

## Fabrication and Characterization of Ordered Oligoaniline Film

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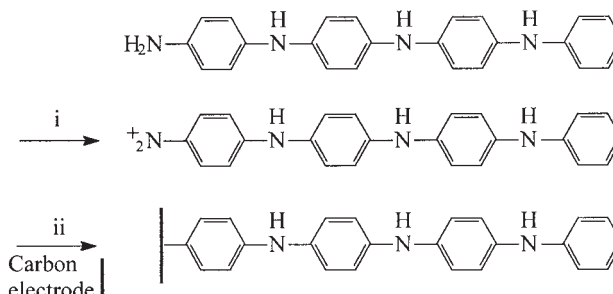
A highly organized phenyl-capped teraniline (PC-teraniline) film at the molecular level was fabricated on carbon surfaces by electrochemical reduction of diazonium salts. Cyclic voltammetry (CV), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) were employed for the characterization of the film.

Electrically conducting polymers have received much attention for their enormous potential applications in serving as molecular electronics, protective coating against corrosion, biosensors, chemical sensors, and media for energy conversion and storage.<sup>1-3</sup> For applications to many devices, it is desirable to have them in a thin film structure, preferably with known thickness and molecular packing.<sup>4</sup> However, the obstacles stemmed from the relatively poor adhesion of polymer films onto solid surface, the lack of fine control on the film thickness and orientation on solid surface and the need to develop methods for their micro- and nanopatterning prevent their wide applications.

Recently, the covalent attachment of a self-assembled monolayer (SAM) containing an electropolymerizable unit on Si<sup>5</sup> or gold<sup>6</sup> surfaces was reported for solving above problems. Moreover, Turyan et al. demonstrated the formation of 2-D polyaniline by the electrochemical polymerization of surface-confined anilinium ions that were electrostatically attached to a negatively charged SAM of  $\omega$ -mercaptodecanesulfonate<sup>7</sup>. However, to our knowledge, until now there is no any report on the precise control of the arrangement and orientation of conducting polymer on solid surfaces.

In this work, we present a new and noncorrosive cathodic approach — the electrochemical reduction of PC-teraniline diazonium salts<sup>8</sup> — for the formation of ordered oligoaniline film as a model of polyaniline film on carbon substrate. The carbon substrate, which has good conductivity and resistance to chemical attack,<sup>9</sup> is an ideal substrate and attractive for various applications in the field of sensors and catalysis. Because of attaching PC-teraniline molecules by C-C covalent bond and normal orientation toward the surface, the obtained film was not only very firm but also high organized at molecular level.

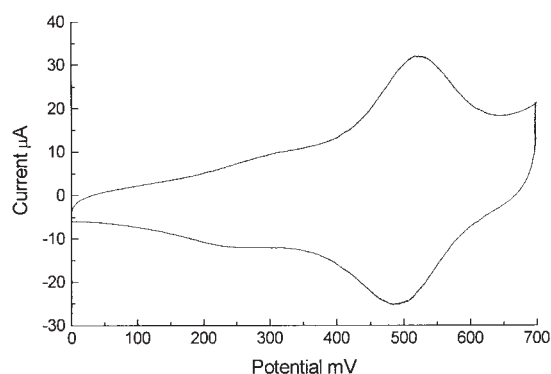
Phenyl-capped teraniline, as a model, was attached on various carbon substrates as depicted in Scheme 1. Instead of using a recrystallized diazonium salt, the diazotation of the parent tetraaniline (synthesized and kindly provided by Dr Z. Sun) was carried out in an ice-cold acidic water for a short period (step (i)). Then the solution was transferred to an electrochemical cell, in which the cathodic functionalization of carbon substrates took place (step (ii)). The cyclic voltammograms recorded at a glassy carbon electrode (GCE) in a solution of the in situ generated diazonium salts present a broad irreversible cathodic peak at about  $-0.4$  V vs Ag/AgCl (sat. KCl), which tends to



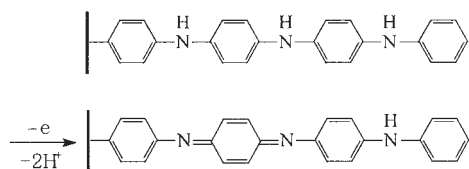
**Scheme 1.** Schematic representation of preparing oligoaniline film on carbon substrates. (i) the parent tetraaniline (2 mmol in 1 M HCl), NaNO<sub>2</sub> (2 mmol), ice-cold, 5 min; (ii) cyclic scanning between 0.0 and  $-0.8$  V vs Ag/AgCl (sat. KCl).

