JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Highly Stable Redox-Active Molecular Layers by Covalent Grafting to Conductive Diamond

Rose E. Ruther, Matthew L. Rigsby, James B. Gerken, Stephanie R. Hogendoorn, Elizabeth C. Landis, Shannon S. Stahl,* and Robert J. Hamers*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

S *Supporting Information*

ABSTRACT: We demonstrate a modular "click"-based functionalization scheme that allows inexpensive conductive diamond samples to serve as an ultrastable platform for surface-tethered electrochemically active molecules stable out to ∼1.3 V vs Ag/AgCl. We have cycled surface-tethered Ru(tpy)$_2$ to this potential more than 1 million times with little or no degradation in propylene carbonate and only slightly reduced stability in water and acetonitrile.

The integration of electrochemically active molecular complexes with electrodes has great potential for the development of electrocatalytic interfaces for applications such as water splitting,[1] organic synthesis,[2] and solar energy conversion.[3] Extensive efforts have focused on tethering electrocatalytically active molecules to carbon-based surfaces;[2c,4] however, sp^2-hybridized materials such as graphite, glassy carbon, and carbon nanotubes are oxidized at modest potentials (>0.6 V vs NHE at pH 1)[5] and rapidly corrode at potentials greater than 1 V vs NHE.[5b,6] In contrast, diamond surfaces are stable to 1.7 V vs NHE,[5a,7] suggesting that diamond may be an ideal candidate for anchoring molecules with the higher redox potentials necessary for applications such as water oxidation (typically >1 V). Inexpensive conductive diamond substrates are available commercially in bulk and thin-film form. Here we demonstrate a modular "click"-based approach to covalently link a Ru coordination complex to conductive diamond surfaces and show that the surface-tethered complex exhibits extraordinarily stable and reversible redox chemistry, as it is able to withstand more than 1 million cycles to strongly oxidizing potentials (∼1.5 V vs NHE) in nonaqueous electrolytes and only slightly reduced stability in aqueous electrolyte solutions.

Figure 1a shows the scheme for anchoring a redox-active Ru complex to diamond via the Cu^{I}-catalyzed azide−alkyne cycloaddition (CuAAC or "click") reaction.[8] We prepared the $[\mathrm{Ru(tpy)_2}]^{2+}$ (tpy =2,2′:6′,2′′-terpyridyl) derivative (**1**) bearing a pendant alkyne group, as reported previously by Ziessel.[9] The unsubstituted parent complex has a Ru^{II}/Ru^{III} couple at a potential of 1260 mV vs NHE in acetonitrile (1250 mV in H_2O),[10] presenting a stringent test of the stability of the interface.

Azide functionalization of sp^2-hybridized carbon surfaces with IN_3 has been reported,[4] but this approach was not effective with the sp^3-hybridized diamond surface. Instead, we adapted a photochemical surface-functionalization method developed previously in our lab.[11] 1-Undecen-11-ol (**2**) was grafted to hydrogen-terminated surfaces of diamond using 254 nm light, producing an alcohol-terminated surface (**3**) [for details, see the Supporting Information (SI)]. The alcohol was converted to an azide (**4**) by mesylation followed by treatment with sodium azide. Ru complex (**1**) was linked to the surface azide groups via the CuAAC reaction to produce (**5**). The results presented here employed commercially available electrochemical-grade conductive diamond (Element Six); similar results for conductive diamond thin films on silicon substrates are presented in the SI.

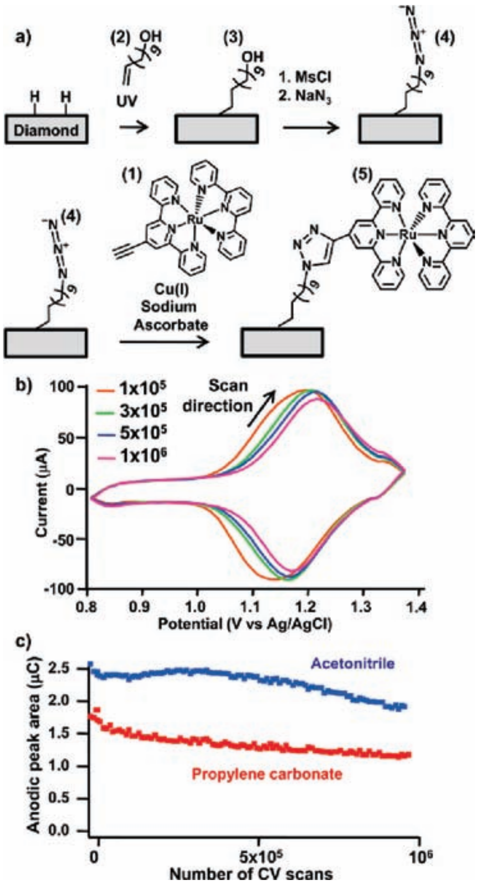

Figure 1. (a) Reaction scheme for anchoring (**1**) to diamond. (b) Cyclic voltammograms in propylene carbonate solution. (c) Anodic peak areas for 10^6 cyclic voltammetry scans in acetonitrile and propylene carbonate.

