CONDUCTIVITY MEASUREMENTS OF POLYANILINE FILMS DOPED AT VARIOUS POTENTIALS BY CURRENT-SENSING ATOMIC FORCE MICROSCOPE

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The polymerization conditions determine morphology of polyaniline (PAn) films, which in turn determines their conductivities.[1] Wrighton et al. reported PAn resistances measured *in-situ* as a function of the applied potential to PAn films formed between interdigitated gold micro-electrodes.[2] In their work, the faradaic currents resulting from electron transfer reactions of degradation products and aniline dimers might have affected the film resistance. Here we now report the conductivities of dry PAn films as a function of the applied potential to achieve varied doping levels, after the degradation products and soluble oligomers are removed, using a current-sensing atomic force microscope.

The PAn films were prepared by the potentiodynamic scanning between -0.10 and 1.2 V *vs.* Ag/AgCl in a solution containing 50 mM aniline and 1.0 M HNO_3. After the degradation products and dimers were removed by washing the film thoroughly with deionized water, various potentials were applied to obtain different doping levels in 1.0 M HNO_3 for 600 s. Fig. 1 shows the ranges of conductivities for PAn films doped at various potentials. The conductivity was calculated from the linear parts of I/V curves obtained at various spots, which had different magnitudes of currents. At -0.10 V the PAn film is in its neutral state (leucoemeraldine), which still has conductive areas in the current image. The conductive areas were seen even at -0.30 and -0.20 V. At 0.30 V, the most conductive protoemeraldine was obtained. When a potential of as high as 0.50 ~ 0.60 V was applied, the entrapped dimers were oxidized and the degradation products are produced, which might have lowered the conductivity.[1] The conductivities of the PAn films at these potential were lower than those at 0.30 V. At 0.80 V the film became almost an insulator with its conductivity of nearly zero. The transition from a conductive to the insulating region takes place at ca. 0.50 V, where the degradation processes also start.

The morphology of the PAn film has been shown to change depending on the electrolytes used during its preparation, and the linear PAn fibers are prepared in the HNO_3 solution.[3] We prepared the PAn nanostructures by oxidizing aniline at a 4-aminothiophenol/n-hexadecane-thiol mixed self-assembled monolayer (SAM) modified Au electrode. Figure 2 shows the topographic and current images recorded at a bias voltage of 50 mV. From the topographic image (Fig. 2a) the PAn nanostructure appears to be a single wire, but one can see from the current image shown in Fig. 2b that the PAn nanorope shown in Fig. 2a is actually made of three pieces of PAn nanostructures.

REFERENCE

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2. W. P. Elizabeth, J. R. Antonio, and M. S. Wrighton, *J. Phys. Chem.*, **89**, 1441 (1985).
3. S.-J. Choi and S.-M. Park, *J. Electrochem. Soc.*, **149**, E26 (2002).

Acknowledgment: This work was supported by the Korea Science and Engineering Foundation through the Center for Integrated Molecular Systems.

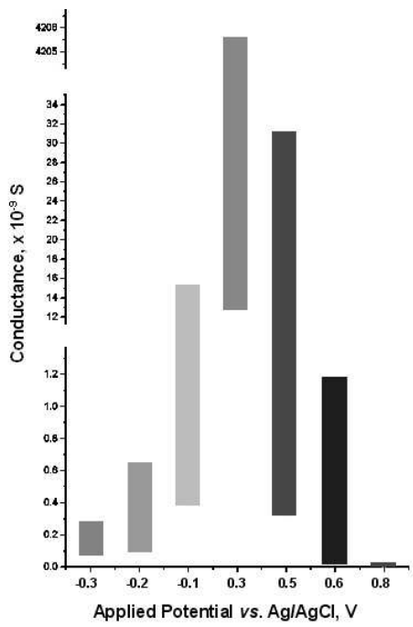

Fig. 1. Ranges of conductivities of PAn films oxidized at various potentials.

(a)

(b)

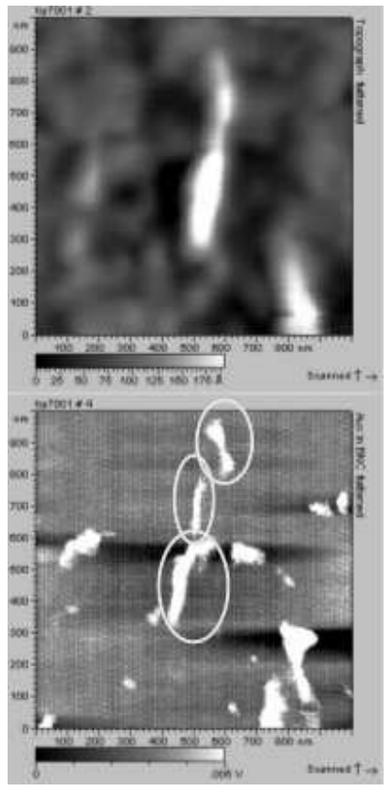

Fig. 2. Topographic (a) and current images (b) recorded for the nanostructures prepared on the mixed SAM modified gold electrode.