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ORIGINAL PAPER

Tunable electrochemical properties of liquid phase deposited TiO_2 films

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Abstract Titanium dioxide (TiO_2) films on glassy carbon (GC) electrode surface were prepared by the liquid phase deposition (LPD) process for different deposition times. The morphological structure, interfacial property and electrocatalytic activity of as-prepared LPD TiO_2 films on GC surface were studied by field-emission scanning electron microscopy (FE-SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The FE-SEM observation showed that the deposition time controlled the morphology of film on GC surface. With increasing deposition time, TiO_2 formed nanoparticles at the initial 5-h stage and compact thick films after 20 h. Due to the semiconducting properties of TiO_2, the LPD films inhibited the electron transfer process of $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ on GC by increasing the redox reaction peak potential separation of CV curve and electron transfer resistance of EIS. The inhibition was increased with TiO_2 film thickness. Nevertheless, the onset reduction potential of maleic acid decreased with increasing LPD TiO_2 film thickness while the cathodic and anodic currents increased, demonstrating the useful electrocatalytic activity of LPD TiO_2 films.

Keywords TiO_2 film · Liquid phase deposition · Electrocatalysis · Maleic acid

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1 Introduction

Titanium dioxide (TiO_2) is a well known metal oxide semiconductor providing extensive applications from photocatalyst to electrode material. Numerous studies have focused on this versatile oxide material to investigate its behaviour. In the field of electrochemistry, TiO_2 has been demonstrated as the most important semiconductor electrode material. By means of electrochemical and spectroelectrochemical methods, several fundamental properties such as surface states [1], electron accumulation [2] and electron traps [3] in nanostructured TiO_2 films have been studied. Meanwhile, some interesting electrochemical and electrocatalytic properties of various TiO_2 electrodes have been demonstrated. On the basis of a simple model, the characteristic experimental voltammogram shapes of nanoporous TiO_2 films have been described and simulated to address the capacitive and reactive properties of nanostructured TiO_2 electrodes in aqueous electrolyte [4]. The electrochemical reactivity of TiO_2 nanoparticles adsorbed onto boron-doped diamond surfaces [5] and electrochemical properties of electrosynthesized TiO_2 thin films [6] have been investigated by cyclic voltammetry. Electrocatalytic properties of TiO_2 electrodes towards the reduction of organic materials such as maleic acid [5, 7, 8], nitroanilines [9], 1-nitroso-2-naphthol [10], nitrobenzene [11] and *p*-nitrobenzoic acid [12] have been reported.

Recently, liquid phase deposition (LPD) of TiO_2 film, developed by Deki et al. [13], has been adopted for electrode surface modification [14], which provides a novel electroactive TiO_2 electrode. By cyclic voltammetry, the influences of electrolyte pH, deposition time and solution concentrations on the voltammetric behavior of LPD TiO_2 electrode have been described [14]. Based on an imprinted LPD TiO_2 film electrode, a phosphonate electrochemical sensor has been obtained [15].

In the present work, we prepared LPD TiO_2 film coated GC electrodes to study the electrochemical properties of LPD TiO_2 films under different deposition times. By means of field-emission scanning electron microscopy and cyclic voltammetry, the deposition time controlled morphology of LPD TiO_2 film showing electrochemical activity on GC was confirmed. The cyclic voltammetric and electrochemical impedance measurements in $K_3[Fe(CN)_6]$/$K_4[Fe(CN)_6]$ solution indicated that LPD TiO_2 film showed a barrier effect on the electron transfer between the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ redox couple and electrode. The electrocatalytic activity of LPD TiO_2 films towards the reduction of maleic acid was also demonstrated. These electrochemical properties were dependent upon the film thickness, which could be easily controlled by the deposition time. Thus, tunable electrochemical properties of LPD TiO_2 films were demonstrated.

