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Carbon Fiber/Epoxy Composite Ring-disk Electrode: Fabrication, Characterization and Application to Electrochemical Detection in Capillary High Performance Liquid Chromatography

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Abstract

Carbon fiber/epoxy composite materials, which are manufactured using the pultrusion process, are commercially available in various shapes and sizes at very low cost. Here we demonstrate the application of such a material as an electrochemical detector in a flow system. Cyclic voltammetry shows that the material's electrochemical behavior resembles that of glassy carbon. Using tube and rod composites, we successfully fabricated a ring-disk electrode with a 20 μm gap between the ring and the disk. The narrow gap is favorable for mass transfer in the generator-collector experiment. This composite ring-disk electrode is assembled in a thin-layer radial-flow cell and used as an electrochemical detector. The disk electrode, placed directly opposite to the flow inlet, is operated as a generator electrode with the ring electrode being a collector. The high collection efficiency on the ring electrode (0.8 for a chemically reversible species) enhances the detection selectivity.

Keywords

microelectrode; dual electrode detection; generator-collector; peptides; biuret; nanoLC

1. Introduction

Carbon composites are composed of carbon and nonconducting binders that are mixed according to specific ratios and allowed to cure to a rigid solid, the shape and size of which are defined by the mold used. Many types of carbon materials can be used in composite fabrication, including carbon fibers[1-4], carbon foam[5], carbon nanotubes[6], and particulate forms of graphite[7-10], glassy carbon[11], and diamond[12]. The composites can be regarded as ensembles of microelectrodes, the properties of which depend on the carbon material used in the composite, the binders, and the volume fraction of conducting material. Carbon composite electrodes are widely used in electrochemistry for sensing and detection applications due to their flexible shape, controllable electrochemical properties and low cost. The binder material and fabrication process affect whether a composite electrode is suitable for detection in a flow system. Some graphite composite electrodes, such as Kel-F graphite[13,14], PVC graphite[15,16], PTFE graphite[17], epoxy graphite[18] and sol-gel derived ceramic graphite [8,10,19], are good for flow system detection purposes, while paraffin carbon paste electrodes suffer practical difficulties.

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Most carbon composites used in electrochemistry are fabricated in individual laboratories and vary in properties, which makes general application difficult. Carbon fiber composites, which are widely used as structural reinforced plastics, are available on a commercial scale at very low cost. They are composite materials combining carbon fibers (short or continuous, unidirectional or multidirectional) and a 'plastic' material such as epoxy or vinyl ester. Carbon fiber composites made from unidirectional carbon fibers have constant cross sections and are usually manufactured using the pultrusion process[20], in which fibers are drawn from spools, passed through resin bath for impregnation, and gathered together to produce a particular shape before entering a heated die. There have been a few studies related to their electrochemical properties[1-3], but the application as electrochemical detectors has not been explored. Taking advantage of their commercial availability in various shapes and sizes, their use in novel detector design for biological environments and miniaturized devices should be favorable.

We report the fabrication of a ring-disk electrode using the carbon fiber/epoxy composite tube and rod and its application as a dual-electrode detector for a capillary HPLC system. The ring-disk electrode in a radial flow cell is equivalent to a dual-series electrode in a thin-layer cross flow cell. When a dual-series detector is assembled in a flow separation system [21-23], the analytes are first oxidized/reduced on the generator electrode and the products stable on the timescale of the transit time from the generator to the collector are then reduced/oxidized on the collector electrode. It has been shown that dual-series/generator-collector detection can reduce noise and increase selectivity. For example, biological samples are complicated matrices containing oxidizable species which results in many overlapping peaks with single electrode detection. Dual-electrode detection is selective for electrochemically reversible analytes (e.g., catecholamines) [24-26]. The selectivity inherent in the dual-electrode approach typically lowers detection limits for electrochemically reversible analytes.