Received: January 9, 2011
Published: March 25, 2011

The functionalized surface was characterized by XPS and Fourier-transform IR spectroscopy. Formation of azide (**4**) produced an IR peak at 2090 cm^{-1}, and this peak decreased by ~70% after reaction with (**1**) (Figure S2), demonstrating that most of the surface azide groups become linked to the Ru complex. XPS measurements showed Ru and aromatic N on the surface, and quantitative analysis of the data yielded a surface coverage of 5×10^{13} molecules cm^{-2}. Control experiments (see the SI) showed that grafting of the alcohol to the diamond substrate was necessary to obtain the surface-bound azide and Ru complex (**1**) (Figures S3 and S6).

The cyclic voltammogram (CV) data in Figure 1b,c demonstrate the remarkable electrochemical stability of the $Ru(tpy)_2$ complex covalently bound to diamond. Figure 1b shows overlaid cyclic voltammograms measured in 1 M $LiClO_4$ propylene carbonate (PC) out to 1 million cycles (scan rate, 10 V/s; voltage range, 0.85−1.36 V vs Ag/AgCl). After 10^6 cycles, the surface complex showed stable, well-defined oxidation and reduction waves with $E_{1/2}$ = 1.18 V vs Ag/AgCl (~1.36 V vs NHE), which is close to the value of 1.26 V vs NHE for the unsubstituted parent compound in CH_3CN.[10] The peak-to-peak splitting of only 45 mV after 10^6 cycles indicates highly reversible electron-transfer kinetics. The peak area of 2.5 μC with our 0.275 cm^2 sample area yielded 6×10^{13} redox groups/cm^2, in excellent agreement with the X-ray photoelectron spectroscopy (XPS) results. Similar voltammograms with slightly increasing peak-to-peak splitting were obtained in $LiClO_4$/acetonitrile (AN) (Figures S7 and S12 in the SI). Figure 1c summarizes the anodic peak areas in PC and AN. In both cases, after an initial loss (presumably due to molecules bonded at less stable surface sites such as steps or defects), the CVs were remarkably stable for more than 1 million cycles.

Diamond's unusually large window of electrochemical stability suggests that surface-tethered complexes might also exhibit stable behavior in water. To test this hypothesis, CVs were obtained in aqueous solutions of 1 M $LiClO_4$. Figure 2a shows CVs out to 1.3 V vs Ag/AgCl, while Figure 2b shows the area under the oxidation wave as a function of cycle number. The CVs showed reversible behavior with $E_{1/2}$ = 1.08 V vs Ag/AgCl (~1.27 vs NHE), which is close to the previously reported value of 1.250 V vs NHE for the unsubstituted $Ru(tpy)_2$ compound.[10] There was a small initial loss of activity, but this was followed by extraordinarily high stability out to >500 000 cycles. Figure 2c shows CVs measured at different scan rates, and Figure 2d summarizes the peak-to-peak splitting (E_{pp}) and peak current (I_{peak}) as functions of the scan rate (R, in V/s). For a surface-tethered redox couple, the peak current should be linear in R, and E_{pp} should go to zero at $R = 0$.[12] Figure 2d shows that I_{peak} was indeed linear with respect to R with zero intercept, following the fitted equation $I_{peak} = (5.2 \pm 0.1) \times 10^{-5}R + (1.0 \pm 1.2) \times 10^{-5}$ with regression coefficient $r^2 = 0.99$. However, at zero scan rate, E_{pp} was ~100 mV rather than zero. This difference could arise from space-charge effects in the (semiconducting) diamond or from imperfections in the molecular layer. The standard electrochemical charge-transfer rate constant k^0_{ct} can be estimated as $k^0_{ct} = R/\Delta E_{pp}$. Using the slope of the plot of E_{pp} versus R from the five points at the highest rate yielded $k^0_{ct} = 620 \pm 30\ s^{-1}$.

Our results demonstrate that molecular complexes can be robustly linked to inexpensive diamond substrates to yield redox-active surfaces with unprecedented electrochemical stability and only minimal perturbation of the complex's redox properties relative to the parent complex in solution. We anticipate that general routes to highly stable, electrochemically active electrodes such as the one described here will provide a convenient way to combine the high selectivity and activity of molecular catalysts with the stability and convenience of inorganic electrodes.