2 Experimental

2.1 Reagents

Maleic acid, H_3BO_3, CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were obtained from Wako Pure Chemicals Ltd., Japan. $(NH_4)_2TiF_6$ was purchased from Aldrich Chemical Co., USA. Acetate or phosphate buffer solution was prepared by mixing stock solutions of 0.2 M CH_3COOH and 0.2 M CH_3COONa or by mixing stock solutions of 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4. All solutions were prepared with ultra-pure water obtained from water purification system (Millipore WR600A, Yamato Co., Japan) to a specific resistivity > 18 MΩ cm.

2.2 Apparatus and procedure

A field-emission scanning electron microscopy (FE-SEM; JSM-7400F, JEOL, Japan) was employed to obtain the FE-SEM images. Electrochemical measurements were performed with an EG & G M263A potentiostat (Princeton Applied Research, USA) and a 5210 lock-in amplifier (Princeton Applied Research, USA) controlled by M270 and M398 programs. A bare or LPD TiO_2 film coated glassy carbon (GC, $1 \times 10 \times 10$ mm, BAS Co.), a platinum wire and an Ag|AgCl (saturated KCl) reference electrode were employed as the working, auxiliary and reference electrodes, respectively. The exposed geometric area of the working electrode surface was 0.0314 cm^2. All measurements were performed at room temperature (22 ± 1 °C). The deaerated solution was acquired by purging the solution with high purity nitrogen gas for 15 min to remove oxygen prior to the experimental runs and blanketed under nitrogen during the experiments.

2.3 Preparation of LPD TiO_2 film on GC

The GC surface was mechanically polished to a mirror-like smoothness with number 2000 and 3000 emery papers and then sonicated in acetone, ethanol and distilled water for 15 min. Following drying with a stream of high purity nitrogen gas, the GC substrate was immersed vertically into an aqueous solution containing 0.1 M $(NH_4)_2TiF_6$ and 0.2 M H_3BO_3 at 25 °C. After 5–40 h, the GC was removed from the deposition solution and thoroughly rinsed with water and dried with nitrogen gas. Thus, a LPD TiO_2 film coated GC electrode was prepared for measurements.

3 Results and discussion

3.1 FE-SEM observation of LPD TiO_2 films on GC surface

Figure 1 shows the surface morphology of LPD TiO_2 films on GC prepared from 0.1 M $(NH_4)_2TiF_6$ and 0.2 M H_3BO_3 for different deposition times. For a deposition time of 5 h, some TiO_2 particles were formed on the GC surface (Fig. 1a). The diameter of most TiO_2 particles was in the range 40–70 nm. When the deposition time was increased to 10 h, the TiO_2 particle size increased to ca. 120 nm and the entire GC surface was almost covered by TiO_2 particles (Fig. 1b). When the deposition time was further increased to 20 h, a compact TiO_2 film was formed (Fig. 1c). At the same time, some small cracks about 50 nm wide appeared in the film, due to film shrinkage by dissociation of water on drying [13]. The film thickness and the width of the cracks clearly increased with increasing deposition time to 40 h (Fig. 1d).

3.2 Electrochemical behavior of LPD TiO_2 films on GC

The voltammetric behavior of LPD TiO_2 films on GC prepared under different deposition times was studied by cyclic voltammetry (CV) (Fig. 2). As recognized from this result, bare GC did not show any faradaic current in the sweep potential range from +0.5 V to −1.0 V (vs. Ag|AgCl) in deaerated acetate buffer solution (pH 4.0) while the LPD TiO_2 film exhibited a characteristic voltammogram shape of TiO_2 film composed of strong cathodic currents in the negative scan and an anodic peak in the reverse scan. The voltammetric response of TiO_2 film is attributed to redox couple of electroactive states of TiO_2 film, namely Ti(IV) and Ti(III), on the electrode surface in contact with electrolyte. Further observation indicated that, with increasing deposition time, the cathodic and anodic currents increased significantly. In addition, at the onset reduction of TiO_2 film,

