Self-Assembled Diode Junctions Prepared from a Ruthenium Tris(Bipyridyl) Polymer, n-Type TiO2 Nanoparticles, and Graphite Oxide Sheets**

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The idea of making molecular rectifiers from bilayers of redox-active polymers, for example Ru- and Os-polypyridyl derivatives, ferrocenes, and viologens, dates to the work of Murray and co-workers[1] and Wrighton and co-workers[2] in the early 1980s. In these devices, the passage of current involves the oxidation and reduction of polymer layers at the anode and cathode, respectively, and the forward bias direction corresponds to electron transfer from the more reducing polymer redox couple to the more oxidizing one. If a polymer with multiple oxidation states is used, then a single-polymer device can pass current when the applied bias approaches the difference in formal potentials. For example, with polymers containing the ruthenium tris(bipyridyl) ([Ru(bpy)3]2+) repeating unit, the difference between the potentials of the RuII/RuIII and RuII/RuI couples is ca. 2.6 V, and the film conductance is low at lower applied bias.[3] At higher voltages, the charge recombination reaction between the RuIII and RuII [Ru(bpy)3] centers results in electron-generated chemiluminescence (ECL), because the emissive metal-to-ligand charge transfer (MLCT) excited state of the RuII form is generated within the film.[4]

Recently, multilayer films that perform this ECL reaction with high external quantum efficiencies (>1 %) have been reported.[5] These polymer films are interesting for potential use in flat-panel electroluminescent displays. One of the problems with these devices is their low conductance, which requires that high voltages be applied in order to generate useful currents. The same considerations apply to thin-film diodes made by sequential adsorption of polymers and semiconductor nanoparticles, which are of interest as components of nanoscale electronic circuits.[6] In this study, we explore the use of TiO2 nanoparticles and graphite oxide (GO) nanoplatelets as electron- and hole-conducting components of such diodes. The rectifying properties of the films depend upon the choice and sequence of components. We find that GO, which is a polyanionic mixed ionic–electronic conductor, forms a rectifying junction with TiO2 and can also act as a charge compensating layer for layers of the [Ru(bpy)3]2+-containing polymer RuP. The conductance of RuP-containing thin-film devices prepared from GO is substantially higher than those containing poly(styrene sulfonate) (PSS), which forms resistive multilayer devices with RuP.

Layer-by-layer self-assembly involved the alternate adsorption of n-type TiO2 particles with poly(diallyldimethylammonium chloride) (PDDA), followed by the adsorption of alternating layers of polycations (PDDA or RuP) and polyanions (PSS or GO). Anatase TiO2 nanoparticles (22 ± 3 Å in diameter) were prepared by the slow hydrolysis of titanium tetraisopropoxide in alcoholic solution.[7,8] Multilayers were grown on conductive indium tin oxide (ITO)-coated glass, antimony tin oxide (ATO)-coated glass, mercaptopentylamine-modified gold, and insulating quartz substrates (see Experimental section).

The growth of PDDA/TiO2 films on quartz substrates was quantified by monitoring the UV absorption band centered at 232 nm, which showed a linear increase with increasing number of layers. The thickness of the PDDA/TiO2 bilayers was estimated from surface plasmon spectroscopy, by using a gold substrate derivatized with a 9 Å thick layer of mercaptoethanol. The PDDA and TiO2 adsorption steps contributed 7 ± 2 Å and 22 ± 3 Å to the bilayer thickness, respectively. The latter is consistent with the TiO2 particle diameter inferred from UV-vis absorption spectra and transmission electron microscopy (TEM). The thickness of films prepared by alternate adsorption of RuP with PSS (sodium salt, Aldrich) or GO (elemental composition C12H2O2, 25 % oxidized)[9] was also linear, as evidenced by the regular increase in absorption bands at 292 and 456 nm. In the case of GO, carboxylic and phenolate groups formed by oxidation of graphite are responsible for strong electrostatic binding with RuP. The pKs of GO is about 6.3,[9b] and the sample used had a proton exchange capacity of 6.0 mmol/g. The electrostatic nature of its interaction with RuP was confirmed by dipping a quartz–PDDA/(GO/RuP)30 film in an acidic solution (pH 1),[10] which induced rapid exfoliation and complete desorption of the film from the substrate. Figure 1 shows the progressive increase of the MLCT band absorbance of RuP as it is alternately adsorbed with GO. Atomic force microscopy (AFM) performed on the multilayer film sequence quartz–PDDA/PSS/RuP/GO showed full coverage by 20 Å thick GO sheets. Importantly, a tiling morphology was observed (Fig. 2), ensuring good compartmentalization of TiO2 and RuP layers in the devices described below.