disappear when cycling the potential repeatedly. This behavior is characteristic of the reduction of an aryl diazonium salt to a highly reactive aryl radical grafted rapidly on the electrode surface.<sup>8</sup> After the reductive current of the characteristic cathodic peak became stable, the electrode was rinsed and ultrasonicated with distill water and acetone (without ultrasonic agitation for the modification on highly oriented pyrolytic graphite (HOPG)).

PC-teraniline modified GCE was first investigated with cyclic voltammograms. Figure 1 shows the CV of the electrode in 0.5 M HCl. A clear reversible wave at 500 mV vs Ag/AgCl is observed and the peak currents show typical surface-controlled behavior with a linear relation with the scan rate (figure not shown). The oxidation/reduction waves are stable over 30 scans between 0 and 700 mV. Moreover, both the oxidation and reduction peak potentials are shifted negatively with increasing pH at a rate of approximately 120 mV/pH. This suggests electron transfer and deprotonation in a 1 : 2 ratio. This behavior was also found with other oligoaniline.<sup>10</sup> The redox reaction of the film is shown to be as follows:



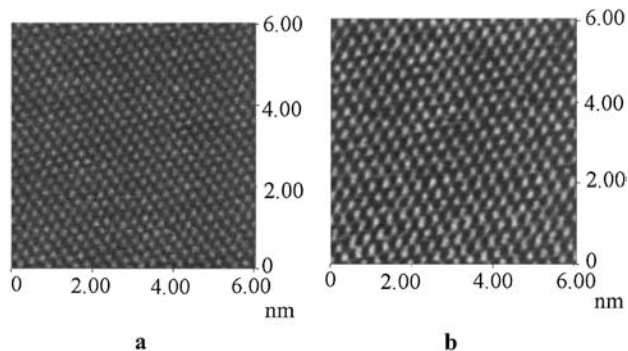
**Figure 1.** Cyclic voltammograms of a GCE modified with PC-teraniline in 0.5 M HCl at a scan rate of 100 mV.



The surface coverage is calculated by integration of the anodic wave (at 500 mV) in Figure 1, and a value of  $14.6 \times 10^{-10} \text{ mol cm}^{-2}$  is obtained. This indicates that PC-teraniline modified on GCE surface forms a compactly packed monolayer.<sup>8b</sup>

The presence of PC-teraniline on the surface of GCE was also revealed by XPS. Before grafting of PC-teraniline, the GCE surface does not show a nitrogen signal. After grafting, rinsing and ultrasonicated in water, ethanol and acetone, and drying, a large signal appears at 399.7 eV, corresponding to N1s core level spectra of PC-teraniline. This demonstrates that the PC-teraniline has been covalently bonded to carbon substrate surfaces.

PC-teraniline modified on HOPG surface was characterized by STM. The atom resolution of a bare and clean HOPG is given in Figure 2a. Figure 2b shows a typical example of a high-resolution image of PC-teraniline modified HOPG surface. It is seen that a highly ordered monolayer is formed. The nearest-neighbor distance between the white spots is  $3.8 \pm 0.1 \text{ \AA}$ , in agreement with the diameter of one phenyl group of oligoaniline



**Figure 2.**  $6 \times 6 \text{ nm}$  STM images of HOPG surfaces. (a) bare HOPG surface, (b) surface derivatized by electrochemical reduction of PC-teraniline diazonium salt.

on the carbon surface. This confirms that PC-teraniline attached to HOPG surface can be precisely arranged at the molecule level and perpendicularly oriented toward the surface.

In conclusion, PC-teraniline was grafted for the first time on carbon substrate by electrochemical reduction of diazonium salts. A highly ordered and very stable oligoaniline film was obtained. Moreover, the film thickness can be controlled by employing different length oligoaniline. The convenient electrochemical grafting of carbon substrates by oligoaniline constitutes a promising versatile platform for the construction of molecular electronics, protective coating against corrosion, media for energy conversion and storage and the study of the factors that govern the electrical properties of conducting polymers.

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