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Monolayer Graphene as Electrode Materials for Electrochemiluminescence Applications

Electrochemiluminescence (ECL) is luminescence phenomenon induced by electrochemical reactions in which species generated at electrodes undergo reactions to light-emitting excited states. The ECL system based on $\text{Ru}(\text{bpy})_3^{2+}$ as emitter and tripropylamine (TPrA) as coreactant using platinum electrodes and photomultipliers, has been utilized for commercial applications in clinical analyses. Graphene grown by chemical vapor deposition (CVD) possesses attractive properties such as transparency and chemical stability, as electrode materials for ECL applications. However, there are only a few reports about ECL using CVD graphene.^[1, 2] In this work, ECL based on the $\text{Ru}(\text{bpy})_3^{2+}$ /TPrA system is demonstrated using CVD-grown graphene electrodes with a CMOS image sensor towards realization of portable and high-sensitive ECL bioanalytical devices using graphene. Monolayer graphene films were grown by CVD method on copper foils and transferred onto quartz glass substrates. A gold film was formed on graphene for electrical contact. The ECL measurement cells made of PTFE were constructed as shown in Fig. 1(a). The custom-made CMOS chips (Fig. 1(b)) were placed under the quartz substrate. Visible, orange light was observed at graphene during the ECL measurements (Fig. 1(c)). Figure 2(a) and (b) show faradaic current and ECL emission as a function of time at potentials of 1.5, 2.0 and 2.5 V for 60 sec. The potentials required for ECL emissions were higher against standard redox potentials ($E^\circ = 1.20$ V for $\text{Ru}(\text{bpy})_3^{2+}$ and $E^\circ = 0.9$ V for TPrA) because of the resistance of the graphene film ($R = 0.5\sim 1$ k Ω/\square) in which applied voltage drops. Consequently, at lower potential, ECL is obtained only by TPrA oxidation, while at higher potential, the ECL process involves two electrochemical reactions (Fig. 2(c)), which result in different time-dependence in the ECL intensity. These results suggest that, with proper cell design, CVD graphene and CMOS image sensor will be excellent combination for portable ECL analytical devices.

References

- [1] N. L. Ritzert et al., *Faraday Discussions*, **172** (2014) 27
 [2] T. C. Cristarella et al., *Langmuir*, **31** (2015) 3999

Figures

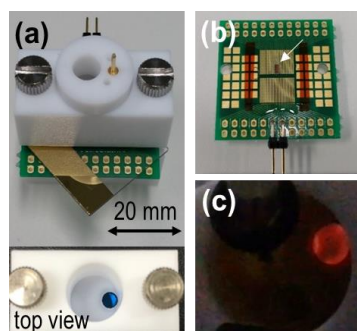


Figure 1: Images of (a) cell for ECL measurement, (b) CMOS chip and (c) ECL at graphene electrode

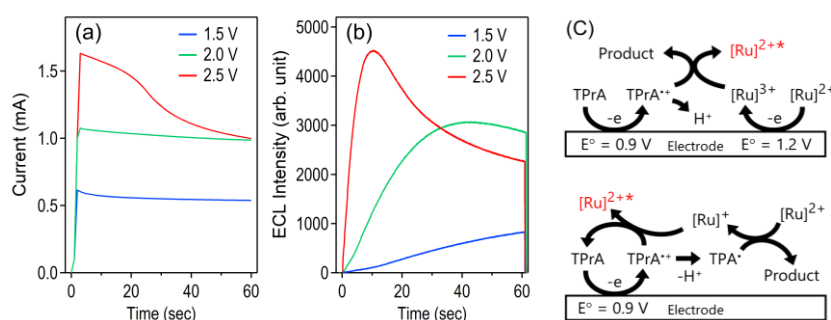


Figure 2: (a) Faradaic Current and (b) ECL emission as a function of time at graphene electrode in a solution of 5 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, 0.5 M TPrA and 0.1 M phosphate buffer (pH 7.0). (c) ECL mechanisms for $\text{Ru}(\text{bpy})_3^{2+}$ /TPrA.