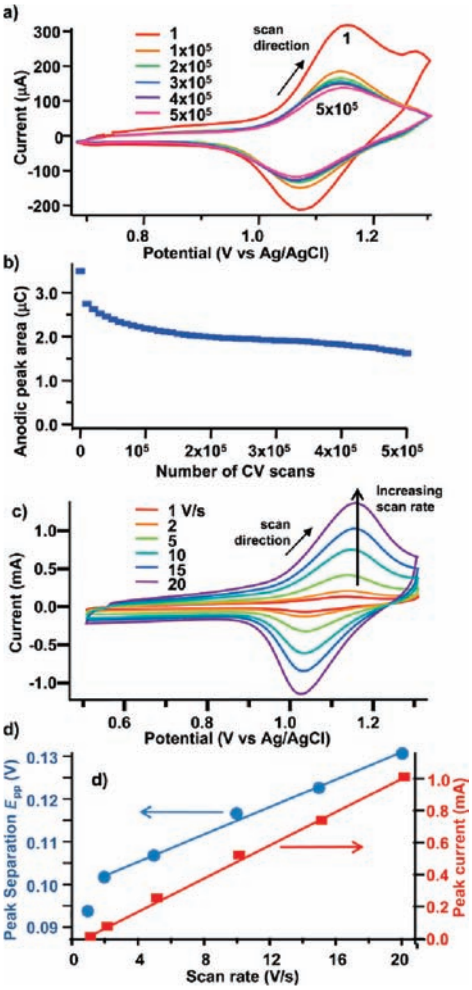

Figure 2. Electrochemical data in 1 M $LiClO_4$: (a) CVs; (b) anodic peak area vs time; (c) CVs at different scan rates in 1 M $HClO_4$; (d) peak-to-peak separation and peak current vs scan rate.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Description of samples; details of functionalization, electrochemical characterization methods, and IR and XPS characterization; electrochemical data before and after cycling; and electrochemical and XPS data for a $Ru(tpy)_2$-modified diamond thin film on a Si substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

stahl@chem.wisc.edu; rjhamers@wisc.edu

ACKNOWLEDGMENT

This work was supported in part by National Science Foundation Grants DMR-0706559 (R.J.H.), CHE-0911543 (R.J.H.), and CHE-0802907 (S.S.S.) and by DOE Basic Energy Sciences BES-SC0002160 (R.J.H.). The authors thank Dr. James Butler for providing diamond films.

REFERENCES

(1) (a) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocinio, A. O. T.; Iha, N. Y. M.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954. (b) Wasylenko, D. J.; Ganesamoorthy, C.; Henderson, M. A.; Koivisto, B. D.; Osthoff, H. D.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2010**, *132*, 16094. (c) Liu, F.; Concepcion, J. J.; Jurss, J. W.; Cardolaccia, T.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2008**, *47*, 1727.

(2) (a) Tucker, J. W.; Narayanam, J. M. R.; Krabbe, S. W.; Stephenson, C. R. J. *Org. Lett.* **2010**, *12*, 368. (b) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 12886. (c) Murray, R. W. *Electroanal. Chem.* **1984**, *13*, 191.

(3) (a) Grätzel, M. *J. Photochem. Photobiol.,C* **2003**, *4*, 145. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (c) Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117.

(4) Devadoss, A.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2007**, *129*, 5370.

(5) (a) Swain, G. M.; Ramesham, R. *Anal. Chem.* **1993**, *65*, 345. (b) Choo, H. S.; Kinumoto, T.; Jeong, S.-K.; Iriyama, Y.; Abe, T.; Ogumi, Z. *J. Electrochem. Soc.* **2007**, *154*, B1017.

(6) Besenhard, J. O.; Fritz, H. P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 950.

(7) Martin, H. B.; Argoitia, A.; Landau, U.; Anderson, A. B.; Angus, J. C. *J. Electrochem. Soc.* **1996**, *143*, L133.

(8) Collman, J. P.; Devaraj, N. K.; Chidsey, C. E. D. *Langmuir* **2004**, *20*, 1051.

(9) Ziessel, R.; Grosshenny, V.; Hissler, M.; Stroh, C. *Inorg. Chem.* **2004**, *43*, 4262.

(10) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(11) (a) Strother, T.; Knickerbocker, T.; Russell, J. N., Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. J. *Langmuir* **2002**, *18*, 968. (b) Wang, X. Y.; Landis, E. C.; Franking, R.; Hamers, R. J. *Acc. Chem. Res.* **2010**, *43*, 1205.

(12) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 19.