

Electrophoretic and Photolithographic Fluorescent Imaging with *t*-BOC-Protected Poly(*t*-BQzMA)-Polyaniline Conducting Particle System

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Among the conducting polymer, polyaniline-based photo-images are important since the conducting properties of polyaniline can be regulated by employing acid/base (doping/dedoping) chemistry.^{1,2} Recently, we reported on noble construction of electrophoretic fluorescence imaging prepared by nano-porous particles of polyaniline-fluorescein complex.³ These conducting particle system hold promise as fluorophores since they are partially polarized and, as a result, they can be electrophoretically deposited onto a film of a micro-patterned polyaniline counter electrode.

In continuing investigations aimed at the development of new systems for producing patterned fluorescence images, we explored the possibility of generating patterned images with conducting particles comprised of an acid-labile *t*-BOC group protected Qz-methacrylate polymer (*t*-BQzMA) and polyaniline.^{4,5} We hypothesized that protonation between the acidic phenol moiety of Qz polymer and a non-conducting polyaniline emeraldine base (EB) would not only render complexation but also the conductivity change of polyaniline by acid/base (doping/dedoping) chemistry.^{1,2} It was assumed that the partially positive-charged polyaniline emeraldine salt (ES) and negatively charged Qz polymers are separated and deposited on the counter electrode during the electrophoretic deposition process, and then patterned fluorescence images could be obtained. In order to demonstrate the feasibility of the above proposal, we developed a method to prepare micro-scale particles from the poly(*t*-BQzMA)-polyaniline system. A schematic of the procedure used for formation of the complex between

the poly(*t*-BQzMA) and polyaniline is shown in Fig. 1.

Polyaniline samples, poly(*t*-BQzMA) and *t*-BOC-polyaniline were prepared as described in detail elsewhere.^{2,6,7} Simply, blending the polyaniline EB and the poly(*t*-BQzMA) (1:2 by weight) in 1-methyl-2-pyrrolidinone (NMP) as solvent enabled the introduction of doped fluorescent labels on the porous structure as a consequence of proton transfer (or doping) under triphenylsulfonium triflate (TPSOTf, 5 wt%) as a photo acid generator (PAG); the solution was irradiated with 250 nm UV for 30 min, and then heated at 70 °C for 1 h to give the deprotected phenol form from the protected Qz polymer. Since the polyaniline in its EB state is basic, acidic phenol moiety of Qz polymers can exist in phenoxy anion forms. Slow addition of NMP solution to ethanol followed by sonification leads to efficient formation of micro-scale particles. Scanning electron microscope (SEM) images, obtained following centrifugation and removal of large aggregates by filtration (1 μm), demonstrate that the micro-sized particles are indeed generated by this method (see the experimental part) as shown in Fig. 2a. An ethanol solution, containing the particles obtained from the poly(*t*-BQzMA) and the EB form of polyaniline, display a purple-pink (Fig. 2b) and bright yellow emission (Fig. 2c). The bright yellow emission indicates that they emit bright yellow fluorescence associated with the deprotected phenol form of poly(QzMA) and, as a result, they can be protonated to the EB form of polyaniline to give the ES form. In addition, the micro-sized particles were found to be stable as ethanol suspensions without aggregation even after heating to reflux condition for 24 h. The particles are also stable in the presence of 5% tetrabutylammonium fluoride salt. The observation of stable particles is significant in that most of conducting polymer particles probed to date tend to aggregate after prolonged storage. It is felt that the approach described above should be

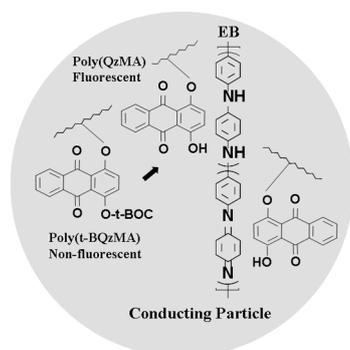


Figure 1. A schematic procedure for formation of the complex and conducting particle system incorporating poly(*t*-BQzMA) and polyaniline.

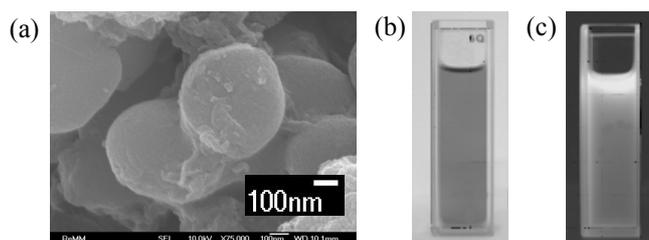


Figure 2. SEM (a), photographs of the conducting particles (ca. 0.5 μm) without irradiation (b) and upon 365 nm irradiation (c).

