Supporting information

Wireless Electrochemical Light Emission in Ultrathin 2D Nanoconfinements

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1. Experimental section

Materials. Sodium dodecyl sulfate (SDS), graphite, glycerol, polyoxyethylene (10) cetyl ether (Brij C10), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate chloride ($Ru(bpy)_3Cl_2$), and 2-(dibutylamino) ethanol (DBAE), sodium phosphate, potassium phosphate and sodium chloride were purchased from Sigma-Aldrich.

Graphene microplatelet solutions. The solution that is used for bubble preparation contains a mixture of 5/4 glycerol/H_2O (phosphate buffer, pH=7.4) together with 2.5 mM tris(2,20-bipyridyl) dichlororuthenium(II) hexahydrate chloride (luminophore); 20 mM 2-(dibutylamino) ethanol (DBAE, co-reactant); 0.125 μg/ml Brij C10 (Polyoxyethylene (10) cetyl ether); and 0.1, 1 or 4 mg ml^{-1} graphene sheets. *Preparation procedure:* grounded graphite powder (10 mg ml^{-1}) was poured into the argon bubbled solution containing a mixture of 5/4 glycerol/H_2O and Brij C10 in a conical tube. The sonication was performed for 20 minutes with a 60-sec rest between each 120-sec sonication pulse, using a custom tip sonicator setup in an ice bath to avoid heating of the samples above 25˚C. The obtained solutions were centrifuged for 2 min at 500 rpm and 80% of the supernatant was collected and used for electrochemiluminescence (ECL) studies without further purification. The desired graphene concentrations were achieved by diluting the obtained solution while keeping a 5/4 glycerol/H_2O ratio and 0.125 μg/ml Brij C10 concentration. The concentration of the graphene particles was controlled by washing/centrifugation the solutions several times using DI water followed by weighting the graphene powder after drying it at 150 ºC for 24h. Next, the luminophore and DBAE were added to the graphene solutions to achieve the abovementioned concentrations.

Bubbles. Bubbles were generated at the tip of a disposable pipette (tip opening: 2 mm) containing ~ 10 µl of the above-described solution. Upon gentle pipetting, a bubble was formed. The bubbles were grown up to a size that fits the bipolar setup (0.3 and 0.6 mm).

Graphene dispersibility. Each of the freshly prepared 0.1, 1 and 4 mg ml^{-1} graphene solution was divided into 4 portions (each 5 ml). The samples were bath sonicated for 20 min followed by removal of the top 30% solution, immediately after sonication, and after 1, 2, and 4 min. The obtained solutions were several times washed by DI water (rpm: 5000, 10 min) and finally dried at 150 ºC for 24h and their weight was compared to the initial concentration. The obtained graphene microplatelets with 0.1, 1 and 4 mg ml^{-1} concentrations demonstrated average sizes of 1.16, 2.26, and 4.92 µm, respectively (DLS measurements).

Electrochemiluminescence (ECL). The ECL measurements were performed using a homemade setup. The setup was designed by punching a circular hole in the middle of a plastic substrate. The two opposite sides of the hole were decorated with carbon paper, acting as feeder electrodes. To avoid any direct contact between feeder electrodes and the bubble, the electrodes were fully covered with Nafion membranes. The membranes have been added to avoid a direct contact between the feeder electrodes and the bubble, to prevent bursting of the bubbles and to ensure that the graphene sheets do not encounter the electrodes. In order to perform the experiments at the desired temperature, a container (radius: 3.5 cm, depth: 3 cm) was first filled with 40 ml liquid nitrogen (LN_2). After evaporation of LN_2, the bipolar setup was placed in the container. The setup was initially soaked in glycerol/H_2O solution to inhibit the immediate freezing of feeder electrodes after placing them in the cold container, to accelerate the charge

transfer between the feeder electrodes and bubbles. The bubble formed at the tip of a disposable transfer pipette was placed inside the bipolar setup. The feeder electrodes were attached to a power supply to apply the desired potentials. Experiments were monitored by using a CCD camera (CANON EOS 70D, Objective Canon Macro Lens 100 mm 1:2.8). Images were processed with Image J software.

