Photoresponse of a Liquid Junction Polyaniline Film

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Polyaniline films give a photoresponse when dipped into an aqueous solution of electrolyte.

Light-into-electricity conversion is attracting interest in conjunction with solar energy conversion and photosensors. Semiconductors can generate photocurrent by utilizing a liquid junction which is formed simply by dipping them into an aqueous electrolyte,[1] however, the number of inorganic semiconductors able to form a stable liquid junction is limited. Recently, a great variety of organic-polymer semiconductors have been synthesized and if they can be used as liquid junction photosensors, a new field of research will be opened.[2] We report here photoresponse of a liquid junction polyaniline film.

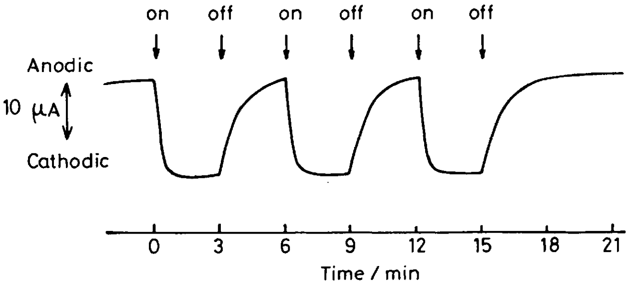

Figure 1. Current change induced by on–off switching of the irradiation with visible light on the surface of a polyaniline film on Pt dipped in $LiClO_4$ (aq. 0.1 M). Applied potential; −0.3 V (*vs.* Ag–AgCl), light intensity; 30 mW cm^{-2}, temp. 20 °C.

The polyaniline film was prepared by electropolymerization of aniline on a platinum plate (1 × 1 cm). The polymerization was carried out in an aqueous solution (pH 6) containing 0.1 M aniline and 0.2 M $LiClO_4$ at an electrode potential of 1 V (*vs.* Ag–AgCl) for 30 min to give a black film coating on the Pt plate. Its i.r. spectrum [ν(C=C) 1598 and 1500, ν(C–N, aromatics) 1310, and $\nu(ClO_4^-)$ 1143 and 628 cm^{-1}], indicated the polyaniline structure containing ClO_4^- as a dopant. The thickness of the film was observed to be 3.7 μm by scanning electron microscopy.

When the film coated on Pt was dipped into an aqueous solution containing 0.1 M $LiClO_4$ and irradiated on the surface with visible light from a 500 W xenon lamp through cut-off filters (Toshiba VY-42 and IRQ-80),† a photocurrent was induced. Figure 1 shows the current change induced by switching the light on and off at an electrode potential of −0.3 V (*vs.* Ag–AgCl). A photocurrent is generated reversibly by repeated on–off cycles of the irradiation. The cycles could be repeated at least 30 times without any appreciable change of the current characteristics. At applied potentials higher than 0 V (*vs.* Ag–AgCl), the irradiation induced a low anodic photocurrent of the order of 1 μA cm^{-2}. At potentials lower

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† VY-42 cuts off u.v. light and IRQ-80 i.r. light: the transmittance of the former filter at 420 nm is 50%, and that of the latter at 800 nm is 2%.

than 0 V, the cathodic photocurrent increased sharply with the decrease of the applied voltage until it reached the value of 21 μA cm^{-2} at −0.5 V. Such a potential dependence of the photocurrent indicates that the polyaniline is working as a p-type semiconductor. A similar film used to coat a transparent Nesa glass electrode induced almost the same photocurrent when irradiated at the film–water interface, however, no photocurrent was generated when irradiated from the Nesa glass side. This fact indicates that the junction formed at the film–water interface is responsible for the photocurrent.

Raising the concentration of $LiClO_4$ in the solution by one order of magnitude produced a *ca.* 30% increase in the cathodic photocurrent, suggesting the participation of the salt in the photoelectrochemical event. Lowering the pH by 3 units gave only a 5% higher cathodic photocurrent, indicating only slight, if any, participation of protons in the process. The film produced a steady photocurrent of 27 μA cm^{-2} for 5 h in a 0.5 M $LiClO_4$ solution at the applied potential of −0.5 V. No gas evolution was observed at either electrode during the illumination. The mechanism of the photoresponse of the present system can not be explained so far, however, the slow response shown in Figure 1 as well as the salt effect described above might suggest the presence of some chemical reaction such as photoelectrochemical doping and undoping of the ions present in the solution.

Thus, it has been shown that a polyaniline film generates a photocurrent by forming a liquid junction on dipping into an aqueous electrolyte.

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