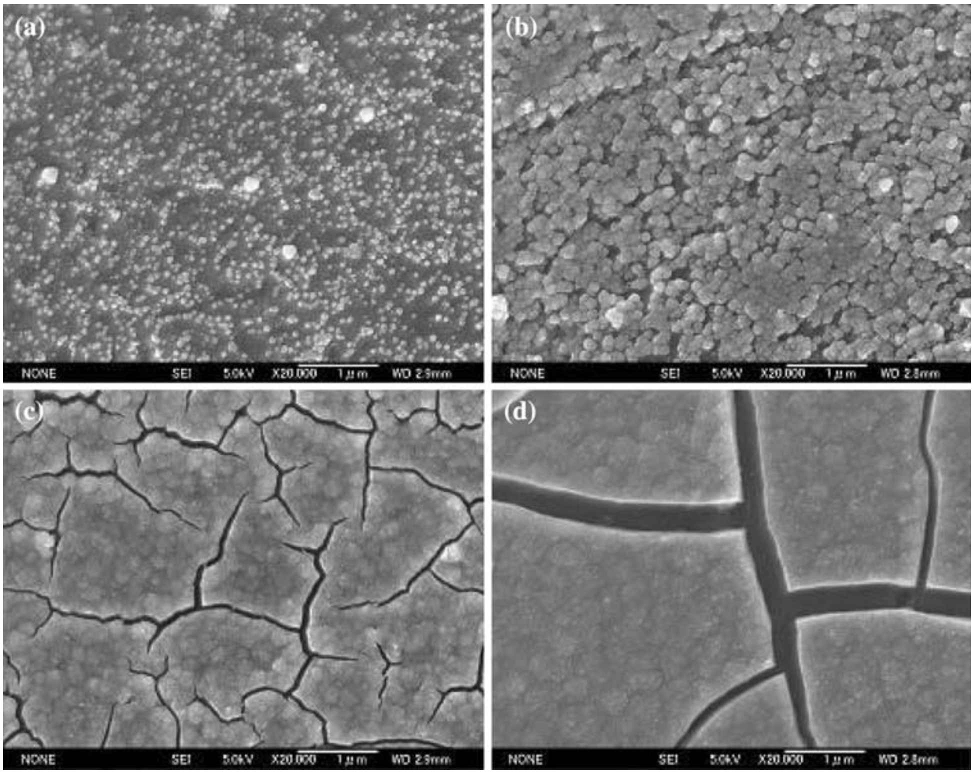

Fig. 1 FE-SEM images of LPD TiO_2 films on GC surface prepared by soaking for (**a**) 5, (**b**) 10, (**c**) 20 and (**d**) 40 h

a small cathodic peak appeared, which was also observed on other types of nanostructured TiO_2 electrodes, attributed to the filling of surface states and the subsequent increase in conductivity [1]. This cathodic peak was shifted negatively accompanied by the enhancement of peak current when the deposition time was increased from 5 h to 20 h. When the deposition time was increased to 40 h, this small cathodic peak was merged in the strong reduction currents of TiO_2. On the other hand, the LPD TiO_2 film showed a stable voltammetric response upon multiple scans. Figure 3 illustrates the CVs of a 20-h LPD TiO_2 film upon the first and second CV scans. The CV curve of the second scan is almost the same as the curve of the first scan except for the disappearance of the small peak on the onset of reduction. This reflects that excellent adherence of TiO_2 film to the substrate is provided by such a LPD approach and no TiO_2 is lost from the electrode surface into the aqueous medium.

3.3 Interfacial properties of LPD TiO_2 film coated GC electrode

The redox behavior of a reversible couple, namely $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$, is effective to evaluate the interfacial properties of electrodes. Figure 4 compares the CVs of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ in phosphate buffer solution (pH 7.0) recorded on bare GC and LPD TiO_2 film coated GC electrodes prepared under different deposition times. On bare GC, the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reaction shows a pair of well-behaved redox peaks with a peak potential separation (ΔE_p) of 150 mV, demonstrating a fast redox process on bare GC. However, the redox process was inhibited when the GC surface was covered by TiO_2 film. Compared with the bare GC electrode, the 5-h LPD TiO_2 film coated GC electrode reduced the redox peak currents and decreased the ΔE_p of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reaction to ca. 480 mV. While at a 10-h LPD TiO_2 film coated GC electrode, the ΔE_p of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ was further decreased to ca. 810 mV. When the deposition time of LPD TiO_2 film was increased to 20 or 40 h, no redox peaks for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ were observable on TiO_2 film.

