Multiphoton-sensitized Polymerization of Pyrrole

Katsumi Yamada,* Yu Kimura, Syoichi Suzuki, Junji Sone, Jun Chen, and Shigeharu Urabe
Department of Photonic Information and Media Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi 243-0297

(Received April 17, 2006; CL-060460; E-mail: kyamada@photo.t-kougei.ac.jp)

An aqueous solution, acting as a photoinduced electron-transfer system, was prepared using tris(2,2′-bipyridyl)ruthenium complex, methylviologen, and pyrrole to demonstrate the multiphoton-sensitized polymerization of pyrrole. A conductive polypyrrole (2.7×10^{-2} S cm^{-1} in free standing state) was obtained on a glass substrate by illumination at 800 nm using a femtosecond pulses laser. The excitation of the ruthenium complex was entailed by two-photon absorption because the ruthenium complex did not have any absorption around 800 nm.

Conductive polymers, such as polypyrrole, polythiophene, polyaniline, and their derivatives, are very useful materials for opto-electronics and nanotechnology. Their applications include molecular wires, semiconductors, display devices, biosensors, and molecular actuators.[1] We have investigated the effect of the preparation conditions on the opto-electronic behaviors of these materials.[2] The chemical and electrochemical polymerizations are usually employed as the preparation method of these materials. In particular, photopolymerization is also an interesting method, which induces the polymer product only at the photoilluminated part. A two-dimensional (2D) pattern of conductive materials can be obtained on the substrate by using photopolymerization. For the photopolymerization of these monomers, a photoinduced electron-transfer process with tris(2,2′-bipyridyl)ruthenium complex [$\mathrm{Ru(bpy)_3}^{2+}$] as the photosensitizer has been adopted, rather than the direct excitation of the monomer. A highly conductive product cannot be expected from the direct excitation of the monomer due to the random bonding positions.[3] The photopolymerization by the indirect process includes the first electron transfer from the excited state of $\mathrm{Ru(bpy)_3}^{2+}$ to the electron acceptor, and the second electron transfer from the monomer to the ground state of $\mathrm{Ru(bpy)_3}^{3+}$. If methylviologen is used as the acceptor, the resulting cation radical is recovered by electron transfer to O_2 in the solution. Repetitions of oxidative quenching of the photosensitizer and electron transfer result in the polymer's growth and the polymer's deposition on the substrate. Actually, several works for photofabrication of polymer materials were reported using the indirect process.[4]

The excited state of the molecule (containing with $\mathrm{Ru(bpy)_3}^{2+}$) is achieved not only by an one-photon process with an ordinary light source, but also by a multiphoton process using a femtosecond laser.[5] By focused illumination with this kind of laser via optics, the multiphoton absorption reaction can take place only in the space narrower than the wavelength of the light source.[6] We describe here a new method for the photopolymerization of conductive polymers, and we adopt a femtosecond laser system and a photoinduced electron-transfer system to demonstrate this method. This method allows a sub-micron patterning of conductive materials on the substrate.

Pyrrole was used as the monomer of the conductive polymer after purification. All other chemicals were purchased and used without purification. Water was deionized with a Millipore purification system. An aqueous solution was used as the polymerization solution that contains 0.1 M of lithium tetrafluoroborate, 0.22 M of pyrrole, 1 mM of methylviologen, and 1 mM of $\mathrm{Ru(bpy)_3}^{2+}$. A glass plate was immersed in the polymerization solution as the substrate for the polymer deposition, and then illuminated to polymerize the pyrrole. Excitation was provided by a mode-locked Ti/sapphire laser (100 fs fwhm). The repetition rate was 80 MHz. The laser beam was tightly focused by the objective lens (N.A. = 0.8). The illuminated areas were transferred under computer-control by shuttering the beam and driving the substrate using an XY stage (Photoscience Co., MPF-130). After illumination, the substrate was immersed in the deionized water to remove any residual monomer and other materials from the surface. The chemical structure of the product on the substrate was evaluated by Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) measurements. The conductivity of the product was measured using an inter-digitated array Pt electrode (spacing: 10 µm).

