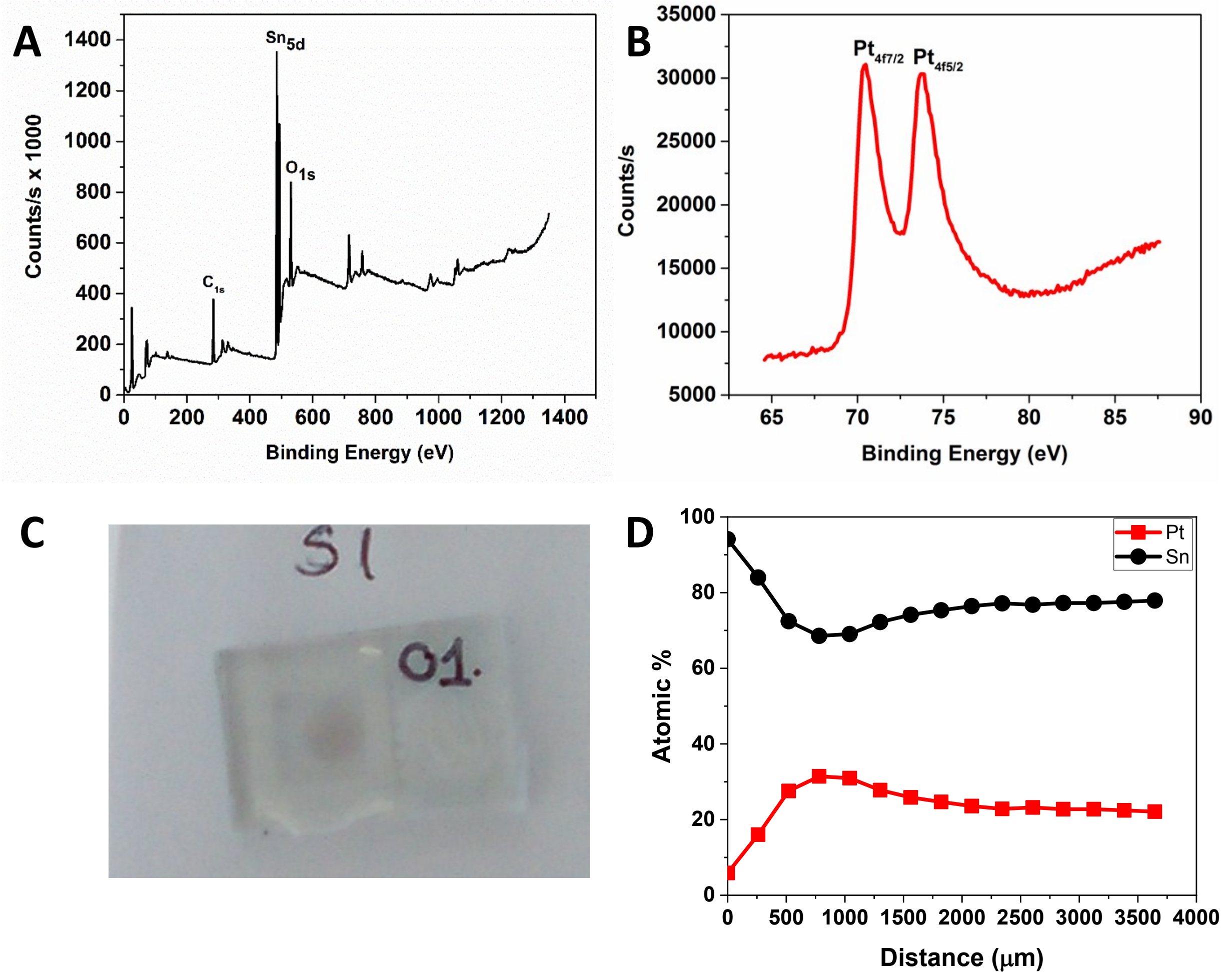


Figure S4. XPS characterization of Pt deposited FTO substrate. Survey scan (A) showing major observed peaks. Narrowed down region showing two peaks for Pt (B). Image of the sample used for XPS characterization (C). Line scan (D) spectra recorded from the edge to centre of the grey spot in (B) shows an increase in Atom % of Pt indicating the presence of Pt.

5. Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS)

SEM and EDS characterization was performed on a JEOL JSM 6010 InTouchScope™ microscope. Pt deposited FTO substrates were loaded onto the SEM sample holder and kept in place by the means of carbon tape. They were placed in the imaging chamber under vacuum. Images were recorded at an acceleration voltage of 20kV at various magnifications. EDS spectra was recorded of the samples by focusing on the region of interest, to obtain a map of elemental distribution (EDS elemental mapping). Particle size analysis was carried out using Fiji (ImageJ V2.0.0-rc-69/1.52i). A total of 100 particles were analysed.

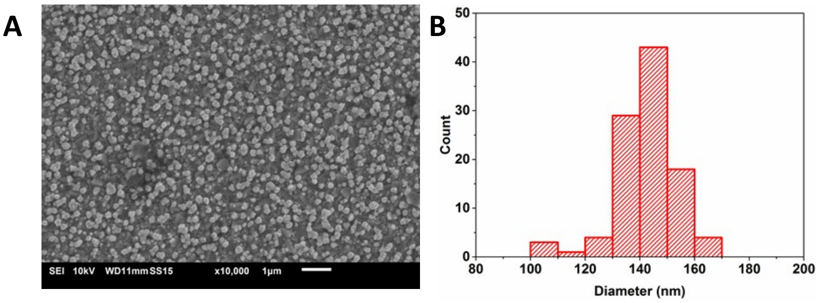
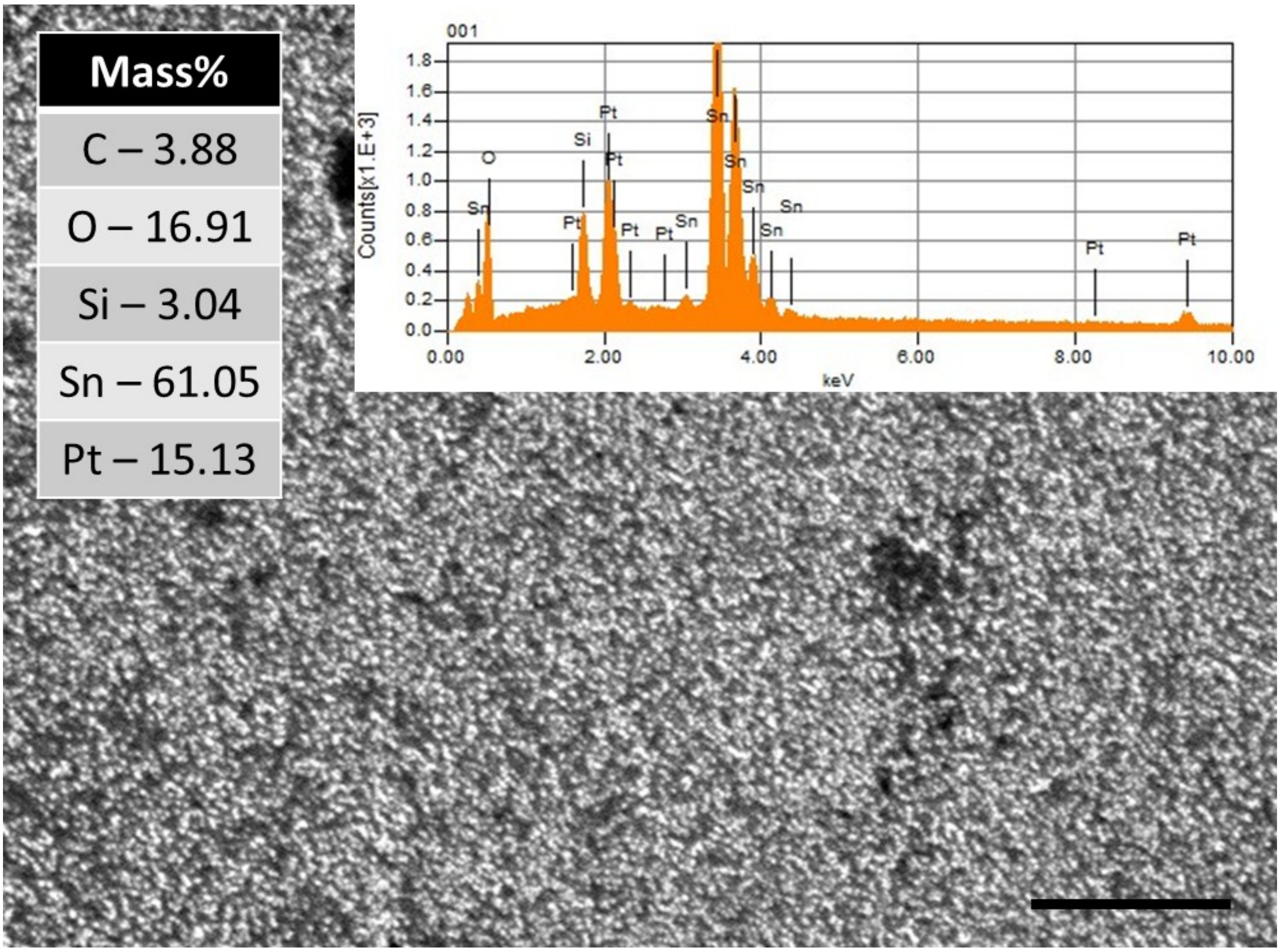


