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Electric field driven protonation/deprotonation of 3,4,9,10-perylene tetracarboxylic acid immobilized on graphene sheets via π–π stacking

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ABSTRACT

The electrochemistry of 3,4,9,10-perylene tetracarboxylic acid (PTCA) immobilized on graphene surface (PTCA/G) via π–π stacking shows four pairs of current peaks in cyclic voltammogram. These peaks are ascribed to sequential protonation and deprotonation of carboxyl groups in PTCA. The distinct differences in four peak potentials demonstrate the existence of electrostatic and hydrogen-bonding interactions between the four carboxyl groups. In addition, it is found that the kinetics for the protonation and deprotonation of PTCA/G changes from surface controlled process at low scan rate to diffusion controlled one at high scan rate.

1. Introduction

Recently, the acid/base properties of surface-immobilized molecules have been extensively studied by diverse techniques, such as contact angle measurements [1,2], quartz crystal microbalance [3], atomic force microscopy [4,5], spectroscopy [6,7] and electrochemical methods [8,9]. Among them, electrochemical methods are simple and useful for qualitative and quantitative measurements of the charging properties of electrode surfaces. Previous reports have shown that surface charge density of acid-terminated self-assembled layers (SAMs) caused by protonation/deprotonation is dependent on not only solution pH, but also on surface electric field [10–12]. It is usually accepted that the surface electric field of an electrode is assumed to drive the protonation and deprotonation processes at constant solution pH. White et al pointed out that sweeping potential to a value negative to the potential of zero charge (pzc) results in protonation of the acid groups for reducing the electrostatic repulsion between the substrate and the deprotonated acid groups of SAMs. Conversely, positive electrode potentials drive the deprotonation process [11]. The electric field driven protonation/deprotonation induces changes of differential capacitance of the modified electrode, resulting in a pair of reversible capacitive current peaks. Theoretical and experimental studies demonstrated that both the peak current and the half-wave potential ($E_{1/2}$) are functions of solution pH [12].

3,4,9,10-Perylene tetracarboxylic acid (PTCA), an aromatic organic perylene dye, has attracted extensive interest due to its outstanding optical and chemical stability [13,14]. It has been used for improving the solubility of graphene and as a biocompatible linker for DNA and other biomolecules through its carboxyl groups when it is immobilized on graphene sheets via π–π stacking [15,16]. Recently, the electrochemical activity of PTCA was reported and the observed electrochemical responses are ascribed to three one-electron transfer process of PTCA although this is difficult to understand [17]. Obviously, exploration and understanding of the electrochemistry of PTCA is urgent for its various applications.

In this communication, the electrochemical property of PTCA immobilized on graphene sheets (PTCA/G) via π–π stacking was investigated. The resultant PTCA/G was characterized by UV–vis spectroscopy and FTIR spectroscopy. Electrochemical titration method using ferricyanide as the probe was used to determine the apparent pKa of PTCA/G. Voltammetric techniques were used to characterize the protonation and deprotonation processes of PTCA at the PTCA/G modified electrode. The electrostatic effect of negative charges, coupling effects between the nearest carboxylic acid groups, the influence of scan rate on the peaks of PTCA/G were discussed.

2. Experimental

Natural graphite powder (99.9995%, 100 mesh) was obtained from Alfa Aesar Company. 3,4,9,10-Perylene tetracarboxylic dianhydride (PTCDA, 97%) was purchased from Sigma–Aldrich. All other reagents were of analytical grade.

Graphene oxide (GO) was synthesized from spectral graphite according to a modified Hummer's method [18,19]. PTCA/G was fabricated by reduction of GO in the presence of PTCA under strongly alkaline conditions [15,20]. In detail, the PTCA was

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dissolved by hydrolyzing PTCDA in 2% KOH aqueous solution at 80 °C for 1 h and then cooled to room temperature. Subsequently, 1 mg/ml GO suspension was added to the above solution. The resulting solution was heated at 80 °C under vigorous agitation for 9 h. The product PTCA/G was centrifuged, thoroughly washed with dilute KOH solution and ultrapure water respectively and then dried under vacuum at room temperature. As a comparison, graphene was fabricated by the same procedure without addition of PTCA.

Glassy carbon (GC) electrode was well polished with 0.05 μm alumina slurry, and then cleaned ultrasonically in ethanol and water for 3 min, respectively. The PTCA/G and graphene modified GC electrodes were prepared by casting 5 μL PTCA/G or graphene suspension onto the pretreated bare GC electrode using a micropipette tip and dried in air.

UV–vis absorption spectra were performed on a UV 3600 spectrophotometer (Shimazu, Japan). FTIR spectra were collected on a Bruker TENSOR 27 spectrometer (Bruker, Germany) equipped with a liquid nitrogen cooled mercury cadmium telluride detector. Electrochemical measurements were carried out on a CHI 660D electrochemical working station (CH instruments) using a three-electrode system with a modified glassy carbon electrode (3 mm in diameter) as the working electrode. A platinum wire and an Ag/AgCl reference electrode (saturated KCl) were used as the counter and reference electrodes, respectively.