Although selectivity is improved with a dual-series detector, the current response is lower on the collector electrode because some of the analyte that is oxidized or reduced at the generator is transported away from the surface and does not reach the collector. Thus, a small gap between the two electrodes is crucial to achieving high collection efficiency on the collector electrode, especially for a capillary HPLC system due to the potentially low solution velocity. The common dual-series electrode composed of two disc electrodes has a relatively large gap between the two electrodes. A ring-disk electrode with proper alignment has the potential to show high collection efficiency. Past efforts towards making ring-disk electrodes include: alternate vapor deposition of insulating and conducting material around a disk electrode (carbon fiber, metal wire, etc.) [21,27,28]; aligning microelectrodes around the disk electrode as the ring electrode[29,30]; using photolithography and dry etching[31,32] or sputtering[33] to fabricate carbon or metal thin film ring-disk electrode. These ring-disk electrodes have been applied in certain areas, but the drawbacks are obvious: vapor deposition results in a very thin conducting layer (micrometers thick) as the ring electrode; thin film electrodes are not polishable and electrochemically less well defined compared to solid electrodes; the fabrication methods involve complicated procedures and expensive equipment (vapor deposition, micromachining, etc.). Based on these reasons, we developed a simple and effective method of making a ring-disk electrode from a carbon fiber/epoxy composite tube and rod. The resulting ring-disk electrode has a relatively thin gap (20 μm). We have applied it successfully as a dual-series detector in a capillary HPLC system.

2. Experimental

2.1 Chemicals and Materials

The reagents used were as follows: $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_3\text{Fe}(\text{CN})_6$ (Fisher Scientific, Fair Lawn, NJ); $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Polysciences, Inc., Warrington, PA); KCl , Na_2CO_3 , NaHCO_3 (EM Science, Gibbstown, NJ); Leu-enkephalin (YGGFL), des-Tyr-Leu-enkephalin (GGFL),

(Bachem, Torrance, CA); copper sulfate pentahydrate (J. T. Baker, Phillipsburg, NJ) was recrystallized once from water and disodium tartrate dehydrate (Baker) was recrystallized from diluted NaOH; all the other chemicals were of analytical reagent grade purity and were used as received. The above solutions were made with 18 M Ω purified water from a Millipore Synthesis A10 system (Millipore, Billerica, MA). Teflon AF 2400 was purchased from DuPont (Wilmington, DE). FC-72 (a mixture of perfluorohexanes) was obtained from 3M (Minneapolis, MN) and was used to dissolve Teflon AF.

The carbon fiber/epoxy composite materials were purchased from A2Z Corp/Peck-polymers (Englewood, CO, USA) – distributor for DPP Pultrusion (Tilburg, the Netherlands). The glassy carbon (dia. 1.00 mm) was obtained from HTW Hochtemperatur-Werkstoffe GmbH (Thierhaupten, Germany).

2.2 Carbon Fiber / Epoxy Ring-disk Electrode Fabrication

The ring-disk electrode was made from a carbon fiber/epoxy composite rod (diameter 0.48 mm) and tube (outer diameter 1.00 mm, inner diameter 0.52 mm). The thin gap between the ring and the disk electrode (20 μ m on average) was achieved through a two-step insulation-adhesion process. The first step was to make a Teflon AF coating on the outer surface of the rod for insulation purpose. The composite rod was dipped in a 10 mg/mL Teflon AF 2400/FC72 solution following which the solvent was allowed to evaporate naturally (room temperature, no forced convection of air). Although we did not treat the surface, it is worthwhile to point out that the adhesion of Teflon AF to the substrate is usually limited, but can be improved by surface treatment and heating the coated surface. This process was repeated 10 times and then the piece was dried in an oven at 110 $^{\circ}$ C for 2 hours to ensure a defect-free Teflon AF thin film coating on the composite surface[25]. The resulting Teflon AF film (dip coat/dry 10 times) was about 7 to 8 μ m thick (the thickness can be adjusted by increasing or decreasing the number of coating cycles applied). The second step involved placing the coated rod into the tube and gluing them together. Because the outer diameter of the coated rod was slightly thinner than the inner diameter of the tube by about 12 μ m, there existed thin space between them when the coated rod composite was inserted into the tube composite. To fill the space and glue the rod and the tube composite together, the whole set was immersed in Spurr low viscosity epoxy resin (Polysciences, Inc., Warrington, PA). The epoxy resin penetrated the space between the coated rod and the tube. The electrode pair was then transferred to the oven (70 $^{\circ}$ C) for the epoxy to cure overnight. A simple test was carried out to examine insulation of the ring-disk electrode by measuring the resistance between the ring and the disk electrode. The few electrode sets that showed measurable resistance were discarded.