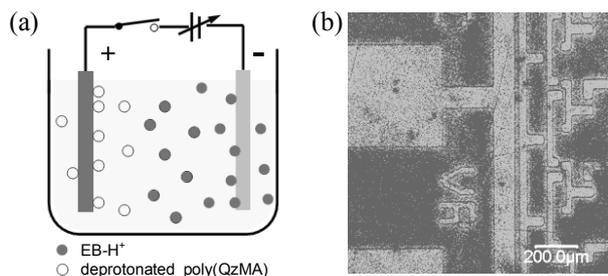


Figure 3. A schematic illustration of the device used for the electrophoretic micro-patterning with a solution containing conducting particles (a). The micro-patterned image obtained after electrophoresis (b).

generally applicable to the fabrication of stable conducting polymer blend system.

In most approaches for chemical patterning, irradiation is responsible for promoting irreversible modifications of photoresists in irreversible patterning processes. In contrast, pH sensitive or electro-sensitive materials which undergo reversible modification of their properties are highly desirable. Polyaniline is known to exist in various oxidation states, such as LB (leucoemeraldine base), EB, and PB (pernigraniline base). Interconversions between these states permit the construction of electrochemically reversible redox cycle. Thus, we envisaged that reversible proton transfer could be constructed based on the control of the electrochemical redox cycle of polyaniline surface properties. Accordingly, the final phase of the current investigation focused on the electrophoretic patterning of the obtained polymer particles. A micro-patterned positive electrode (anode) was prepared according to the previously described method.³ Electrophoretic deposition on the micro-patterned polyaniline film with the polymer particles is illustrated schematically in Fig. 3a. When an electric field is applied, the positively charged polyaniline are collect on the cathode, whereas the negatively charged Qz particles are deposited on the surface of the anode. Indeed, application of electric field to the solution of the particles leads to generation of patterned fluorescence images as displayed in Fig. 3b.

To extend the photoimaging capability of the unique polyaniline-Qz polymer system, soluble polyaniline was synthesized by modifying with a *t*-BOC group; while unmodified polyaniline is not soluble in common organic solvents. The prepared *t*-BOC-polyaniline⁵ is highly soluble in common solvents such as THF and chloroform. As a result of this solubility difference, conducting patterns can then be achieved in a photo-lithographic process by employing the Qz polymer, thereby capable of generating conducting and fluorescence patterns. To investigate the feasibility for potential application of microelectronic devices, thin films were prepared by spin-coating a THF solution containing poly(*t*-BQzMA), *t*-BOC-polyaniline, and PAG (TPSOTf, 5 wt%) on quartz substrates. The polymer film was irradiated with 250 nm UV for 1 min through a photo-mask in a contact mode followed by post-exposure-bake (PEB) at 120 °C for 1 min. As shown in Figure 4a, after PEB treatment and HCl vapor exposure, complete deprotection of *t*-BOC groups in polymer films was confirmed by UV spectral data. The unexposed film displays two absorption bands around 320 nm and 550 nm. Upon exposure to UV light, the exciton

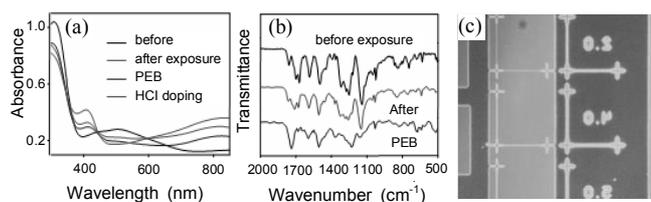


Figure 4. UV absorption spectral changes of a conducting polymer film containing *t*-BOC-polyaniline and poly(*t*-BQzMA) on a quartz plate (a) and the corresponding IR spectral change. The micro-patterned fluorescent image obtained by a photo-lithographic method (c).

band around 580 nm decreases and two new bands appearing around 400 and 800 nm slightly increase with increasing exposure dose. These bands are usually assigned to polaron bands originated from the conducting structure of polyaniline, *i.e.*, doped, emeraldine salt.³ Further, visual inspection of the film showed color changes at the exposed areas. In addition, the deprotection of *t*-BOC groups in the polymer films were monitored by IR spectral changes (Figure 4b). During UV exposure and PEB, the absorption bands at 1770 cm⁻¹ associated with carbonyl of *t*-BOC groups gradually decreased with the PEB process. Simultaneously, the C-O bond (banding) intensity at 1120 cm⁻¹ related to of *t*-BOC group decreased by removal of *t*-BOC group in the polymer. The deprotected polymer complex is insoluble in common organic solvents, and the un-irradiated part is soluble in THF solvent. Consequently, THF solution has been used as a developer to obtain good quality negative-tone patterns with fluorescence (Figure 4c). As expected, the fluorescence was effectively quenched when the fluorescent image patterns were treated with a NaOH solution since the base inhibits the intramolecular hydrogen bonding of the Qz moiety. Furthermore, fluorescence was recovered by acidic HCl treatment. These results imply that the fluorescence and conductivity property can be controlled by acid/base chemistry.

In summary, application of an electric field to the solution containing the conducting particles enables formation of patterned fluorescence images by electrophoretic method. The results of electrophoretic fabrication and photo-lithographic imaging should stand as interesting and potential contributions to the fields of recording and sensing.

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