Scanning Electron Microscopy (SEM). SEM experiments were carried out using a Vega3 Tescan 20.0 kV microscope.

2. Exfoliation of graphite

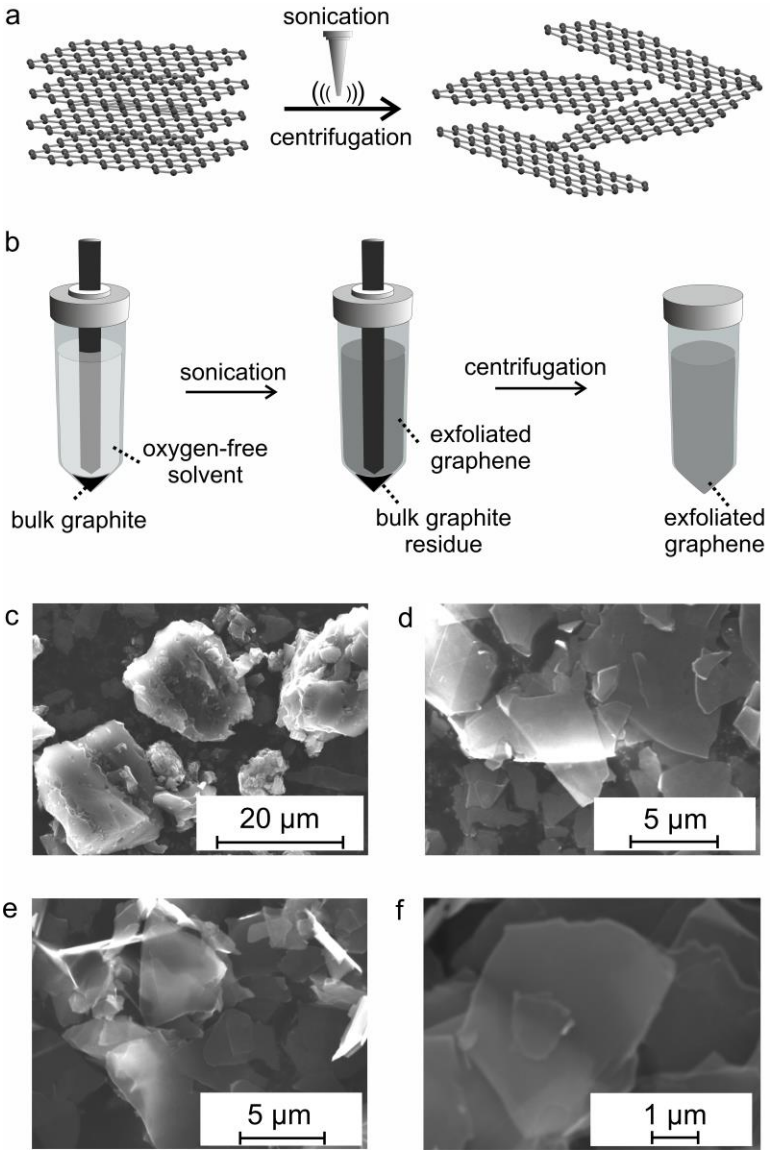

Figure S1. Exfoliation of graphite particles. a) Exfoliation of graphite with a layered crystal structure by a sonication/centrifugation procedure. b) Schematic illustration of the tip sonication setup by minimizing the exposure to ambient air. SEM images of graphite particles (c) and exfoliated sheets (d-f).

3. Bubbles shrinkage/bursting

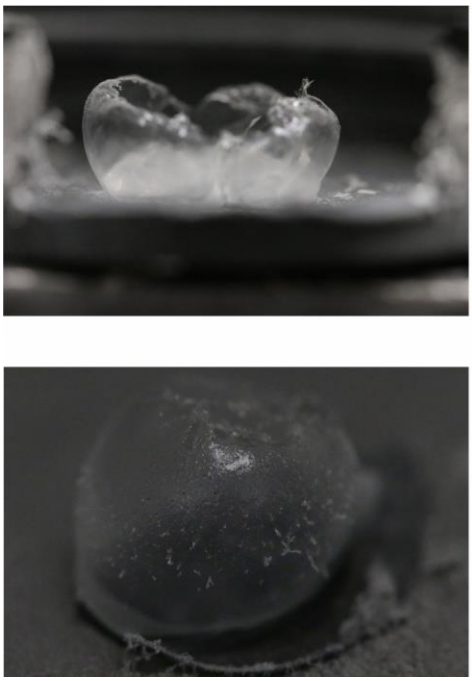

Figure S2. The stability of bubbles in a -24 ºC environment. Bubbles shrink (top) or burst (bottom) at low temperatures; 6 mm bubbles.