Electrical contact was made by connecting each carbon fiber/epoxy composite piece to a nichrome wire with silver epoxy H20E (Epoxy Technology Inc., Billerica, MA) (cured at 80 $^{\circ}$ C overnight). The electrode was insulated either in a glass tube with Torr Seal (Varian, Inc., Lexington, MA) for voltammetry, or in a Kel-F block with EPO-TEK 353ND epoxy (Epoxy Technology, Billerica, MA) for flow experiments. Before electrochemical experiments, the electrodes were wet polished with 0.05 μ m γ -alumina slurry (Buehler Ltd., Lake Bluff, IL, USA) and rinsed and sonicated with deionized water.

2.3 Microscopy characterization

Scanning electron microscopy (SEM) images were obtained using a Philips XL-30 field emission scanning electron microscope. The samples were sputter coated with Pd before SEM. Compositional analyses were done by the affiliated energy-dispersive X-ray spectroscopy (EDX). Optical microscopy images were obtained using an inverted fluorescent microscope (Model IX71) with Olympus U Plan Apo 4 $\times$ and 20 $\times$ objective lenses.

2.4 Capillary liquid chromatography and electrochemical detection

The capillary HPLC system was described before[35,36], so the process is briefly summarized as follows.

The mobile phase (0.1% TFA, 3% 1-propanol, 23% acetonitrile) was pumped through a homemade capillary column slurry packed with 3.2 μm prototype bridged hybrid C18 (Waters, Milford, MA) reversed-phase particles using 100 μm ID, 360 μm OD fused-silica capillary (Polymicro Technologies, Phoenix, AZ) as the column blank. A Waters 600 E quaternary pump (Milford, MA) with a simple tee as a flow splitter delivered mobile phase at 1 $\mu\text{L}/\text{min}$. The injected samples were peptide solutions in aqueous 0.1 % TFA. Two μL were injected. A Picoplus syringe pump (Harvard Apparatus, Holliston, MA) was used to deliver the biuret reagent (0.24 M carbonate buffer, 12 mM disodium tartrate, and 2.0 mM copper sulfate, pH 9.8) at 0.3 $\mu\text{L}/\text{min}$ into a home-made Y-shape post column reactor[37], where the biuret reagent was mixed with the chromatographic eluent after the column. The Y-shape reactor was composed of three silica capillary tubes (ID = 75 μm , OD = 360 μm), with the junction fixed in a piece of dual shrink/melt tubing (Small Parts, Miami Lakes, FL). The reaction length was 8 cm measured from the confluence. The post column reaction derivatizes peptides and produces electroactive Cu(II)-peptide[38], which makes peptides electrochemically detectable.

The electrochemical detector was composed of a BAS radial-style thin layer auxiliary electrode, a 13 μm thick Teflon spacer and the homemade carbon fiber composite ring-disk electrode block described on section 2.2. The disk electrode was placed centered and directly opposite to the flow inlet. The electrode block was polished with 0.05 μm alumina slurry and sonicated in DI water before being assembled in the flow cell. The detection potential was + 0.6 V at the disk electrode, + 0.05 V at the ring electrode. The potential was controlled by a BAS (W. Lafayette, IN) Epsilon potentiostat. A Ag/AgCl reference electrode (3M NaCl, BAS) was used as a reference electrode. All stated potentials are referred to this reference electrode.

3. Results and discussion

3.1 Carbon fiber/epoxy composite electrode characterization

The carbon fiber/epoxy composite material used in this study is made from unidirectional continuous carbon fibers and epoxy as the binder resin. SEM shows the cross-sectional and longitudinal images of this material (Figure 1). The average diameter of the carbon fibers is 7~8 μm and they are densely packed. The area percentage of carbon fibers calculated from the SEM cross section image is 50~60 %, which agrees with the manufacture's value of carbon fiber volume loading.

