ECL is a means of converting electrical energy into light (chemiluminescence). It involves the production of energetic intermediates from stable precursors at the surface of an electrode. These intermediates then react under a variety of conditions to form excited states that emit light. For example, application of a voltage to an electrode in the presence of Ru(bpy)$_3^{2+}$ (where bpy = 2,2'-bipyridine) results in light emission and allows one to detect the emitter at very low concentrations (~10$^{-11}$ M). By employing ECL-active species as labels on biological molecules, ECL has found application in immunoassays and DNA analyses. Commercial systems have been developed that use ECL to detect many clinically important analytes (e.g., R-fetoprotein, digoxin, thyrotropin, protein and steroidal hormones, and various antibodies) with high sensitivity and selectivity. Our goal is to study ECL at a small electrode with a well-defined geometry using combined electrochemistry and spectroscopy tools.

**ECL generation**

ECL generation through an oxidative-reduction mechanism

ECL of Ru(bpy)$_3^{2+}$ utilizing tripropylamine (TPrA) as coreactant is generated through an oxidative-reduction mechanism given by,

1. Ru(bpy)$_3^{2+}$ + e$^- \rightarrow$ Ru(bpy)$_3^{3+}$ (1)
2. Ru(bpy)$_3^{3+}$ + TPrA$^- \rightarrow$ Ru(bpy)$_3^{2+}$ + TPrA$^-$ (2)
3. TPrA$^- \rightarrow$ TPrA + H$^+$ (3)
4. Ru(bpy)$_3^{3+}$ + TPrA$^- \rightarrow$ Ru(bpy)$_3^{2+}$ + product (4)
5. Ru(bpy)$_3^{2+}$ + TPrA$^- \rightarrow$ Ru(bpy)$_3^{2+}$ + hv (5)

**New ECL electrode preparation**

Gold was deposited from 1% HAuCl$_3$ onto an anodized 100 µm Ti wire (99.99%). The anodization was done in 0.15 M NH$_4$F solution of ethylene glycol containing 0.08 M oxalic acid at 20 V (DC) for 12 hours. Cyclic voltammetry (CV) of anodized Ti wire in 1% HAuCl$_3$, scan rate: 0.1 V/sec.

ECL generation from TiO$_2$/Au wire electrode: a) A typical SEM image of a gold-coated 100 µm (in diam.) TiO$_2$ wire electrode; b) photoluminescence (PL) under 488 nm excitation; c) ECL image of the wire electrode in 50 mM Ru(bpy)$_3^{2+}$/0.1 M TrPA with 10 msec binning time per pixel (Scan area: 100 µm×100µm; resolution: 50×50 pixels); d) ECL and c) current of control experiments.

**ECL stability test**

ECL generation from TiO$_2$/Au thin film electrode modified with Au particles

A) Schematic drawing of the experimental setup for local ECL generation and collection setup from single gold particles. B) Typical SEM image of a TiO$_2$/Au thin film electrode. C) Typical PL image under 488 nm laser excitation with an intensity of 5 µW and D) ECL image obtained from the TiO$_2$/Au electrode in 50 mM Ru(bpy)$_3^{2+}$/0.1 M TrPA solution. Binning time: 10ms; scan area: 50 µm ×50 µm; resolution: 50×50 pixels, electrode potential=1.5 V. E) Current from the whole TiO$_2$/Au substrate and ECL from a single gold particle under applied potential scanning. Scan rate: 0.1 V/sec.

**Conclusion**

We present that gold particle deposition onto TiO$_2$ thin film can switch on ECL from Ruthenium complex. Local ECL and PL information at each gold particle can be studied using spectroelectrochemical approach. Future applications of the substrate include spectroelectrochemistry and photoelectrochemistry of a well-defined electrode as well as new electrochemical sensors.