A systematic investigation of the rectifying properties of the different layer sequences of these polyelectrolytes was conducted, beginning from the simplest and progressing to more complex devices. The system ITO/(PDDA/TiO2)10/Au, reported in a previous paper, exhibits rectifying behavior (current flows when the ITO electrode is biased negative, but not in the opposite direction) indicative of the formation of a Schottky diode at the TiO2/Au interface.[8] In contrast, the system ITO/(PDDA/GO)30/Au gave linear I–V behavior, consist-
tent with ohmic ITO/GO and GO/Au interfaces. The TiO₂/GO interface was specifically studied by preparing the system ITO/(PDDA/TiO₂)₁₀/(PDDA/GO)₃₀/Au. Figure 3 (curve 1) shows current flow at negative bias originating from this rectifying interface. In this case the forward bias current can be thought of as a redox process in which TiO₂ reduces GO with minimum overpotential, and electrons travel through the film to Au, where the reduced GO is re-oxidized. A barrier height energy of 0.42 eV, which corresponds to the difference in Fermi levels[8] at the TiO₂/GO interface, was calculated by fitting the $I-V$ characteristics to the Schottky diode equation. This gives a work function for GO in the multilayer film of 4.8 eV below the vacuum level (Fig. 4).

As a prelude to the study of nanoparticle/polymer diodes containing TiO₂, GO, and RuP, cyclic voltammetry was performed in solution on multilayer films grown on ATO-coated glass electrodes. At negative bias, the electrode ATO/(PDDA/TiO₂)₁₀, showed a reversible reduction at –1.13 V vs. saturated calomel electrode (SCE), corresponding to a redox level and conduction band edge 3.6 eV below the vacuum level. The cathodic current began to increase at the flat band potential (estimated to be –0.5 V vs. SCE[11]). When 10 bilayers of (RuP/PSS) were added to ATO/(PDDA/TiO₂)₁₀ with a terminal layer of PSS or 30 bilayers (RuP/GO) with a top layer of GO, additional redox waves were observed at –1.38 V (Ru I/II vs. SCE) (reversible wave) and +1.00 V (Ru II/III vs. SCE, quasi-reversible wave). The positions of these waves correspond to those of RuP (–1.52 V and +1.12 V, respectively) in solution. Consistent with this assignment, the quantity of charge passed in the cathodic wave for the RuIII/RuII process ($1.07 \times 10^{-8}$ mol/cm² for a 10 bilayer PSS/RuP film) agreed closely with the amount of RuP determined by UV-vis spectroscopy ($1.04 \times 10^{-8}$ mol/cm²). These results show that, in contact with a liquid electrolyte solution, charge transfer through the multilayer and oxidation/reduction of the RuP film are facile processes. This was found to be the case for both polyelectrolytes (GO and PSS) used as charge-compensating layers for RuP.

In contrast, dry films prepared with Au top contacts showed substantial differences between PSS and GO polyanions as charge compensating layers. The system ITO/(PDDA/TiO₂)₁₀/(RuP/PSS)ₓ/Au with $n = 10–30$, showed exhibit resistive behavior. Interestingly, ITO/(PDDA/TiO₂)₁₀/(RuP/GO)₃₀/GO/Au was rectifying at both positive and negative voltages and the $I-V$ curve was dissymmetric (Fig. 3A, curve 2). The emergence of current in the positive branch (at bias >1.8 V) is consistent with electron injection into TiO₂ via the RuI/II
couple, whereas the negative branch corresponds to electron transfer from TiO$_2$ to GO and/or Ru$^{III}$. It should be noted that this result was obtained after pre-cycling the films 10 times between 0 and 2 V. A pronounced charging hysteresis was observed during this pre-cycling treatment. Subsequent to this treatment, however, the electrical response of the junctions was reproducible and reversible. We believe that the thinness of the bilayer RuP/GO and the fact that GO platelets are both electronically and ionically conductive might explain the fast reversal of the concentration gradients upon further cycling. This procedure is reminiscent of that used by Murray and co-workers, who made poly[Ru(vpy)$_3$](PF$_6$)$_2$ diodes (where vpy=4-vinyl-4'-methyl-2,2'-bipyridine) with fixed ion concentration gradients by first polarizing the devices in an electrolyte solution. In the present case, the availability of mobile cations (H$^+$, Na$^+$ present at the surface and within the GO sheets) allows for the establishment of the necessary ion and potential gradients within the film.

Several control experiments were conducted with the fixed-site strong acid polyelectrolyte PSS in place of TiO$_2$ or GO, or with PDDA in place of RuP. These experiments underscore the necessity for electronically conducting TiO$_2$ nanoparticles and mobile ions from GO layers in making high conductance devices. The film ITO/(PDDA/(RuP/GO)$_{30}$/Au (Fig. 3A, curve 3) shows poor conductivity relative to ITO/(PDDA/TiO$_2$)$_{10}$/(RuP/GO)$_{30}$/Au, and no current rectification. The conductivity becomes progressively lower with ITO/(PDDA/PSS)$_{10}$/(RuP/GO)$_{30}$/Au (Fig. 3B, curve 4) and ITO/(PDDA/PSS)$_{10}$/(RuP/PSS)$_{30}$/Au (Fig. 3B, curve 5), which contain isolating PDDA/PSS sequences.

