Spontaneous Formation and Electrogenerated Chemiluminescence of Tris(bipyridine) Ru(II) Derivative Nanobelts

Jiaguo Yu,[†,‡] Fu-Ren F. Fan,[†] Shanlin Pan,[†] Vincent M. Lynch,[†] Khalid M. Omer,[†] and Allen J. Bard*,[†]

Center for Electrochemistry, Department of Chemistry and Biochemistry and Center for Nano-and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712, and State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R. China

Received February 27, 2008; E-mail: ajbard@mail.utexas.edu

In recent years, one-dimensional nanostructured materials have been extensively studied because of their distinctive geometries, novel physical and chemical properties, and potential applications in nanoscale optical and electric devices. Most research, however, has focused on inorganic compounds, polymers, or low-molecular-weight organic compounds.[1–3] Fewer studies have been performed on ionic compounds, such as $Ru(bpy)_3(ClO_4)_2$ (bpy = 2,2′-bipyridine) and its derivatives, which have been widely used in electrogenerated chemiluminescence (ECL) studies,[4] for example, commercially as a highly sensitive analytical method for immunoassay and DNA analysis.[5] We report here a simple reprecipitation method for fabricating nanoscale nanobelts (NBs) from such an ionic compound and the strong photoluminescence (PL) and ECL that can be obtained from these in aqueous solution. The compound used is the water-insoluble derivative of tris(bipyridine) Ru(II), $[Ru(bpy)_2(4,4′-(CH_3(CH_2)_{14}COO)_2-bpy)](ClO_4)_2$, (Ru-LC, see Scheme 1 for structural details).[6] The observation of ECL in such nanostructures leads to the development of a new class of ECL systems that may prove useful for a variety of purposes. To our knowledge, this is the first report of ECL of a single nanoparticle of this type. These can be useful in the study of the electrochemistry of nanoparticles, as well as the basis of highly sensitive electroanalytical methods, with a small amount of material concentrated on an electrode surface.

Ru-LC was synthesized by a previously reported method.[6] It is totally insoluble in water, but very soluble in polar organic solvents, such as acetonitrile (MeCN) and acetone. Ru-LC nanobelts were prepared by a simple reprecipitation method from a 4% w/v solution in MeCN at room temperature. In a typical preparation, 4 μL of this solution was rapidly injected into 10 mL of highly pure (Millipore) water under ultrasonic agitation at room temperature for 30 s, followed by aging in a closed vial at room temperature for 24 h. The resulting colloid solution is a transparent orange-yellowish solution that exhibits strong light scattering (see Supporting Information, Figure S1), confirming the formation of nanoparticles. The concentration of Ru-LC monomers in the colloidal suspension was 1.35×10^{-5} M. With increasing aging time (a month), a small amount of orange-yellow precipitate occasionally settled. However, the deposited nanobelts could be easily dispersed and a clear solution obtained again by slight agitation. This stability is important for applications and is probably related to the negative ζ potential of the surface of the NBs (ca. −11.2 mV).

The morphology and microstructure of the products were studied by field-emission scanning electron microscopy (FESEM) and

† The University of Texas at Austin.
‡ Wuhan University of Technology.

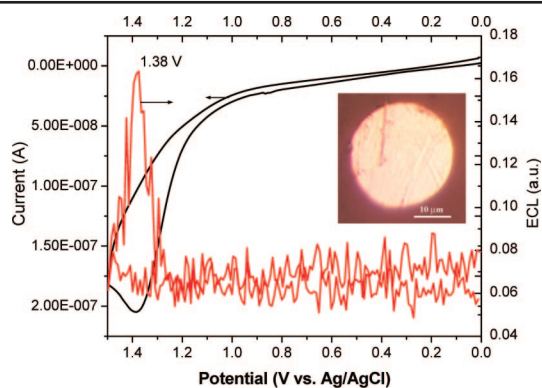**Scheme 1.** Structure of $[Ru(bpy)_2(4,4′-(CH_3(CH_2)_{14}COO)_2bpy)]^{2+}$
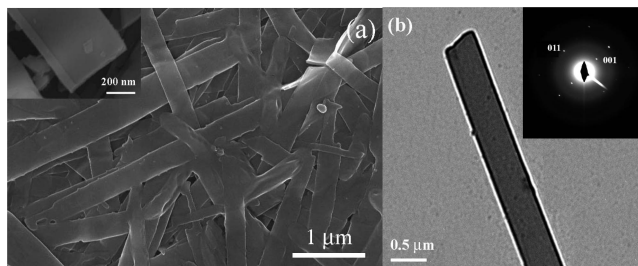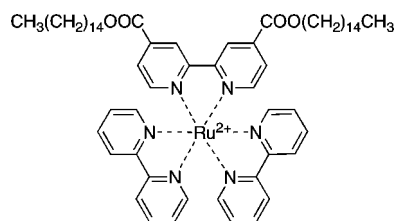
Figure 1. SEM (a) and TEM (b) images of the product. Insets in panels a and b show side-face SEM image and SAED pattern of single nanobelt, respectively.

