

## Electronic supplementary information

### Enhanced oxygen reduction reaction activity and durability of Pt nanoparticles deposited on graphene-coated alumina nanofibres

Sajid Hussain,<sup>a</sup> Nadezda Kongi,<sup>a</sup> Alexey Treshchalov,<sup>b</sup> Tauno Kahro,<sup>b</sup> Mihkel Rähn,<sup>b</sup> Mairo Merisalu,<sup>b</sup> Aile Tamm,<sup>b</sup> Väino Sammelselg<sup>b</sup> and Kaido Tammeveski<sup>a,\*</sup>

<sup>a</sup>*Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia*

<sup>b</sup>*Institute of Physics, University of Tartu, W. Ostwald Str. 1, 50411 Tartu, Estonia*

\*Corresponding author. Tel.: +372 7375168; E-mail: [kaido.tammeveski@ut.ee](mailto:kaido.tammeveski@ut.ee)

#### Plasma-assisted synthesis

A simple, one-step plasma-assisted synthesis (PS) method similar to that described in our previous works<sup>1-3</sup> was applied for the synthesis and simultaneous decoration of fibres by well-dispersed Pt nanoparticles (NPs). Briefly, an atmospheric pressure pulsed (13 kHz) discharge in He/H<sub>2</sub> (95/5) gas jet with a continuous gas flow of 150 sccm was used for the net injection of electrons into the solution. The current flow was arranged from a thin stainless-steel capillary (inner diameter of 150 μm) served as a cathode through a plasma jet (a distance between the capillary and the liquid surface was about 6 mm) and over the electrolyte to a grounded Pt foil counter electrode immersed in the liquid. A 1.8 MΩ resistor was used to limit the current peak value to about 2 mA (the current density on the surface of the electrolyte was estimated as 0.2 A cm<sup>-2</sup>). The temperature of the liquid did not exceed 40 °C during the plasma treatment. After the plasma processing during 15 min, the characteristic absorption band of PtCl<sub>6</sub><sup>2-</sup> species at 261 nm was no longer detectable,<sup>4,5</sup> suggesting that these anions were completely reduced. During plasma processing, a high local density of solvated electrons is generated at the plasma-liquid interface. Thus, we consider that Pt NPs nucleate and grow predominantly in a very small volume close to the interface layer due to the reduction of PtCl<sub>6</sub><sup>2-</sup> anions by solvated electrons e<sup>-</sup><sub>aq</sub>. This localized zone can be qualified as a nanosized electrochemical reactor.<sup>6,7</sup> According to Rumbach et al.,<sup>8</sup> the penetration depth of e<sup>-</sup><sub>aq</sub> is only 10 to 100 nm due to the diffusion-limited second-order recombination process:



Besides, due to the low initial concentration of PtCl<sub>6</sub><sup>2-</sup> species, their transport-limited depletion layer near the plasma-liquid interface is of the same order of magnitude.<sup>9</sup> Therefore, the size of the synthesised Pt NPs is inherently limited by the amount of reactants in the depletion layer.

It was noticed that the higher is the discharge current density as well as the concentration of the  $\text{PtCl}_6^{2-}$  anions in the start solution, the larger Pt NPs were produced during the plasma processing. We suggest that the growth of Pt NPs is stopped by the electrostatic stabilisation mechanism<sup>10</sup> until sufficient negative surface charge on the Pt NPs is accumulated in a strongly alkaline interface layer.<sup>11</sup> Conductive fibres, which penetrate from the acidic bulk solution into the interfacial layer due to ultrasonic mixing, have a positive surface charge. The opposite charges of Pt NPs and support is a good prerequisite for the effective binding of Pt NPs to the graphenated fibre surface due to the electrostatic attraction. The low-power ultrasonic waves do not play a sonochemical role here, but rather a mechanical role of forced convection of the solution by cavitation micro jets.<sup>12,13</sup> After the plasma treatment procedure, acidic suspension was formed (pH 3.4) which was precipitated after several hours.

### **Sonoelectrochemical deposition**

In sonoelectrochemical deposition (SD), Pt-based nanocomposite was synthesized by a modified pulsed electrodeposition procedure combined with a low-power ultrasound. The commonly used sonoelectrochemical technique is based on applying a cathodic electric current pulse to the electrode to nucleate and grow NPs from the electrolyte, followed by a burst of ultrasonic wave to remove NPs from the surface.<sup>13</sup> The distinct differences between the technique in our report and previous sonoelectrochemical methods are the use of alternating electrodeposition current and the absence of any special synchronisation between the pulses of electrodeposition current and bursts of ultrasonic waves.<sup>12,14</sup> This simple, one-step technique allows decorating the surface of conductive graphenated fibres suspended in an electrolyte solution with small Pt NPs in situ, upon their synthesis while Pt particles have inherently good electrical contact with the support. The loading of Pt NPs in this nanocomposite was easily changed from a homogeneous widespread distribution to rather dense multilayers of NPs by controlling the current amplitude, concentration of electrolyte and fibres as well as duration of the processing.