The electrochemical behavior of carbon fiber/epoxy composite electrode was evaluated through cyclic voltammetry (CV) in ferrocyanide-containing and ruthenium(III) hexamine-containing solutions at scan rates 20, 50, 100, 200 mV/s (Figure 2A and 2B). The same experiments were carried out on a glassy carbon electrode with the same geometrical area (both 1.00 mm in diameter) for comparison (Figure 2C and 2D), as glassy carbon is by far the most commonly used electrode material for electroanalytical purposes. The resulting voltammetric profiles recorded at a carbon fiber composite electrode and a glassy carbon electrode are very similar: the voltammograms display well-defined peak shapes; the peak-to-peak separation is about 65 mV; the peak current is dependent on scan rate (v) in the following way. For the composite electrode: in a solution of $\text{Fe}(\text{CN})_6^{4-}$ current is proportional $v^{0.43}$, for $\text{Ru}(\text{NH}_3)_6^{3+}$ the exponent is 0.44. For the glassy carbon electrode the exponents are 0.46 and 0.45 respectively (see supplementary Figure S1 for more details). The peak current dependence of sweep rate indicates that the current is limited by linear diffusion to the electrode instead of radial diffusion. Also, the similar peak current on carbon fiber composite and glassy carbon

electrode indicates that the “effective” electrode area of the carbon fiber composite is the same as the measured physical area. These CV characteristics suggest that the carbon fiber composite material, despite its appearance as a bundle of carbon fibers, behaves like a solid electrode.

As the ‘active’ component of the carbon fiber/epoxy composite electrode, the carbon fibers are usually considered as microelectrodes, the general concept of which is that the electrode is smaller than the scale of the diffusion layer developed in readily achievable experiments[39]. When bundles of carbon fibers are embed within insulating matrix, the diffusion layer of individual microelectrodes can either be isolated or overlapping with each other depending on the gap between the microelectrodes and the experimental time scale. The experimental time scale determines the diffusion layer thickness at individual microelectrodes, which is on the order of $(Dt)^{1/2}$. For a species with a diffusion coefficient of $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $(Dt)^{1/2}$ is about 30 μm for an experimental time of 1 s. Thus, in an experiment on a carbon fiber composite electrode with a similar or longer time scale, the diffusion layers of the individual carbon fiber microelectrodes start overlapping because the distance between individual carbon fibers in the composite is only 10 μm on average (seen from SEM). In fact, the distance between microelectrodes has to be at least 12 times the radius of microelectrodes[40] for it to behave like a microelectrode array, in which case the total current is the sum of individual microelectrode steady-state current response. The characteristic dimensions of the carbon fiber/epoxy composite determine that it acts like a macroelectrode on the seconds timescale. This explains the similarity between carbon fiber/epoxy composite and the glassy carbon electrode in the current response observed in Figure 2.

3.2 Carbon fiber composite ring-disk electrode fabrication and characterization

Carbon fiber composite material is commercially available in many shapes and sizes, including rods, tubes, rectangular, strips, etc. Different electrode designs can be fabricated from this composite material taking advantage of its variety in shapes and sizes. A carbon fiber composite ring-disk electrode is composed of a rod fitted inside a tube and separated by an electrically insulating material. The gap spacing between the ring and the disk electrode is determined by the diameters of the rod and the tube. A minimum gap is desirable when the ring-disk electrode is operated in generator-collector mode because of the favorable high collection efficiency. For this reason, we chose a rod and tube pair with these dimensions: Diameter (rod) = 0.48 mm; Inner diameter (tube) = 0.52 mm; Outer diameter (tube) = 1.0 mm. If the rod is fixed perfectly concentrically inside the tube, the gap will be 20 μm . The gap can be filled by allowing a resin, for example, an epoxy adhesive, to penetrate and then cure for hardening. Because the average distance between the rod and the inner tube is only 20 μm , this one-step method can easily fail to form an effective insulation due to the high chance of the rod and the inner tube contacting each other before the epoxy is cured. To prevent this, we added an insulation step before fixing the rod into the tube with the epoxy resin treatment by coating the rod surface with a Teflon AF film. The insulating Teflon AF coating is crucial in the ring-disk electrode fabrication: not only does it create an insulating layer; this step also ensures proper alignment between the rod and the tube.

