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Wireless Electrochemiluminescence at Functionalised Gold Microparticles Using 3D Titanium Electrode Arrays

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1. Experimental

1.1 Reagents and Materials. 45 μ m diameter gold particles (Goodfellow) were cleaned by boiling it in concentrated HCl until the supernatant became clear. The gold microparticles (AuMP) were then isolated by centrifugation and repeatedly washed using Milli-Q water (resistivity = 18 M Ω cm). 0.5 g of the clean gold microparticles were functionalised with 10.2 nmols of 11-mercaptoundecanoic acid, MUA (30 mL, dilute acetic acid), by stirring the reaction mixture for 72 h. Thereafter the MUA modified gold microparticles, AuMP-MUA, were washed three times in H₂O using the centrifugal precipitation and re-dispersion approach.

1.2 Instrumentation. All conventional electrochemical experiments were performed using a CH Instruments, Model 760B Electrochemical Workstation in a three-electrode cell setup comprising the 3D titanium array as the working electrode, a CH Instruments silver/silver chloride (Ag/AgCl) as the reference electrode and a platinum wire (Sigma Aldrich) as the counter electrode. For bipolar experiments, two 3D titanium arrays were used as feeder electrodes and a direct current power supply (Tenma Bench, Output 0 to 30 V dc, 0 to 2A)

was employed to generate the electric field required between the two arrays. The two titanium feeder arrays were interdigitated and placed on a plastic platform 2 cm above the bottom of a 25 cm³ cell. This allowed the AuMP-MUA particles to be kept in suspension by gentle stirring. The intensity of the ECL was measured with an Oriel 70680 photomultiplier tube (PMT) biased at -850 V using a high-voltage power supply (Oriel, Model 70705) and an amplifier/recorder (Oriel, Model 70701). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) was performed using a Hitachi S5500 Field Emission SEM. Particle sizing was carried out by dynamic light scattering on a Delsa Nano C submicron particle size and zeta potential particle analyzer with the standard size cell accessory. Confocal imaging was carried out using a Leica TSP DMi8 confocal microscope with immersion objective lenses between 10 and 100 x.

1.3 Fabrication of 3D-Printed electrode. 3D printed titanium electrodes were fabricated according to a procedure reported previously.¹ The electrode design was drawn using SolidWorks modelling software. Metal 3D printing was carried out with a Realizer SLM50 metal printer (Realizer, Germany) using selective laser melting (SLM). A focused, high-energy laser beam fused and linked Ti alloy (Ti-6AI-4V) powder on a printing stage in a layer by layer fashion to create an array of 25 vertical round microcylinders (0.015 cm radius, 0.8 cm high) spaced evenly on a 0.48 x 0.48 cm square base that contained 0.75 x 0.75 mm holes.

2. Characterisation and Stability of Titanium Electrodes. As shown in Figure S1(a), the surface of the individual grains within the titanium electrode show roughness on the micrometre length scale. Significantly, as shown in Figure S1(b), using the titanium electrodes as feeder electrodes for 60 minutes with a potential difference of 100 V causes only minor changes in the surface topography inducing only moderate smoothing of the electrode. Moreover, SEM reveals that the width of the microcylinders does not change (to within 10%) after the application of the voltage. These results suggest that the titanium electrodes are stable at the voltages needed to generate ECL in the $[Ru(bpy)_3]^{2+}$ -TPA system using the AuMP-MUA as microemitters.

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Figure S1. SEM images of the surface of the titanium feeder electrode, before (a) and after (b) application of a voltage of 100 V for 60 minutes.

3. Stability of the Ruthenium Emitter Under Application of an Electric Field. Figure 3 shows that increasing the electric field strength causes I_{ECL} to increase for potential differences up to approximately 45 V. However, as shown in Figure S2, the ECL intensity observed at a potential difference of 50 V decreases by approximately 50% over 330 s. This decrease could arise from decomposition of the $[Ru(bpy)_3]^{2+}$ luminophore, e.g., due to the production of hydroxyl radicals. However, Figure S2 shows that the absorbance of the ruthenium containing solution decreases by less the 5% when exposed to the approximately 770 V cm⁻¹ electric field for 330 s suggesting that decomposition of the complex is not solely responsible for the decrease in the intensity of the electrochemiluminescence. The voltage at the anodic pole of the MUA coated gold microparticles is approximately +3.6 V which will drive oxidation of the gold surface as well as stripping of the MUA monolayer. The formation of an oxide layer that hinders heterogeneous electron transfer appears to be the dominant cause of the decreasing intensity of the ECL under the most intense electric fields investigated.



Figure S2. Time dependence of the electrochemiluminescence intensity (\blacklozenge , y-axis to left) from a suspension of microparticles in a solution containing 1 mM [Ru(bpy)₃]²⁺ and 25 mM tripropylamine at a voltage difference between the two feeder electrodes of 50 V. The time dependence of the absorbance of the solution diluted 50-fold is also shown (\blacksquare , y-axis to the right). The solution has not been purged to remove oxygen.

4. Impact of Deoxygenation on ECL intensity. Each MUA functionalised gold microparticle acts as an electrochemical cell with oxidation occurring at the anodic pole and reduction at the cathodic pole. Thus, it is possible for the ECL intensity to be controlled by reduction reactions rather than the oxidation reactions that would lead to ECL, i.e., oxidation of $[Ru(bpy)_3]^{2+}$ and TPA. The reduction reactions typically involve oxygen reduction or reduction of protons in acidic solutions. Figure S3 shows the effect of deoxygenating the solution on the ECL intensity as the pH is changed where the voltage difference between the two feeder electrodes is 45 V.



Figure S3. Electrochemiluminescence intensity at 45 V from a suspension of AuMP-MUA particles in a solution containing 1 mM $[Ru(bpy)_3]^{2+}$ and 25 mM tripropylamine for oxygenated solutions (blue bars) and deoxygenated solutions (brown bars).

Figure S3 shows that the presence of oxygen influences the ECL intensity observed at pH values above approximately pH 5. It is important to note that the presence of oxygen does not cause the ECL intensity to decrease, i.e., the dominant effect of oxygen is not excited state quenching as might be expected for optical excitation. Rather, it appears that oxygen can be reduced at the cathodic pole of the AuMP-MUA particles allowing the metal complex and co-reactant to be oxidised. Removing oxygen blocks reduction which limits the generation of Ru³⁺ and TPA radicals needed for ECL generation. However, if the solution is acidic, protons can be reduced at the cathodic pole of the cathodic pole of the microparticles and the ECL intensity is essentially unaffected by deoxygenation of the solution.

Zhao, C., Wang, C., Gorkin III, R., Beirne, S., Shu, K., & Wallace, G. G. (2014). Three dimensional (3D) printed electrodes for interdigitated supercapacitors. Electrochemistry Communications, 41, 20-23. doi:doi.org/10.1016/j.elecom.2014.01.013