3. Results and discussion

Fig. 1A shows the UV–vis absorption spectra of graphene, PTCA and PTCA/G. The characteristic absorption peaks of PTCA at 439 nm, 467 nm and 551 nm and the characteristic absorption peak of graphene around 245 nm are observed in the spectrum of PTCA/G, indicating the formation of PTCA/G nanocomposite. The FTIR spectra of PTCA, graphene and PTCA/G are shown in Fig. 1B. For the FTIR spectrum of graphene, the peak at 1597 cm^{-1} is assigned to the aromatic ν(C=C) stretching vibration in graphene and PTCA. The peak at 1691 cm^{-1} in the spectrum of PTCA is ascribed to ν(C=O) vibration of carboxyl groups. The characteristic peaks of graphene and PTCA are all observed in the spectrum of PTCA/G. However, their band centers shift to lower wavenumbers (1594 cm^{-1} and 1664 cm^{-1}), which might be attributed to the π–π stacking interaction between PTCA and graphene. These results demonstrate that reduction of graphene oxide to graphene and immobilization of PTCA on graphene sheets occur simultaneously in the present one-step synthesis method.

For acid-terminated SAMs, the surface property can be studied by electrochemical titration method using ferricyanide/feerocyanide redox probe. In our experiment, $K_3Fe(CN)_6$ was used as the electroactive probe to determine its interaction with the surface of PTCA/G in solutions with different pH values. Consistent with the reported results [8], the peak current of $Fe(CN)_6^{3-/4-}$ probe changes remarkably with solution pH values (as shown in Fig. 2). At lower pH (<4), the carboxyl groups of PTCA/G are fully protonated, which hardly affects or inhibits the electron transfer between the probe and the electrode. Thus, a pair of well-defined peaks appears and the peak current of the probe changes slightly to show a plateau (stage I in Fig. 2B). With the increase of pH (4–6.5), the carboxyl groups gradually deprotonate to yield a negatively charged carboxylate ion on the surface of PTCA/G. The formed negative charges will increase the electrostatic repulsion between the negatively charged probe and the negatively charged carboxylate groups. Therefore, a prominent decrease in peak current occurs in this pH range (stage II in Fig. 2B). Further increasing the solution pH higher than 6.5, all the carboxyl groups will be fully deprotonated and the electrostatic repulsion between the probe and the electrode is almost unchanged. Thus, another current plateau appears (stage III in Fig. 2B). From the obtained electrochemical titration curve, the apparent p*K*a for the PTCA/G is determined as 5.45 ± 0.05, the midpoint of the sigmoid curve [8]. It is reported that a maximum peak current is obtained for a SAM-modified electrode when the solution pH is equal to the $pK_{1/2}$ [12]. Therefore, it is more convenient to discuss the protonation/deprotonation processes of PTCA/G in a solution pH of 5.5.

Fig. 3A compares the cyclic voltammograms (CVs) of PTCA/G and graphene modified GC electrodes in phosphate buffer (pH 5.5). No obvious current peaks are observed at the graphene modified electrode (the H_2 evolution is not observed in the studied potential window). However, four pairs of irreversible current peaks located at −0.67 V (peak A), −0.55 V (peak B), −0.21 V (peak C), and −0.05 V (peak D) appear clearly for the PTCA/G modified electrode. It has been reported that the derivatives of perylene (aromatic core of PTCA) show a pair of reversible redox peaks at ca. −1.68 V versus SCE [21], which is more negative than the observed pairs of current peaks in the present case (Fig. 3A). Therefore, the four pairs of current peaks observed for PTCA/G should be attributed to the electric-field-driven protonation and deprotonation of four carboxyl groups in PTCA rather than the redox processes of PTCA. The different half-wave potentials ($E_{1/2}$) suggest that the energy barrier of protonation and deprotonation of PTCA/G is different for each carboxylic acid group, because PTCA has four instinctive p*K*a values and distinct energy barriers for dissociating any one of protons in essence. The difference in anodic peak potentials of peaks A and B is 120 mV, which is approximately equal to the anodic peak difference between peaks C and D. This difference in peak potential could be

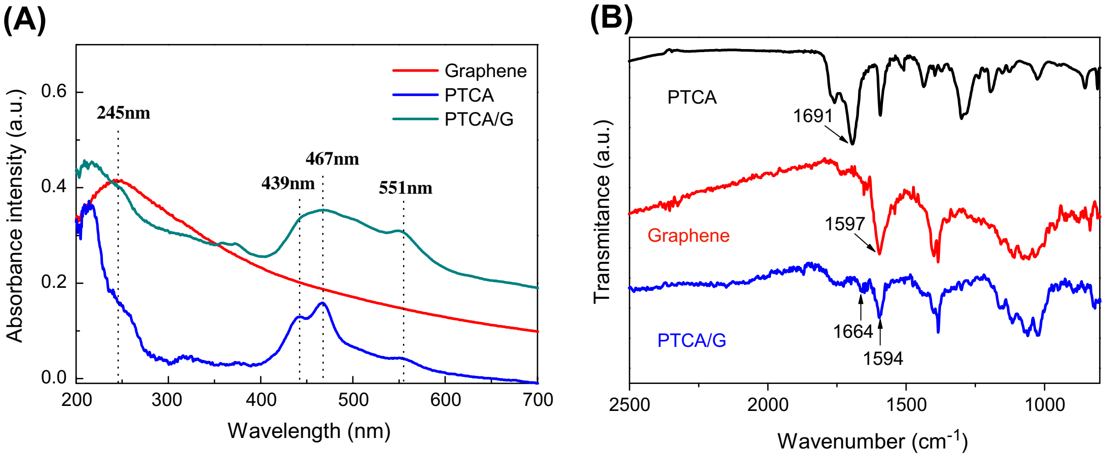

Fig. 1. (A) UV–vis absorption spectra of PTCA, graphene and PTCA/G. (B) FTIR spectra of PTCA, graphene and PTCA/G.