Formation of a Light Image in a Polyaniline Film containing Titanium(IV) Oxide Particles

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High-resolution light images are formed in polyaniline films containing TiO_2 particles when the film is immersed in an aqueous neutral solution containing methanol.

Electrochemically synthesized polyaniline films possess high redox reactivities in aqueous acidic solutions, and the oxidized and reduced forms of the film exhibit vivid green and yellow, respectively.[1,2] We have previously reported that such colour changes of the film caused by the redox reaction can be utilized for electrochromic display devices because of its fast response and high durability.[3] The present communication describes the preparation of polyaniline films that can be reduced with light illumination under open circuit (*i.e.* no applied bias potential) to give light images of high resolution. The strategy employed in the present study is to incorporate TiO_2 particles into polyaniline films during the course of the electrochemical polymerization of aniline. Photogenerated electrons in the TiO_2 particles incorporated in the resulting polyaniline films are used to reduce polyaniline, but in order to have light images of high resolution the films have to satisfy the following two contradictory prerequisites. One is that the polyaniline films must have low conductivity which can prevent spreading of the photogenerated electrons from the periphery of the illuminated area, and the other is that such films should have high electrochemical activities when illuminated. We have discovered that such events can be achieved if we use aqueous neutral solutions containing alcohols as electrolyte solutions.

The polyaniline films containing TiO_2 particles (PAn/TiO_2) were prepared by electrolysis at 0.2 mA cm^{-2} for 100 mC cm^{-2} of aqueous 2 mol dm^{-3} HCl solution containing 1 mol dm^{-3} aniline and 30 g dm^{-3} TiO_2 particles (Aerosil P-25) under N_2. The TiO_2 particles used have the anatase structure and have an average particle size of 21 nm. An indium–tin oxide coated glass plate was used as the anode, and the deposition bath was stirred during the course of the electropolymerization. Observations of the resulting polyaniline films with a scanning electron microscope and X-ray microanalyses revealed that the TiO_2 particles were distributed uniformly in the film. The amount of the incorporated TiO_2 determined calorimetrically[4] was as high as 70 wt% of the resulting films, but the films were a vivid green. The incorporation of TiO_2 into polyaniline must have occurred owing to participation of Cl^--adsorbed TiO_2 particles as in the case of the incorporation of TiO_2 into polypyrrole.[4]

Illumination for 15 s with a 500 W xenon lamp of the PAn/TiO_2 in aqueous 1 mol dm^{-3} HCl containing 20 vol% of methanol under open circuit caused complete changes in the film colour from green to yellow. The photoreduced film could be re-oxidized to green by polarization at 0.5 V *vs.* SCE in the dark. The photoreduction of polyaniline is rationalized by such energetic correlations between TiO_2 and polyaniline that the potential of the bottom of the conduction bands of anatase-TiO_2 at pH 0 is less than −0.29 V *vs.* SCE,[5] which is negative enough to reduce polyaniline. The photogenerated positive holes in the TiO_2 particles must be consumed by oxidation of methanol dissolved in the solution. The use of 1 mol dm^{-3} HCl containing 20 vol% methanol, however, was

Fig. 1 Light image formation on PAn/TiO_2 film immersed in 0.5 mol dm^{-3} phosphate buffer (pH 7) containing 20 wt% methanol by projecting the positive image on the PAn/TiO_2 film with illumination by a 500 W xenon lamp for 1 min

not successful for producing light images. The reduced area was steadily spread over the entire film with increased illumination time, because the oxidized form of polyaniline possesses high conductivity, which allows easy diffusion of photogenerated electrons beyond the periphery of the illuminated area.

It is well known[6] that the conductivity of a polyaniline film can be remarkably decreased by immersing it in aqueous neutral solutions; as a result of deprotonation. The film changes from green to blue in that case. Illumination of the PAn/TiO_2 film in 0.5 mol dm^{-3} phosphate buffer solution (pH 7) containing 20 vol% of methanol caused a change from blue to yellow in the illuminated area alone, and light images could be produced as shown in Fig. 1. The polarization of the film at 0.5 V *vs.* SCE was again enough to erase the light image and turn it blue again. The light image was produced by projecting the positive image on the PAn/TiO_2 film for 1 min using the 500 W xenon lamp as a light source and an enlarger for printing photographs. The shade of the obtained picture resulted from difference in the degree of reduction of polyaniline, which depended on the intensity of irradiated photons. The produced images were very stable and no change in their contrast was noticed for at least 2 weeks if the film was kept under open circuit in the N_2-purged solution. Considering that deprotonated polyaniline films have no redox activity,[1,7] it is unlikely that polyaniline films in the deprotonated state were photoreduced to give the light images. It is more likely that deprotonated films were converted into the protonated form only in the illuminated area with the mechanism that protons which are released from methanol on its oxidation with involvement of photogenerated positive holes attach to the deprotonated polyaniline at the place where the proton-release occurs, resulting in photoreduction of the film as observed. The 'write–erase' cycle was successfully repeated for more than 100 cycles, though gradual oxidative degradation of polyaniline was noticed from changes in its absorption spectrum.

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