4. Bubble stability

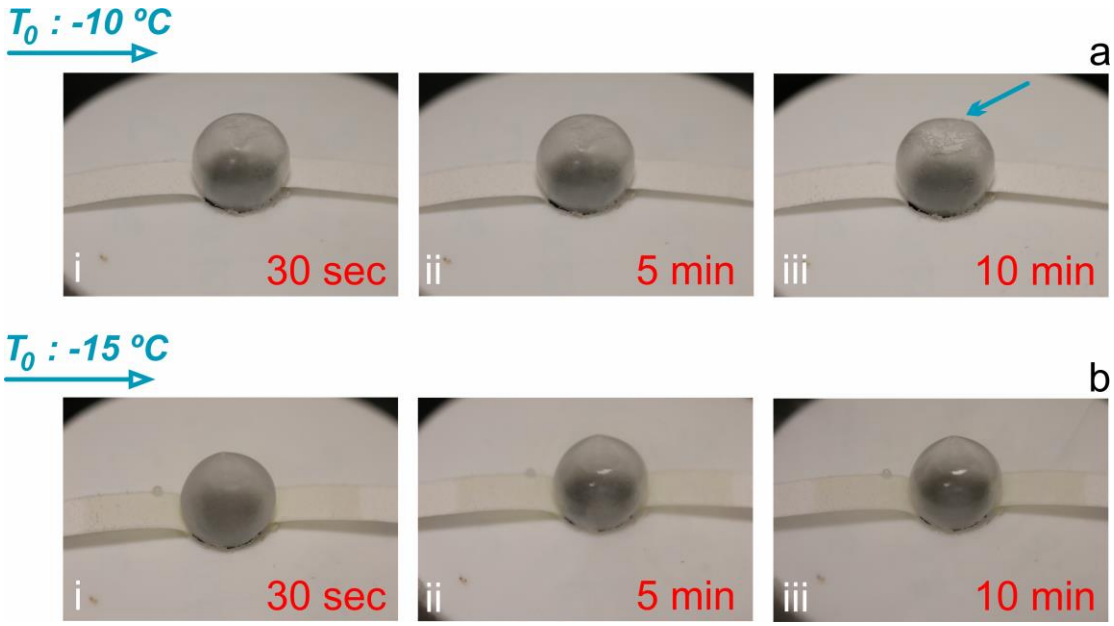

Figure S3. The stability of bubbles at an initial ambient temperature of -10 ºC and -15 ºC in a bipolar setup without applying potential. Bubble breaking occurs after 10 min for the sample that was kept in a container with an initial temperature of -10 ºC, while the sample in the -15 ºC container was still stable after 10 min. As can be seen, the breaking/melting starts from the top part (a-iii, blue arrow), where the bubble warms up first; 6 mm bubbles.