Figure S5. Full scale SEM image from Figure 1C (A) and histogram (B) of particle sizes based on image analysis.



Mass%
C – 3.88
O – 16.91
Si – 3.04
Sn – 61.05
Pt – 15.13

Figure S6. SEM image of the FTO modified with Pt NPs from 1 mM K_2PtCl_6 solution with corresponding EDS spectra (right inset). Table available in the left corner of the figure gives mass%.

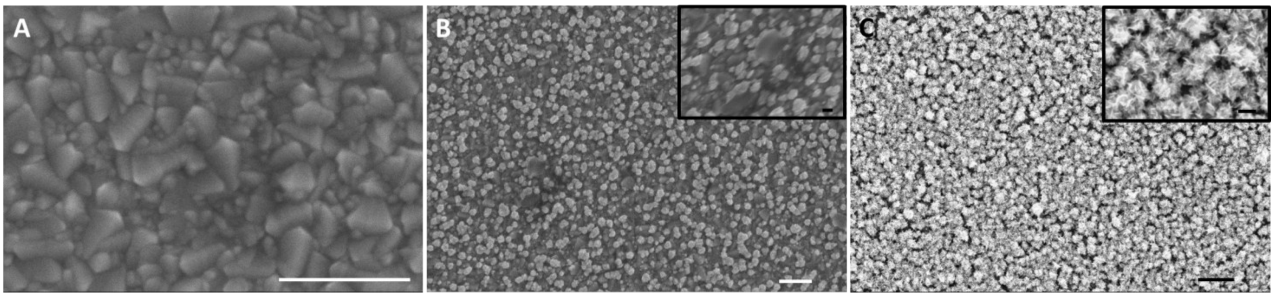


Figure S7. SEM image of the A – bare FTO; B – FTO modified with Pt NPs after 10 minutes deposition time and C – FTO modified with Pt NPs after 20 minutes deposition time. $E_{deposition}$ = – 1.5V from 1 mM K_2PtCl_6 in 0.25 M $NaNO_3$.Scale bars correspond to 1 μm (inset 200 nm).

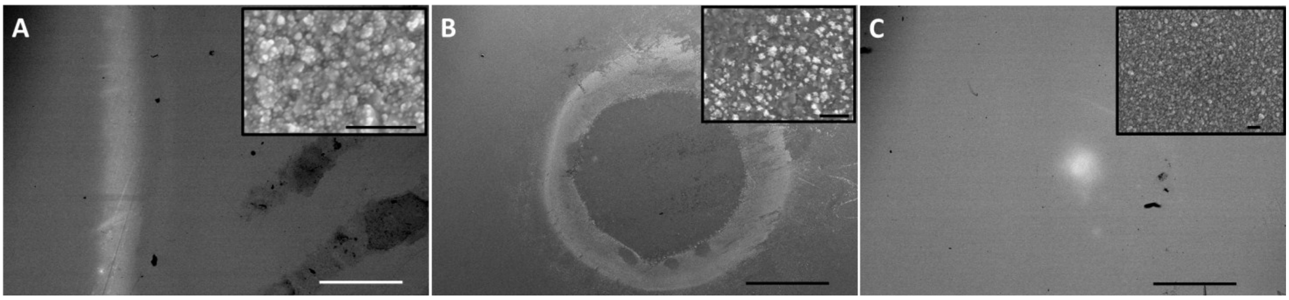


Figure S8. SEM image of the A – Pt NPs stripe ($t_{deposition}$ = 10 min, $E_{deposition}$ = – 1.5V); B – Pt NPs ring ($t_{deposition}$ = 10 min, $E_{deposition}$ = – 1.5V); and C – Pt NPs μ-spot ($t_{deposition}$ = 20 min, $E_{deposition}$ = – 1.5V). Concentration of $BTPPA_2PtCl_6$ in DCE was equal to A – 1 mM and B and C – 5 mM. Insets shows the regions with Pt NPs. Scale bares: 500 μm (inset 1 μm).