The electrochemical impedance spectra (EIS) for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ on bare GC and LPD TiO_2 film coated GC electrodes were also measured (Fig. 5). The charge transfer resistance (R_t) estimated from the diameter of the semi-circle (arc) of EIS for bare GC was drastically increased when the GC surface was covered with LPD TiO_2 films. At the same time, the double-layer capacitance (C_d) calculated according to the following equation for EIS measurement on bare GC decreased after coating with TiO_2 films

$$C_d = \frac{1}{\omega_{\max} R_t} \tag{1}$$

where $\omega_{\max}$ is the maximum angular frequency for arc. The apparent heterogeneous rate constant (k_{app}) for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reaction on bare GC and LPD

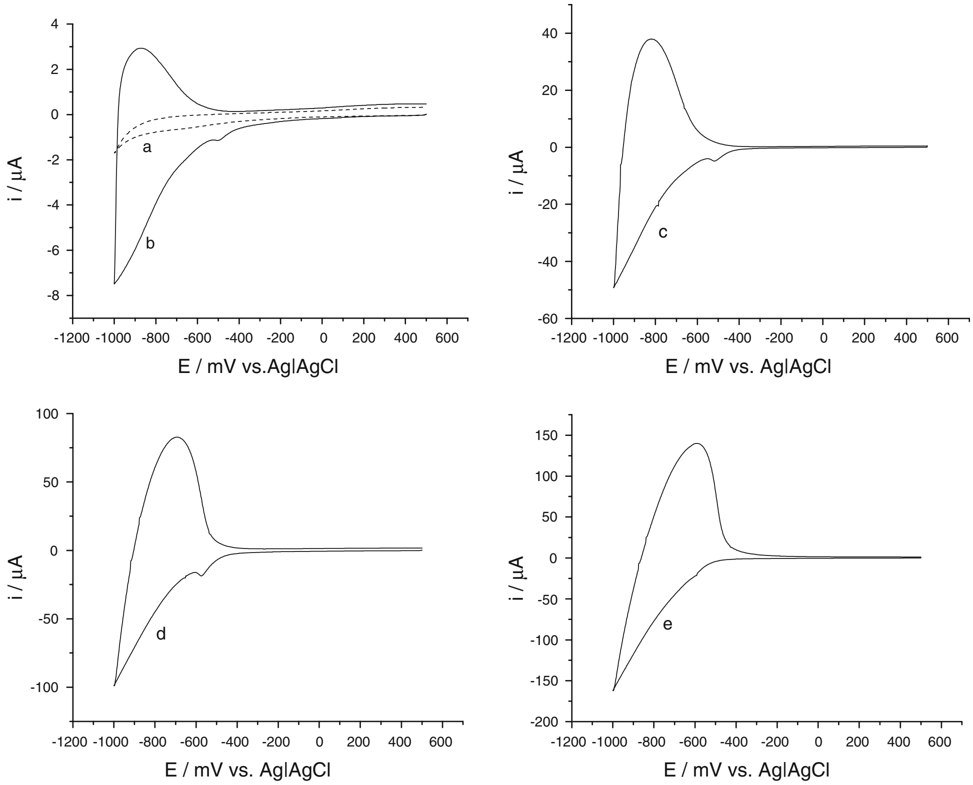

Fig. 2 CVs of bare GC (**a**) and LPD TiO_2 film coated GC (**b–e**) electrodes in 0.2 M deaerated acetate buffer solution (pH 4) at 0.1 V/s. The LPD TiO_2 films were prepared by soaking for (**b**) 5, (**c**) 10, (**d**) 20 and (**e**) 40 h