5. Graphene microplatelet aggregates: DLS measurements

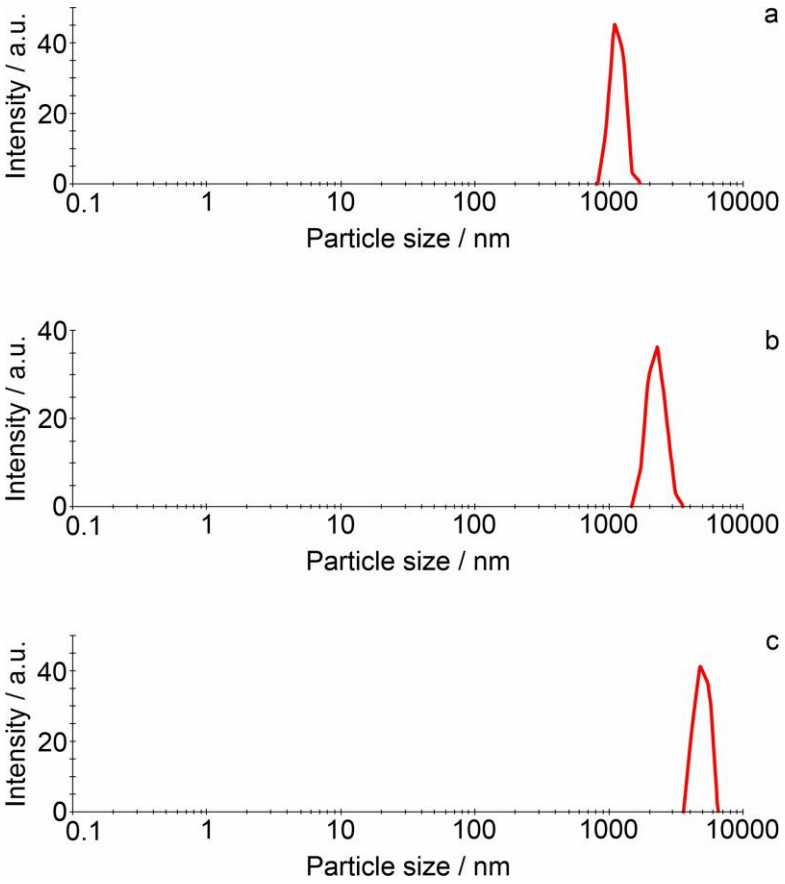

Figure S4. Dynamic light scattering (DLS) of exfoliated graphene microplatelets with 0.1 (a), 1 (b) and 4 (c) mg ml^{-1} concentrations with average sizes of 1.16, 2.26, and 4.92 µm, respectively.

6. Bipolar setup

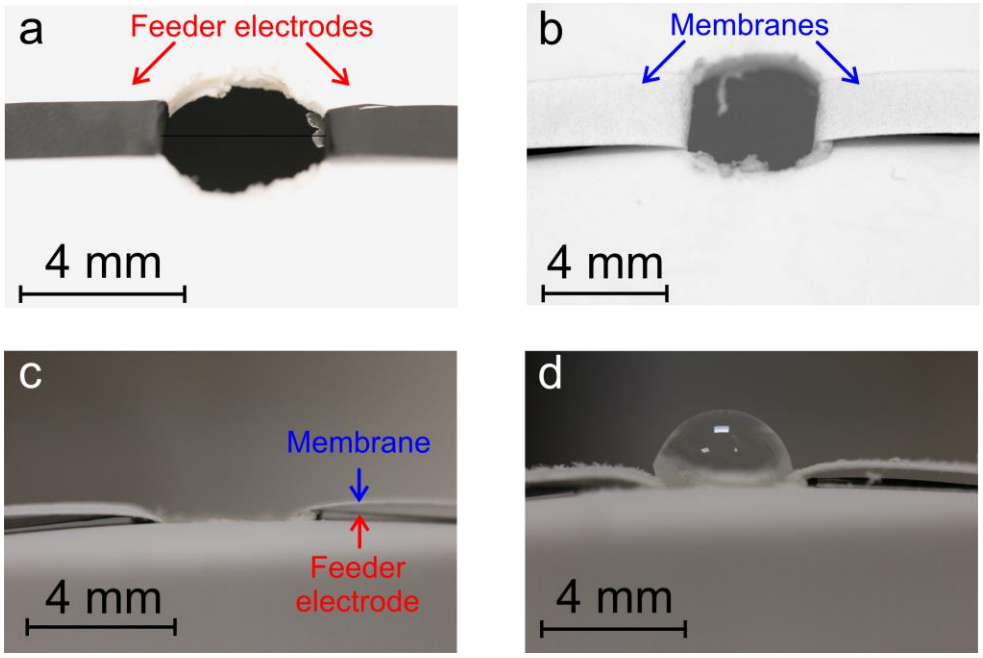

Figure S5. Experimental bipolar electrochemical setup. Carbon feeder electrodes (a) covered by a membrane (b, c). d) A bubble positioned between the two membranes, protecting the feeder electrodes.