6. Transmission Electron Microscopy (TEM) & Cryo-TEM

Pt NPs deposited over Formvar® coated Cu grids were imaged in a JEOL JEM 1400 Plus electron microscope equipped with a TViPs 4K camera and EDS detector at an acceleration voltage of 120V using a single-tilt holder. Deposition was performed from 1 mM H_2PtCl_6 in 250 mM $NaNO_3$ solution at E = –1.5V for 10 min. For Cryo-TEM experiments, Quantifoil^{TM} R1.2/1.3 100 Holey carbon Cu 200 mesh grids were first coated with Pt The coated grids were held on a forcep and placed inside a solution of gelator precursor and electrolyte (setup shown in **Figure S8B**). Hydrogel was deposited through Linear-Sweep Voltammetry (Grid – WE, Pt strip – CE & RE) at the rate of 10mV/s from 0 to 1.8 V. The grids were then loaded onto the loading station of a Leica Vitribot with Cryogen (liquid ethane maintained -185°C using liquid Nitrogen). The grids were immediately plunged into the Cryogen and transferred to the electron microscope. Images were recorded at an acceleration voltage of 120V under low dose conditions.

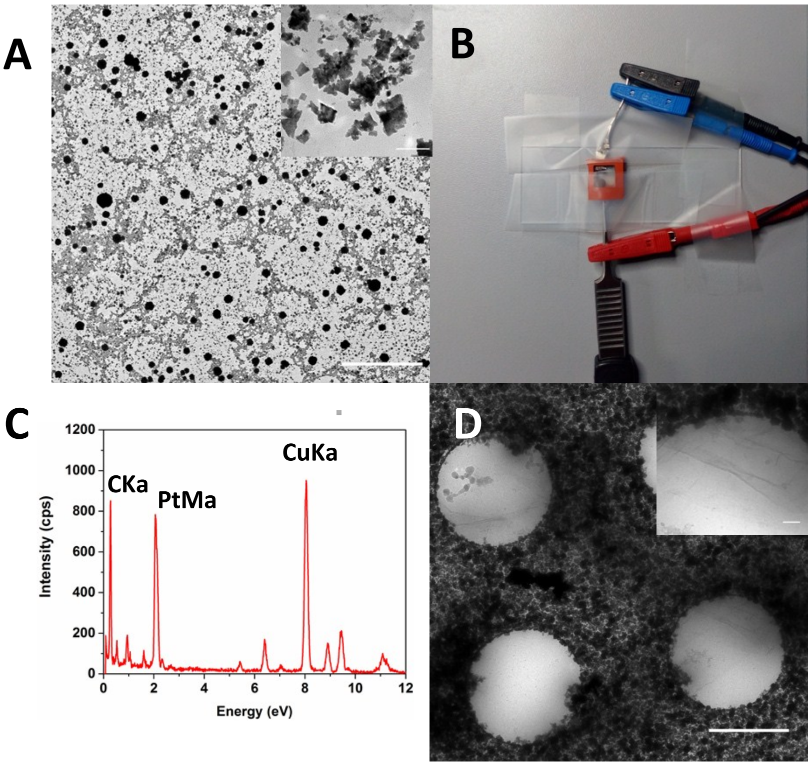


Figure S9. Transmission Electron Microscopy Characterization of Pt NPs (A) which were used in this work. Optical image (B) showing electrode configurations, red – working electrode, blue and black – counter and reference electrode respectively. EDS spectra shows presence on the Platinum (NPs), Carbon (from TEM grid) and Copper (from TEM grid). Cryo-TEM images shower hydrogel fibers formed using linear-sweep voltammetry. Scale bars are: 2 µm and 1 µm (A & D) and inset scale bars are 50 nm (A) and 100 nm (D) respectively.

7. Polarization Optical Microscopy (POM)

For Optical and Polarization microscopy measurements, Nikon Eclipse E600 POL microscope was used. Pt NPs coated FTO substrates were fastened to a slide by means of a scotch tape. The unit was then placed under the objective of the microscope. For electrochemical hydrogel formation, two rubber square spaces were placed on top on the FTO substrate in order to hold the gelator salt solution (40mM Na_2DBC in 250mM $NaNO_3$). To prevent lensing effect from the solution, a glass coverslip was placed on top. All connections were then made with the potentiostat. Illumination was provided using the microscope on Diascopic mode. Hydrogel formation was observed at different magnifications (5 – 20X) both under normal and polarized (polarizer and analyser were 90° to each to other) conditions.