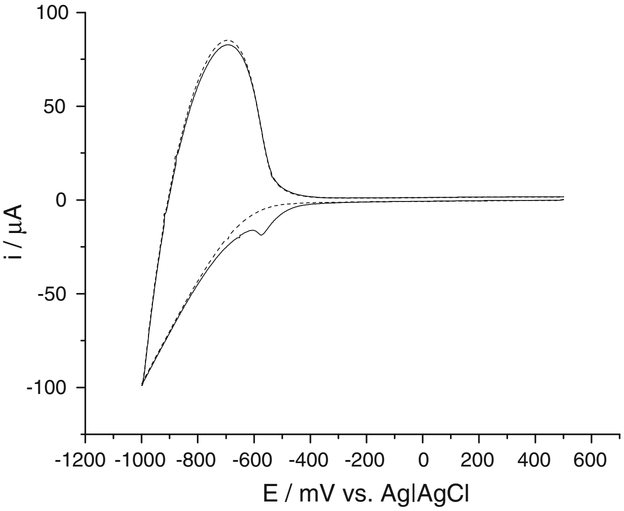

Fig. 3 CVs of 20-h LPD TiO_2 film in 0.2 M deaerated acetate buffer solution (pH 4) at 0.1 V/s upon the first scan (*solid line*) and the second scan (*dashed line*)

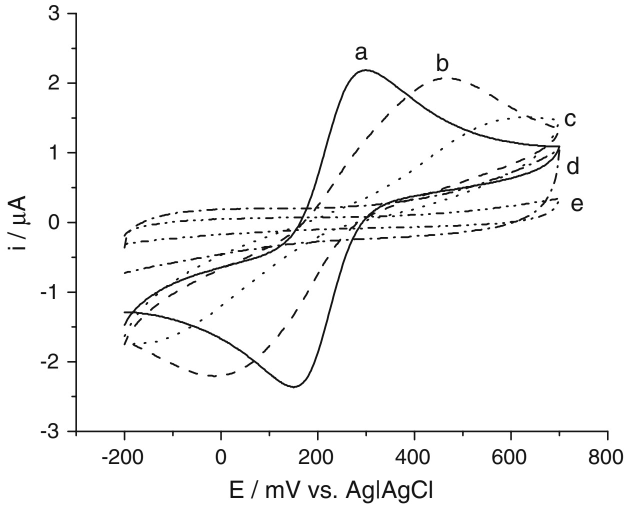

Fig. 4 CVs of bare GC (**a**) and LPD TiO_2 film coated GC (**b–e**) electrodes in 0.1 M phosphate buffer solution (pH 7.0) containing 0.5 mM $[Fe(CN)_6]^{3-}$ and 0.5 mM $[Fe(CN)_6]^{4-}$ at 0.05 V/s. The LPD TiO_2 films were prepared by soaking for (**b**) 5, (**c**) 10, (**d**) 20 and (**e**) 40 h

TiO_2 film coated GC electrodes was estimated from the equation expressed as [16]

$$K_{\text{app}} = \frac{RT}{F^2 R_t C*} \tag{2}$$

where R is the gas constant, T is temperature, F is Faraday constant and C^* represents the concentration of redox couple. Table 1 summarizes these EIS parameters corresponding to Fig. 5.

The above electrochemical experimental results reveal that the LPD TiO_2 film inhibit the electron transfer process of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. The inhibition increases with deposition time; this is attributable to the semiconducting