The absorption and the emission spectra of the $\mathrm{Ru(bpy)_3}^{2+}$ in the aqueous solution are shown in Figure 1. The present setup of our Ti/sapphire laser provides a photoillumination at 800 nm. In spite of the absence of the absorption around 800 nm, the emission spectrum was observed in the solution only by the photoillumination of over 20 mW. The shape of the emission spectrum is almost the same as that from the excitation of $\mathrm{Ru(bpy)_3}^{2+}$ at 400 nm with a xenon lump. These results indicate that the two-photon excitation of $\mathrm{Ru(bpy)_3}^{2+}$ occurs in this system. A previous work of the two-photon excitation of $\mathrm{Ru(bpy)_3}^{2+}$ concluded that the generated excited state displays the same photophysical characteristics as those obtained by the one-photon excitation.[7] Therefore, the deactivation process of the excited state of $\mathrm{Ru(bpy)_3}^{2+}$ could be utilized for the sensitized polymerization of pyrrole in the same way as the one-photon-sensitized polymerization.

A glass substrate was immersed in the polymerization solution, and then illuminated by the same light source. The laser

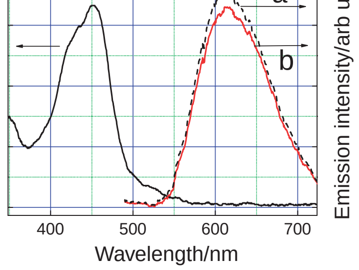

Figure 1. Absorption and emission spectra of $\mathrm{Ru(bpy)_3}^{2+}$ in aqueous solution. Emission spectra were observed by photoexcitation at 400 nm (a) and 800 nm (b).

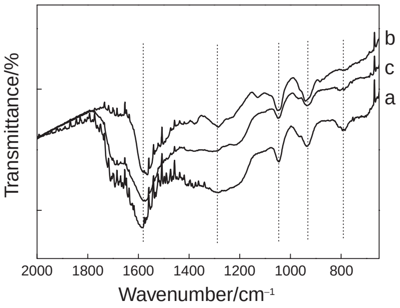

Figure 2. FT-IR-RAS spectra of the deposition from excitation at 800 nm (a), 400 nm (b), and an electropolymerized polypyrrole (c).

beam was focused on the surface of the substrate (solution side). As a result of the illumination (130 mW) for 60 s, a cylindrical deposition was found on the substrate. From the microscopic measurements, the diameter and the height were estimated to be about 1.1 and 0.9 µm, respectively. A longer illumination (for 300 s) induces further growth of the deposit. The diameter and the height then increased to 2.2 and 2 µm, respectively. It was confirmed that no deposition was obtained on the substrate using the same illumination from the solution without pyrrole or $Ru(bpy)_3{}^{2+}$.

Figure 2 shows the FT-IR spectrum of the deposit on the ITO substrate obtained by illumination at the wavelength of 800 nm. This spectrum includes some peaks which have the same wavenumber as the polypyrrole obtained by electro-polymerization or a one-photon excitation (400 nm). Their peak values are 1583, 1285, 1024, 932, and 788 cm^{-1}, and they are due to the C–C stretching vibrations in the pyrrole ring, the C–H or C–N in-plane deformation mode, the C–H and N–H in-plane deformation vibrations, the C–C out of plane ring deformation vibrations and the C–H out-of-plane deformation vibrations, respectively. The peak at 1700 cm^{-1} corresponds to carbonyl group formed by nucleophilic attack of water during the polymerization. And, the peak at 1024 cm^{-1} includes the signal of $BF_4{}^-$ as the dopant anion for oxidized PPy.[8] We concluded that the product by illumination at 800 nm was the conductive polypyrrole.

Although oxidative quenching of $Ru(bpy)_3{}^{2+}$ could be estimated as the electron-transfer mechanism, reductive quenching via $Ru(bpy)_3{}^{+}$ could be also one of the mechanism.

To cover the two electrodes with polypyrrole, an illumination at 800 nm was carried out on the inter-digitated electrodes in the polymerization solution. The electric conductivity of the obtained polypyrrole was evaluated using this electrode, and a value of 2.7×10^{-2} S cm^{-1} was obtained for the free standing state.