transmission electron microscopy (TEM), as shown in Figure 1 panels a and b, respectively. These images indicate that the particles have a long, straight, and belt-like morphology with widths of ca. 200−1000 nm and lengths of ca. 5−15 μm. The thickness of the NBs range from around 50 to 120 nm, as estimated from the side-face FESEM images of NBs (see inset in Figure 1a), and the width-to-thickness ratios are about 5 to 10. The selected-area electron diffraction (SAED) pattern (inset in Figure 1b) reveals that the as-prepared NBs have single crystal structures and grow along the [001] direction. This can also be proven by the contrast of the X-ray diffraction (XRD) pattern (see Figure S2), which indicates the preferential orientation of (001) lattice planes in the NBs. The strong and sharp XRD signals suggest a highly crystalline structure of Ru-LC NBs, and the main peak at 2.231° corresponds to the preferential [001] growth plane of the Ru-LC single crystal. According to cell volume and NB size $(10000 \times 500 \times 100$ nm$^3)$, a single NB contains about 3.0×10^8 Ru-LC molecules, Therefore, the concentration of NB suspension is very dilute and about 3×10^7 particles/cm^3 $(4.5 \times 10^{-14}$ M in NB particles). Compared to the usual nanowires with a round cross section, a nanobelt structure should provide a large area interface when deposited on electrodes, thus facilitating the fabrication of devices with improved electrical contact.

Figure 2. CV (black) and ECL curve (red) of a single Ru-LC nanobelt deposited on a platinum UME in 0.1 M phosphate buffer solution (pH 7.2) containing 0.1 M TPrA. Potential scan rate, 0.1 V/s. The inset is the optical microscope image of UME with single NB.

The formation mechanism of the NBs was elucidated by TEM analysis of structures isolated from the reaction mixture for various aging times. Samples collected after 5 min consisted of ca. 10 nm sized nanoparticles of amorphous Ru-LC (see Figure S3a,b), which subsequently aggregated within 30 min into a belt-like structure (see Figure S3c). Extending the aging time to 2 h resulted in a progressive increase in the length of the nanobelts (see Figure S3d). SAED analysis indicated that the initially formed NB was amorphous. Extending the aging time to 24 h resulted in a progressive increase in the crystallinity of the NBs. According to the above observations, we suggest that formation of the single-crystalline NBs involves a multistep process involving nucleation, oriented assembly, and mesoscale restructuring of initially formed nanoparticle building blocks.[7]

The absorption and PL spectra of Ru-LC NBs and the corresponding monomers in solution were measured (see Figure S4). The monomer in MeCN exhibits a wide intramolecular charge-transfer absorption band (360−480 nm), which is assigned to the metal-to-ligand charge-transfer (MLCT) transition (that is $d\pi \rightarrow \pi^*$).[8] However, the lowest energy $d\pi \rightarrow \pi^*$ MLCT transition of NBs in aqueous solution exhibits an obvious blue-shift (from 480 to 458 nm). The PL spectra of the nanobelts also show a similar hypsochromic shift as the absorption spectra and an enhanced PL emission (at about 640 nm); a fluorescence image of a NB can be easily observed (see inset in Figure S4).

Two methods were used to observe ECL of the NBs at a Pt electrode or ultramicroelectrode (UME) (see Supporting Information). First, ECL from the NBs dispersed in water containing 0.1 M tripropylamine (TPrA) as a coreactant and 0.1 M phosphate buffer could be easily observed during potential scans (from 0 to 1.5 V) or pulses (−1.25 to 1.25 V) (see Figure S5). Second, the ECL curve of a single Ru-LC NB deposited on a platinum UME was also observed (Figure 2). The cyclic voltammogram (CV) shows a rather broad irreversible anodic wave due to the direct oxidation of TPrA, and the single Ru-LC NB has little influence on the CV current. The oxidation current starts to rise at ∼1.1 V, and its peak potential is ∼1.38 V. This completely irreversible anodic oxidation behavior is similar to that of TPrA in acetonitrile solution on a Pt electrode[9a] and in neutral aqueous solution on a glassy carbon electrode.[9b] The mechanism probably follows that of $Ru(bpy)_3^{2+}$ in solution, where scanning the electrode potential positive of 1.25 V causes the oxidation of $Ru(bpy)_2(bpy-C_{15})^{2+}$ in the adsorbed NB to the +3 form, either directly or via TPrA radical cations.[10] Reaction of the +3 form with either the reducing TPrA• radical or the +1 form produces the excited state. The ECL emission intensity increased with increasing potential. Note that no ECL is seen for an aqueous solution that is saturated with $Ru(bpy)_2(bpy-C_{15})^{2+}$ prepared by putting a glass slide with a film of this material (cast from an MeCN solution) in the solution overnight with gentle stirring, so soluble monomer makes no detectable contribution to the ECL.

Organic nanoparticles, including NBs, have potential applications in electronics, optics, sensors, and analysis. While most of this research has focused on the properties of ensembles,[3] the exploration at the single nanoparticle level is also of interest.[11] Experimental difficulties at the single particle level usually involve problems in generating, locating, and characterizing it, especially at the nm scale and in measuring the very small currents or optical signal associated with these electrode reactions.[11] Further studies are underway to elucidate the ECL mechanism of organic NBs.

In summary, a new class of ECL system has been developed from Ru-LC single crystalline nanobelts, which were fabricated by a simple reprecipitation method. The prepared nanobelts show an enhanced fluorescence emission and relatively strong ECL that have potential analytical applications. More interesting, ECL of a single nanobelt deposited on UME was observed.

Supporting Information Available: Detailed experimental section, light scattering, absorption and PL spectra, XRD, TEM, and ECL results. This material is available free of charge via the Internet at http://pubs.acs.org.

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