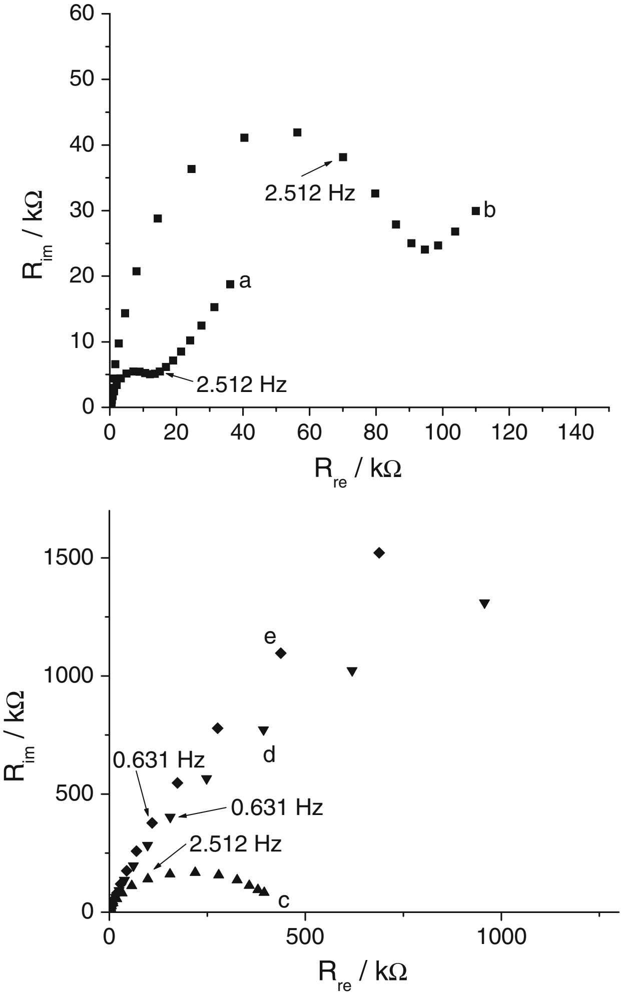

Fig. 5 EIS of bare GC (**a**) and LPD TiO_2 film coated GC (**b**–**e**) electrodes in 0.1 M phosphate buffer solution (pH 7.0) containing 0.5 mM $[Fe(CN)_6]^{3-}$ and 0.5 mM $[Fe(CN)_6]^{4-}$. The LPD TiO_2 films were prepared by soaking for (**b**) 5, (**c**) 10, (**d**) 20 and (**e**) 40 h. E_{DC} = 0.23 V. Frequency range: 100 kHz–0.1 Hz

Table 1 EIS parameters of $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ on different electrodes

Electrodes	R_{ct}/Ω	C_d/F	k_{app}/cm s^{-1}
Bare GC	1.15×10^4	5.54×10^{-7}	1.48×10^{-3}
5-h LPD TiO_2 film	1.1×10^5	3.64×10^{-7}	1.55×10^{-4}
10-h LPD TiO_2 film	4.4×10^5	3.62×10^{-7}	3.86×10^{-5}
20-h LPD TiO_2 film	4.1×10^6	–	4.15×10^{-6}
40-h LPD TiO_2 film	7.0×10^6	–	2.43×10^{-6}

properties of TiO_2 film. Further comparison between the electrochemical measurement and SEM observation reveals that when compact TiO_2 films are formed on GC under deposition times longer than 20 h, the redox peaks of CV curve for $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ are completely lost while the k_{app} value (cm s^{-1}) for $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ reaction is decreased to the order of 10^{-6}. On the other hand, though the SEM observation also shows the increase of crack width with deposition time, no significant cracking effect is observed for these electrochemical experiments conducted with wet films.

3.4 Electrocatalytic activity of LPD TiO_2 films

Although the semiconductor properties of TiO_2 film is disadvantageous to the interfacial transfer between the electrode and reaction species, TiO_2 is actually a useful electrode material because of its electrocatalytic activity toward the reduction of some organic materials. The typical example is the electrocatalysis of maleic acid on various electroactive TiO_2 electrodes. To evaluate the electrocatalytic properties of as-prepared LPD TiO_2 films, we studied the electrochemical behavior of maleic acid on LPD TiO_2 film coated GC electrodes. Figure 6 compares the CVs of maleic acid on bare GC and various LPD TiO_2 film coated GC electrodes. On bare GC the reduction of maleic acid in acetate buffer solution (pH 4.0) started at ca. −0.7 V. When GC was coated with 5-h LPD TiO_2 film, the onset reduction potential was decreased to ca. −0.55 V. The onset reduction potential value was further decreased to ca. −0.45 V, −0.4 V and −0.35 V when 10-h, 20-h and 40-h LPD TiO_2 films were deposited. At the same time, the cathodic and anodic currents increased remarkably with increase in deposition time, demonstrating the excellent electrocatalytic activity of LPD TiO_2 film.