The fabrication of the 2D patterns was tested by driving the laser focus in the *XY* directions. In order to improve the deposition of polypyrrole, a thin polymer layer (about 200 nm) was coated on the glass substrate. Figure 3 shows an example of these results. The minimum resolution of the polypyrrole pattern is less than 800 nm. This indicates that the two-photon process occurs within the diffraction limit of the light sources in the present system. Further fine pattern will be obtained in the near future by the optimization of the illumination conditions. We are presently fabricating of three-dimensional (3D) patterns by moving the beam focus in the *Z* direction.

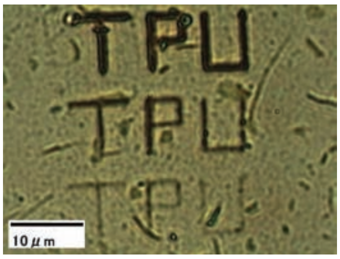

Figure 3. Micrograph of polypyrrole patterns on the glass substrate obtained by two-photon-sensitized polymerization with different driving rates of the laser focus (Top: 250 nm/s, Middle: 500 nm/s, Bottom: 1000 nm/s).

We have demonstrated a new approach for patterning a conducting polymer. This method was the photoinduced oxidation of a monomer by multiphoton excitation of the sensitizer. From comparison with the one-photon process, the method proposed can provide a higher-space (3D) selectivity of reaction sites and a finer resolution of the pattern. In the near future, the 3D nanofabrication of conductive polymers will be accomplished by driving the focal point in the *XYZ* directions. The electroactivity of these nanoparts obtained from this system will contribute to provide attractive targets such as 3D electronic circuits, biosensors, rechargeable batteries, and actuators for nanorobots.

References

1 a) K. Yamada, H. Koizumi, K. Ikeda, Y. Ohkatsu, *Chem. Lett.* **1997**, 201. b) K. Yamada, Y. Kume, H. Tabe, *Jpn. J. Appl. Phys.* **1998**, *37*, 5798.
2 a) K. Yamada, K. Teshima, N. Kobayashi, R. Hirohashi, *J. Electroanal. Chem.* **1995**, *394*, 71. b) K. Teshima, K. Yamada, N. Kobayashi, R. Hirohashi, *J. Electroanal. Chem.* **1997**, *426*, 97.
3 I. Rodriguez, J. Gonzalez-Velasco, *J. Chem. Soc., Chem. Commun.* **1990**, 387.
4 a) M. Okano, K. Itoh, A. Fujishima, K. Honda, *Chem. Lett.* **1986**, 469. b) H. Segawa, T. Shimizu, K. Honda, *J. Chem. Soc., Chem. Commun.* **1989**, 132. c) H. Yoneyama, N. Takahashi, S. Kuwabata, *J. Chem. Soc., Chem. Commun.* **1992**, 716. d) K. Teshima, K. Yamada, N. Kobayashi, R. Hirohashi, *J. Chem. Soc., Chem. Commun.* **1996**, 829. e) K. Yamada, H. Tabe, *J. Electroanal. Chem.* **2003**, *560*, 13.
5 a) W. Denk, J. H. Strickler, W. W. Webb, *Science* **1990**, *248*, 73. b) G. S. He, L. X. Yuan, Y. P. Cui, M. Li, P. N. Prasad, *J. Appl. Phys.* **1997**, *81*, 2529. c) T. Tanabe, M. Oyamada, K. Fujita, P. Dai, H. Tanaka, T. Takamatsu, *Nat. Methods* **2005**, *2*, 503. d) O. Mongin, T. R. Krishna, M. H. Werts, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Chem. Commun.* **2006**, 915.
6 a) D. A. Parthenopoulos, P. M. Rentzepis, *Science* **1989**, *245*, 843. b) S. Kawata, H. B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, *412*, 697.
7 F. N. Castellano, H. Malak, I. Gryczynski, J. R. Lakowicz, *Inorg. Chem.* **1997**, *36*, 5548.
8 a) B. Tian, G. Zerbi, *J. Chem. Phys.* **1990**, *92*, 3886. b) H. Kato, O. Nishikawa, T. Matsui, S. Honma, H. Kokado, *J. Phys. Chem.* **1991**, *95*, 6011. c) M. Omastova, M. Trchova, J. Pionteck, J. Prokes, J. Stejskal, *Synth. Met.* **2004**, *143*, 153.

Published on the web (Advance View) July 8, 2006; doi:10.1246/cl.2006.908