The carbon fiber composite ring-disk electrode is characterized using optical microscopy (Figure 3A). The magnified image (Figure 3B) shows the junction between the ring and the disk, which is clearly composed of two layers. EDX results confirm that the layer around the disk periphery is the Teflon AF film, which contains fluorine and carbon as the main elements, and the layer surrounding the Teflon AF film is epoxy. The gap spacing is fairly uniform and is estimated from the micrograph to be around 20 μm , with Teflon layer around 7 - 8 μm and Epoxy layer 10 - 12 μm thick (as measured on Figure 3B). We have fabricated three ring-disk electrodes with the same gap spacing as judged by the optical micrographs.

The voltammetric/amperometric experiment[41] in a quiescent solution is a simple and effective method to characterize the quality of a dual-electrode, especially a ring-disk electrode, and demonstrate the thin gap between the two electrodes[29]. In the experiment, the potential at the disk electrode is scanned (voltammetric), while the ring electrode is kept at a certain potential (amperometric) to oxidize or reduce the analyte that is produced from potential scanning on the disk electrode and reached the ring electrode by pure diffusion. Figure 4 shows this voltammetric/amperometric experiment in 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ 0.1 M KCl solution. When cathodic current on the disk electrode increases, the anodic current on the ring electrode starts increasing because of the oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ that is produced from $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction on the disk electrode.

The peak-shaped voltammogram on the disk (generator) electrode resembles that on a single electrode (Figure 2B) with a lower peak current value due to the difference in electrode area. The current-potential curve from the ring (collection) electrode, on the other hand, is sigmoidal reaching a steady-state beyond about -0.25 V. The collection efficiency, the ratio of the steady state current on the collector to the peak current on the generator ($i_p = 0.215 \mu\text{A}$), is 0.404 ± 0.005 . Note that this is a ratio of an amperometric steady-state current and a voltammetric peak current.

The same experiment was repeated on another ring-disk electrode fabricated from a composite tube and rod with the same diameters (see supplementary Figure S2). The collection efficiency is 0.382 ± 0.005 . The very similar collection efficiency, and indeed the similarity of the current magnitudes, indicates the reproducibility of the electrode areas and the gap spacing between the disk and the ring electrode.

3.3 Carbon fiber composite ring-disk electrode detection of peptides following capillary HPLC

One application of the carbon fiber composite ring-disk electrode is using it as a dual-electrode detector for a flow system, e.g., flow injection analysis, capillary electrophoresis and liquid chromatography. Because the diameter of the disk electrode ($480 \mu\text{m}$) is in the same range of a silica fused capillary lumen (tens to hundreds of micrometers), the ring-disk electrode should be readily applicable for a capillary HPLC separation system. In this experiment, the composite ring-disk electrode was assembled in a thin-layer radial-flow cell with the disk electrode centered and opposite to the flow inlet so that the flow impinges directly on the disk. The disk anode is the generator electrode while the ring cathode is the collector electrode.

Capillary HPLC separation of des-Tyr-Leu-enkephalin (GGFL) and Leu-enkephalin (YGGFL) is shown in Figure 5. The peptides (GGFL and YGGFL) are separated on the capillary column. The separated peptides react with biuret reagent in the post column reactor, where the basic copper tartrate solution yields electroactive copper-peptide complexes[22,38,42,43]. The biuret solution is an effective post-column derivatizing reagent for peptides. It interacts with the backbone of the peptides and is thus effective for peptides containing more than two amino acids. The resulting $\text{Cu}(\text{II})$ -peptide is oxidized to $\text{Cu}(\text{III})$ -peptide on the disk/generator electrode and reduced back to $\text{Cu}(\text{II})$ -peptide on the ring/collector electrode. The ratio of current on the collector electrode to that on the generator electrode is defined as collection efficiency. The difference in collection efficiency for GGFL (0.8) and YGGFL (0.05) results from the homogeneous chemical reactions that follow the anodic oxidation of YGGFL. We note that a similar ring-disk electrode showed a collection efficiency value near 0.40 in a voltammetric experiment. The large difference between the collection efficiencies in the quiescent solution experiment (0.40) and the flowstream experiment (0.80) results from the faster mass transport carrying the product of the disk electrode to the ring electrode in the latter case.