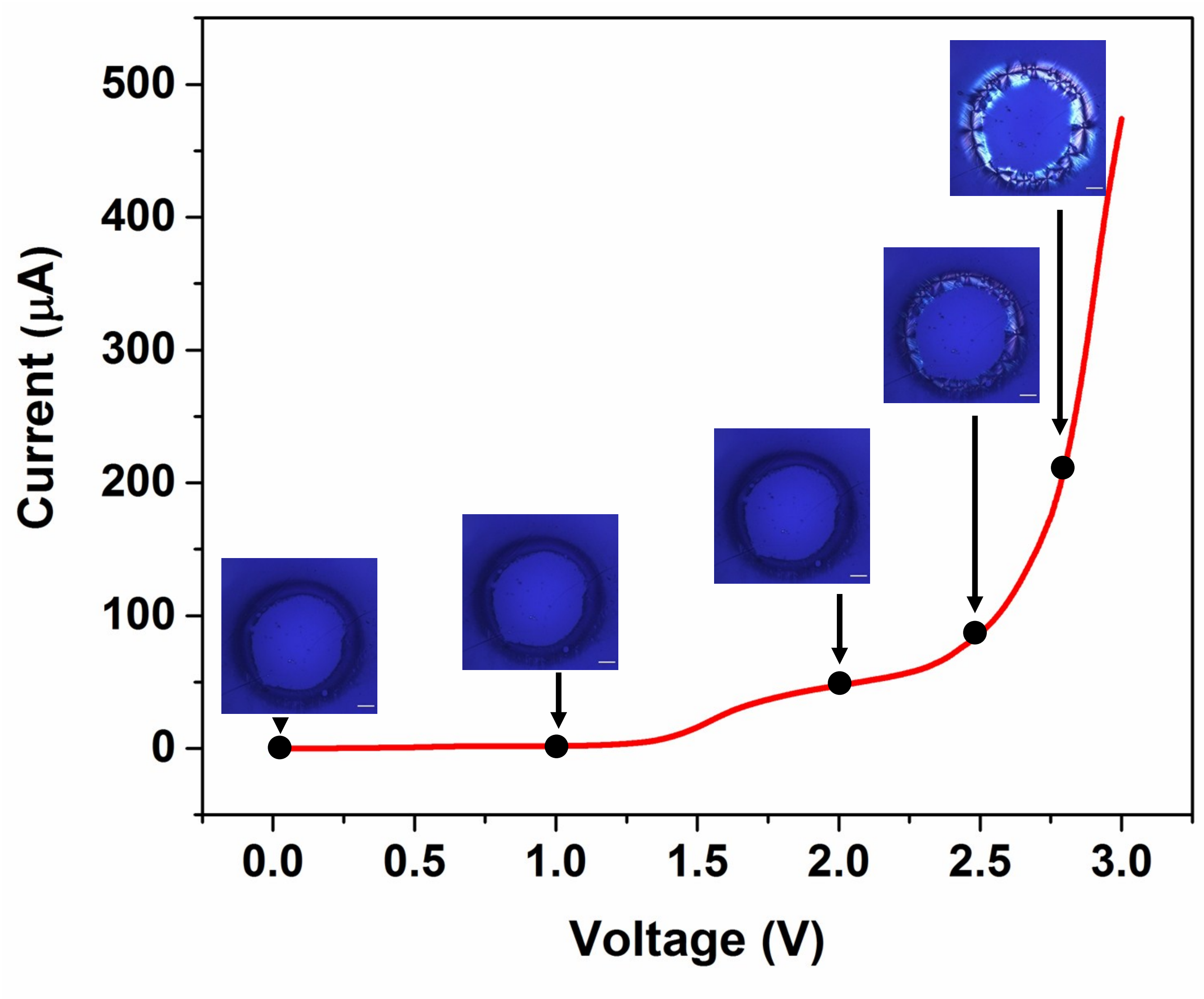


Figure S10. Linear sweep voltammogram with forward polarization towards anodic potential and scan rate equal to 10mVs^{-1} recorded atFTO electrode decorated with Pt NPs in the shape of a ring. Hydrogel formation as followed by optical microscopy under cross-polarizers progressively increases with time as indicated by the increase in the current intensity (increase in number of oriented fibres). Scale bar of microscopy images is 200 μm.

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