4 mL of 0.05 mM  $\text{H}_2\text{PtCl}_6$  aqueous solution with small additives of the nanofibres was used as an electrolyte in a sealed quartz cell. After the deaeration procedure by He, the same He gas was passed above the solution during the electrodeposition process. Two Pt foil electrodes, each with a surface area of 0.5 cm<sup>2</sup> were immersed into the electrolyte. The distance between the electrodes was 0.9 cm. During the synthesis, the electrodes were connected to the 50 Hz sin wave alternating current source operating at 30 V and the processing current was 10 mA. Visually no bubbles were observed on the electrodes due to electrolysis of water. Sonication

of the solution was arranged by a low-power ( $\sim 1$  W) ultrasonic (1.7 MHz) transducer contacted the bottom of the quartz cell. After the sonoelectrochemical processing during 30 min the characteristic absorption band of  $\text{PtCl}_6^{2-}$  anions at 261 nm disappeared,<sup>4,5</sup> suggesting that these Pt species were completely reduced. The temperature of the solution did not exceed 30 °C during the sonication treatment.

The principal role of the ultrasound is the increase in mass transfer induced by extreme solution mixing caused by cavitation micro jets.<sup>12</sup> These jets initiate very intense motion of fibres near the electrode surface. When conductive fibres come into contact with Pt foil during the cathodic 10 ms half-period pulse, they serve as cathode and electrodeposition current is mainly concentrated to these fibres. Despite rather small average current density ( $\sim 20$  mA  $\text{cm}^{-2}$ ), the local current density, which is a driving force for the nucleation and growth of Pt NPs was several orders of magnitude higher on fibres than on the flat surface of the foil. This regime of high overpotential, high current density and very short electrodeposition time (much less than 10 ms due to 1.7 MHz bursts of ultrasonic waves) provides ideal conditions for the nucleation and growth of small Pt NPs at high density over the surface of fibres.<sup>15</sup>

When fibres with Pt NPs come into contact with the electrode during the anodic polarisation pulse the electrochemical oxidation of the surface of Pt NPs takes place. The thin oxide layer easily reduces under cathodic polarisation pulse. We suggest that after 30 min of pulsed electrodeposition the vast majority of nanofibres inside 4 ml bulk solution have equalised probability for contacting the electrodes due to stochastic averaging caused by intense ultrasonic agitation of the solution. Multiple cycles of oxide formation (anodic polarisation) – reduction (cathodic polarisation) lead not only to the cumulative formation of high density of Pt ad-islands, but also to substantial “roughening” of the surface of nanoparticles.<sup>16,17</sup>

## Surface morphology of the graphene-coated alumina nanofibres

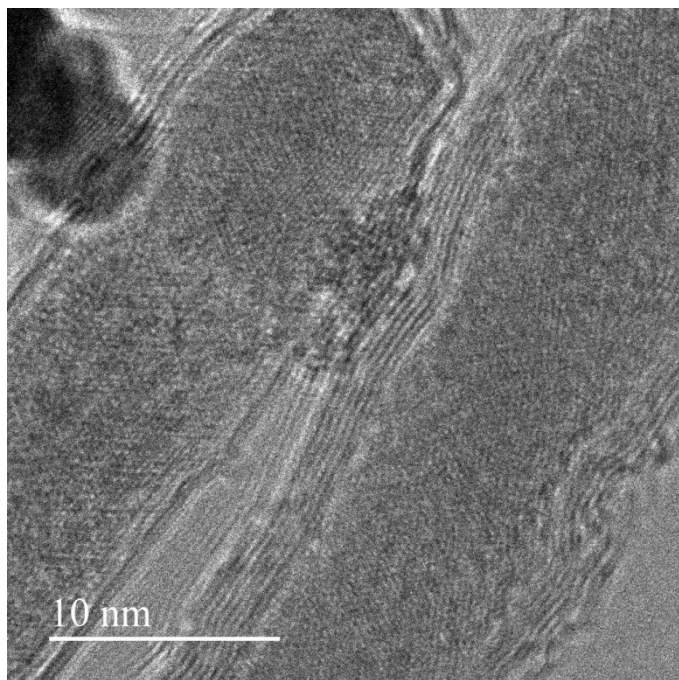


Figure S1. HRTEM image of the alumina nanofibres covered with few-layer graphene.

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