The Cu-GGFL^{3+/2+} reaction is a reversible one-electron redox process on the timescale of this experiment[44], which means that the current response on the collector electrode is controlled by mass transfer only. Ring-disk electrode and flow cell parameters, as well as flow velocities, affect the collection efficiency. In general, increasing the area of the downstream electrode and reducing the gap between two electrodes[29] are favorable for achieving high collection efficiency. The collection efficiency cannot be simply compared with literature values because of the differences in flow cell design (distance between flow inlet and the electrode), flow rate, etc. In one example of the ring-disk electrode fabricated through vapor deposition, the collection efficiency is reported to be ~0.3[21]. The limited collection efficiency is due to the fact that the ring electrode is only a thin CVD film. Ring-disk electrodes fabricated through micromachining have a higher collection efficiency (close to 0.9) because the gap is small (5 μm)[31].

The electrochemistry of Cu-peptide^{3+/2+} is reversible, but there are possible complications especially for the peptides that contain the amino acids tyrosine and tryptophan. In the case of YGGFL, the cathodic current on the ring electrode is much lower than for GGFL due to the homogenous chemical reaction that occurs after the oxidation of Cu(II)-YGGFL on the disk electrode. The current response on the disk electrode comes from the reduction of Cu(II) to Cu (III). In addition, tyrosine can be oxidized at the disk. However, tyrosine oxidation is chemically irreversible on our experimental time scale. Thus, the only carrier of signal for the cathode is Cu(III). At the same time, there is an intramolecular reaction between Cu(III) and a reaction product resulting from the oxidation of the tyrosinyl residue[45] that forms an electroinactive product. The presence of the homogenous chemical reaction is responsible for the low current response on the collector electrode.

The results on the peptide solution demonstrate the ability of the ring electrode to emphasize signals from analytes that are chemically reversible. This is advantageous in biological sample analysis. There are many oxidizable species present in typical biological samples which would result in many overlapping peaks with single electrode detection. The fraction of oxidizable species that is chemically reversible is unknown, but small. The dual-electrode detection in the generator-collector mode enables selective detection of reversible species, e.g., Cu-peptide^{2+/3+}, as the chromatogram on the second (collector) electrode will be free from interfering peaks of irreversible species, thus reducing noise and increasing selectivity. The high collection efficiency ensures high sensitivity on ring collector electrode which is crucial for low concentration detection.

4. Conclusion

A carbon fiber/epoxy composite ring-disk electrode has been fabricated with thin gap between the disk and the ring electrode. The fabrication process is simple and does not require complicated machinery. The composite electrode is commercially available at very low cost and demonstrates well-behaved electrochemistry. The ring-disk electrode features high collection efficiency for electrochemically reversible species.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix

There are supplementary data (Figure S1 and S2) associated with this article.

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Figure 1. SEM images of a carbon fiber/epoxy composite with the 50-μm scale bar: cross-sectional (A) and longitudinal (B).

Figure 2.

Cyclic voltammograms of a carbon fiber/epoxy composite electrode in Fe(CN)_6^{4-} solution (A) and $\text{Ru(NH}_3)_6^{3+}$ solution (B); a glassy carbon electrode in Fe(CN)_6^{4-} solution (C) and $\text{Ru(NH}_3)_6^{3+}$ solution (D). Fe(CN)_6^{4-} solution was 1 mM $\text{K}_4\text{Fe(CN)}_6$ 0.1 M KCl solution; $\text{Ru(NH}_3)_6^{3+}$ solution was 1 mM $\text{Ru(NH}_3)_6\text{Cl}_3$ 0.1 M KCl solution. Scan rates were: 20 mV/s (—); 50 mV/s (---); 100 mV/s (....) and 200 mV/s (— · —). Both the composite electrode and the glassy carbon electrode have diameters of 1.00 mm.

Figure 3.

Optical microscopy images of carbon fiber/epoxy composite ring-disk electrode: whole ring-disk electrode surface (A) and magnified area showing the 20- μm gap between the ring and the disk (B).

Figure 4. Voltammetric/amperometric experiment in 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ 0.1 M KCl solution: cyclic voltammetry on the disk electrode (—), scan rate is 10 mV/s; amperometry on the ring electrode (---), potential = 50 mV.

Figure 5. Chromatogram of a standard solution containing 1 μM GGFL and YGGFL. The potentials at the disk and the ring electrode are 0.6 V and 0.05 V, respectively.