7. ECL intensity for bubbles in a 3 mm setup

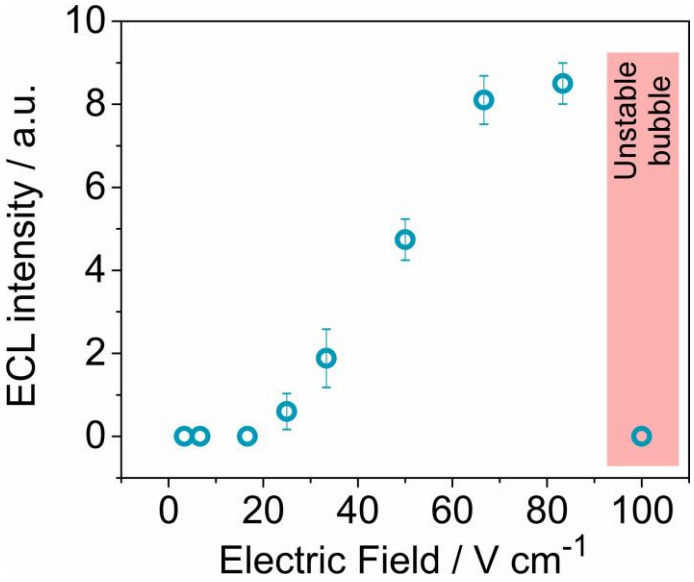

Figure S6. Effect of the magnitude of the electric field on the ECL intensity of 3 mm diameter bubbles in the presence of 1 mg ml^{-1} graphene microplatelets. In comparison to the 6 mm diameter bubbles, applying the same range of potentials (1 – 30 V) on the smaller bubbles resulted in ECL at lower potentials and higher intensities. This behaviour is explained based on Equation S1, where the value of an electric field (ε) between two feeder electrodes is a function of the difference of potential between the feeder electrodes (ΔE) and the distance between two electrodes (d):[1]

$$\varepsilon = \frac{\Delta E}{d} \qquad \text{Eq. S1}$$

Although higher ECL intensities were observed for the smaller bubbles, the intensity enhancement does not scale linearly with the distance between the feeder electrodes. This is attributed to the faster melting of bigger bubbles upon applying potential, due to the Joule effect

and hence an accelerated mass transfer in the walls. The frozen bubbles typically start to melt from the top (Figure 2b).

8. ECL of coupled bubbles

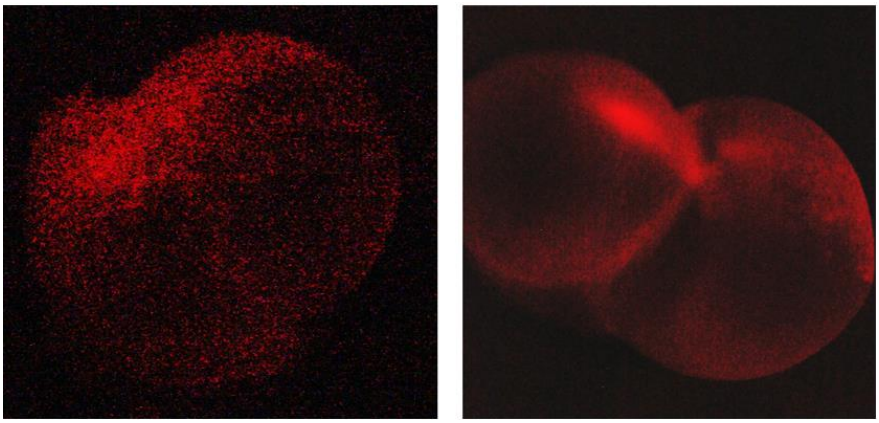

Figure S7. Two examples of ECL generated with coupled bubbles recorded at 33 V cm^{-1} using a bubble solution with 4 mg ml^{-1} graphene sheet content.

1. L. Bouffier, D. Zigah, N. Sojic and A. Kuhn, in *Encyclopedia of Electrochemistry*, DOI: https://doi.org/10.1002/9783527610426.bard030112, pp. 1-53.