Although these two systems differ only by the nature of the spacer between the RuP layers, the dramatic change observed upon substituting GO for PSS shows that in the dry state PSS cannot rearrange to provide the ion gradient necessary for re- dox conduction in the RuP layers. Layer-by-layer assembly of polyelectrolyte films is based on the displacement of their counterions, and the process often leads to multilayers containing few or no mobile ions. However, a recent study has shown that when poly(acrylic acid) is used, non-ionized acid groups, in addition to the small number of free ions present in the films, can act as potential proton donors to restore local charge neutrality as the voltage is applied, improving the performance of the devices. In the present case, GO is both electrically conductive and can act as a reservoir of mobile ions to allow electrochemically driven rectification in the systems ITO/(PDDA/TiO$_2$)$_{10}$/PDDA/(PSS/RuP)$_{30}$/PSS/Au to be observed at low voltage.

In summary, we have demonstrated, using a layer-by-layer assembly method, that: i) a direct contact between quantum-size TiO$_2$ particles and RuP is not required for promoting efficient electron transfer in a diode-like junction; ii) the interconnection of the RuP layers via thin GO sheets allows the electroactivity of the junction to be observed at positive bias; and iii) the interface TiO$_2$/GO is also rectifying at negative bias.

Fig. 3. $I$–$V$ characteristics of A) rectifying junctions: ITO/(PDDA/TiO$_2$)$_{10}$/(PDDA/GO)$_{30}$/Au, curve 1 (inset shows the reverse bias region on a larger scale); ITO/(PDDA/TiO$_2$)$_{10}$/(RuP/GO)$_{30}$/Au, curve 2; ITO/PDDA/(GO/RuP)$_{30}$/Au, curve 3; and B) junctions with fully reversible interfaces: ITO/(PDDA/PSS)$_{10}$/(RuP/GO)$_{30}$/Au, curve 4; ITO/(PDDA/PSS)$_{10}$/(RuP/PSS)$_{30}$/Au, curve 5; and ITO/(PDDA/TiO$_2$)$_{10}$/PDDA/(PSS/RuP)$_{30}$/PSS/Au, curve 6.

Fig. 4. Energy level diagram of the different materials used in the construction of the rectifying devices (ITO, TiO$_2$ nanoparticles, GO, RuP, and Au) at zero applied potential. All energy levels are calculated relative to the vacuum level. $E_a$ is the electron affinity (or work function in the case of a metal), $E_g$ is the band gap energy, c.b. is the conduction band, and v.b. is the valence band. The dashed line below the conduction band edge of TiO$_2$ corresponds to the Fermi level.
Experimental

Titanium tetrakisopropoxide, 97% ; 11-ammoniumdodecanodic acid, 99% ; mercaptoethylinamine hydrochloride (MEA); poly(styrene-4-sulfonic acid), sodium salt (PS-S), 20% solution in water; PDDA, 20 wt.-%. ; graphite powder (1-2 μm); RuCl3; 2,2'-bipyridine; LiCl; KPF6; and tetra(n-butylammonium) bromide were purchased from Aldrich and used as received. Ru(bpy)3Cl2·2H2O and Me-bpy(CH2)5bpyMe were available from a previous study [13]. All aqueous solutions were prepared in 18 MΩcm water obtained by purification of distilled water with a Millipore Mill-Q system. Soda lime float glass, coated with SiO2, and ITO, with R < 125 Ω/cm2 and >87% transmission were a gift from Photocon. Quartz slides were purchased from Chemglass, Inc. S0/300 (ATO) coated slides, 100 μm were purchased from Delta Technologies Ltd. All substrates were cleaned with a fresh piranha solution (75% H2SO4/25% H2O2) for few seconds prior to being used for the self-assembly.

GO colloidal suspensions were prepared by exfoliating GO powder [9] in a 0.1 M NaCl solution. TiO2 nanoparticles were prepared as previously reported [8]. A Ru(bpy)3Cl2·2H2O (ZnO) was used as the positive lead while Au, coated with a mercaptoethylamine layer prior self-assembly [6a], was used as a conductive substrate, a metallic top layer M (i.e., Au) completes the junction with an electrical contact. Note that each slash, /, represents the junction with an electrical contact. Each stacked bilayer M/S/.../M; where S refers to the substrate (ITO, ATO, quartz, etc.) onto which the film is grown. A first series of bilayers comprising a titanium dioxide layer (10 Å) and a gold layer (450 Å) were used in this study, coated ITO and ATO electrodes were the “working” lead while the reference and counter electrodes were connected to the gold electrode. This is, at positive voltage values in the I-V plots, ITO or ATO electrodes were biased positive relative to Au.

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[10] The notation used to account for the nature and relative ordering of the bilayers (or sequences) adsorbed onto the substrate is as follows: S(PF6-)/BPb2Cl20_x/M; where S refers to the substrate (ITO, ATO, quartz, etc.) onto which the film is grown. A first series of bilayers comprising a binder (polyelectrolyte) and a building block BB, typically particle or platelet, is then sequentially grown on a few times to place the system S(PF6-)/BPb2Cl20_x.

In some cases, a second series of bilayers can be adsorbed onto the first film, and so on, until the different components of the device are properly integrated along the vertical axis to the substrate. Finally, when ITO was used as a conductive substrate, a metallic top layer M (i.e., Au) completes the junction with an electrical contact. Note that each slash, /, represents an interface between two different materials.