We also observed the electrocatalytic responses of maleic acid in different amounts on a 20-h LPD TiO_2 film coated electrode (Fig. 7). LPD TiO_2 film shows a sensitive response to the concentration of maleic acid. With

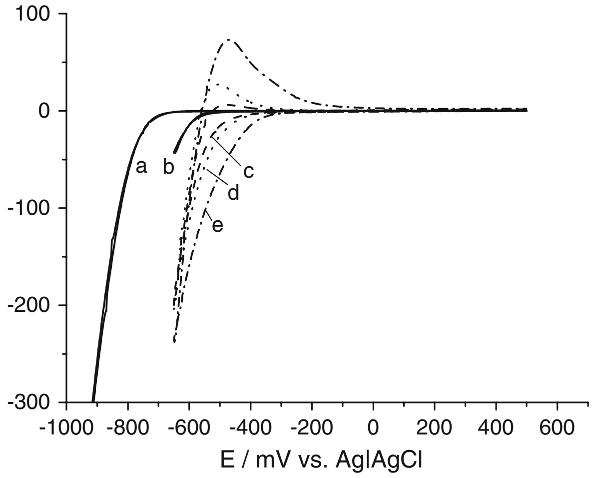

Fig. 6 CVs of bare GC (**a**) and LPD TiO_2 film coated GC (**b**–**e**) electrodes in 0.2 M deaerated acetate buffer solution (pH 4.0) containing 0.2 M maleic acid at 0.1 V/s. The LPD TiO_2 films were prepared by soaking for (**b**) 5, (**c**) 10, (**d**) 20 and (**e**) 40 h

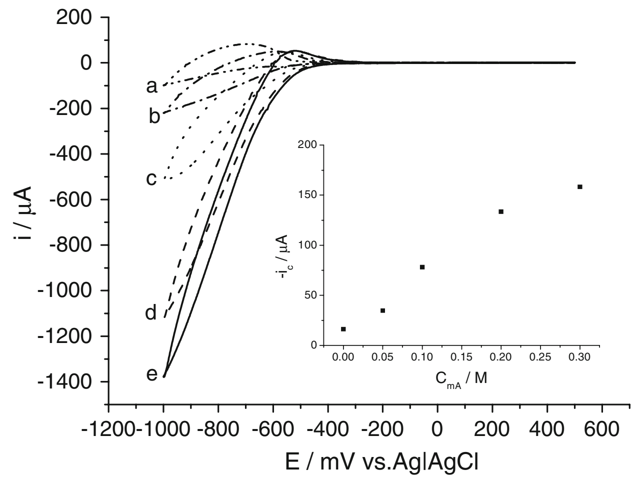

Fig. 7 CVs of 20-h LPD TiO_2 film at 0.1 V/s in 0.2 M deaerated acetate buffer solution (pH 4.0) containing (**a**) 0, (**b**) 0.05, (**c**) 0.1, (**d**) 0.2 and (**e**) 0.3 M maleic acid. *Inset*: Increase of cathodic current at −0.6 V with the concentration of maleic acid

increasing concentration of maleic acid, the cathodic current is markedly increased while the peak anodic current is decreased, illustrating the heterogeneous electrocatalytic behavior of maleic acid on LPD TiO_2 film, which is attributed to the electroactive TiO_2 film catalyzing the reduction of maleic acid expressed by the following reaction [8].

$$\begin{aligned}&2\mathrm{Ti(III)} + (\mathrm{CHCOOH})_2 + 2\mathrm{H}^+ \\ &\quad \rightarrow 2\mathrm{Ti(IV)} + (\mathrm{CH_2COOH})_2 \qquad (3)\end{aligned}$$

4 Conclusions

This work studied the electrochemical interfacial properties and catalytic activity of LPD TiO_2 films combined with a deposition time controlled film morphology on GC electrodes. With increasing LPD TiO_2 film thickness, the electron transfer kinetics of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ were decreased while the electrocatalytic activity of LPD TiO_2 films toward the reduction of maleic acid was improved due. These results demonstrate that tunable LPD TiO_2 film is an interesting and useful electrode material, which may provide promising applications in increasing the selectivity for electroanalysis and improving the efficiency for electrocatalysis.

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