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Electrochemical instability of indium tin oxide (ITO) glass in acidic pH range during cathodic polarization

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Abstract

Indium tin oxide (ITO) glass substrates are widely used in electrochemical devices and as substrates for *in situ* spectro-electrochemical experiments owing to their interesting optical, electrical and electrochemical properties. In this work, we found ITO surfaces to undergo substantial changes in their properties on potentiodynamic stresses in the acidic pH range. The surface changes occurring during cathodic cycling of ITO were characterized by redox couples in cyclic voltammetry, and the resultant surfaces examined by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical transmittance measurements, X-ray diffraction (XRD) and the compositional changes by X-ray fluorescence spectroscopy (XRF). The studies of electrical, optical and structural properties of ITO during cathodic cycling in the acidic pH range clearly point to a set of conditions that help retaining the stability of ITO substrates intact for electrochemical applications.
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1. Introduction

Indium tin oxide coated glasses are widely used as substrates for depositing thin films of electro-active materials such as conducting polymers, semiconductors like CdTe [1,2], etc. which are part of electrochemical and optoelectronic devices and solar cells [3]. ITO glass substrates are generally prepared by sputter-coating a thin conductive layer of indium tin oxide on a high-quality glass substrate [4,5]. These substrates are commonly used for spectro-electrochemical studies of electroactive thin films which undergo redox transitions involving changes in the optical absorbance [6]. The chemical stability of the interfaces involving ITO surfaces is an important factor determining its use in various application areas. More often, electro-deposition of metal oxides such as Cu_2O, ZnO or TiO_2 films by cathodic electro-deposition from aqueous acidic bath solutions are reported without paying much attention to the electrochemical stability of substrates [7–10]. Electrodeposition of lead on ITO is described by Avellaneda et al. [11]. In many of these papers, the researchers use cathodic potential up to -1.2 V

in acid medium to perform electrodeposition of the semi conducting metal oxides. One of the primary criteria for the use of these substrates is the electrochemical stability of the underlying ITO film under the experimental conditions of formation of electroactive films. The first work by Kraft et al. [12] reported the instability of ITO during anodic potential cycling. The instability of ITO electrodes during anodic oxidation during oxygen evolution reaction is proposed as due to the anodic dissolution of the ITO coating [13]. The comparison of properties of ITO and boron-doped diamond electrodes under very aggressive acidic or alkaline conditions, leading to total deterioration of surface has been reported recently [14].

The surface condition of any electrode is normally assessed by examining the voltammetric response of standard redox couples such as ferri-/ferro-cyanide. During the course of examining a few redox couples on ITO glass substrates, we found the responses are affected considerably depending on the solution pH and the extent and time duration of potential excursions into the cathodic regime. This led us to examine in detail the electrochemical nature of the surface under the above conditions. In this communication, we report the stability aspects of ITO during excursions into the cathodic potential region in the acidic pH range. The instability in terms of changes in the electrical, optical and structural properties was char-

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acterized using SEM, AFM, optical transmittance and XRF measurements.

2. Experimental

The ITO substrates (Nippon Sheet Glass Co., Japan) were cleaned by sonication for 10 min using ultrasonic cleaner (Ralsonics, Mumbai) at frequency of 20 KHz in a commercial detergent solution (Pril) containing non-ionic surfactants, followed by sonication in ethanol and water mixture for 2 min each and dried in air oven at 60–70 °C. The resistance of the cleaned ITO varied between 20 and 25 Ω cm^{-1}. Thickness of the ITO coating on glass is around 100 nm. All ITO glass samples used in our experiments were from the same lot. All solutions were prepared in Milli-Q water using Analar-grade reagents. The reference electrode used was a calomel electrode fabricated in our laboratory. Scanning electron micrographs were obtained using Hitachi Model electron microscope (S-3000H) and atomic force microscopic (AFM) images were recorded with the Molecular Imaging PicoSPM 2100 using gold-coated silicon nitride (30 nm) cantilevers (force constant of 0.12 N m^{-1}). UV–vis transmittance measurements were carried out for ITO cycled for different time durations in solutions of pHs with an Ocean Optics SD 2000 fibre-optic spectrophotometer. XRD measurements were made using a Jeol X-ray diffractometer between 10° and 80° with Cu Kα radiation and the compositional data were obtained using X-ray fluorescence spectrometry (Horiba XGT-2700). The cyclic voltammetric measurements were carried out using a potentiostat (Autolab PGSTAT 30, The Netherlands) controlled by a computer. Area of the ITO electrodes used in our experiments was fixed as 0.5 cm^2. The electrical contacts to the working electrodes were made with the help of a clip and a copper strip. A large area Pt electrodes were used as counter electrode.

3. Results and discussion

Fig. 1(a–c) shows cyclic voltammograms of 1 mM potassium ferricyanide in 1 M KCl on ITO between −0.2 and 0.6 V versus SCE at a scan rate of 0.02 V s^{-1} with and without treatment. A reversible redox peaks characterized by a peak-to-peak separation (ΔE_p) of ~60 mV was observed agreeing with the reported data [15] characterizing an ideal diffusion controlled reversible redox reaction on ITO substrate. On treatment by

Fig. 2. Cyclic voltammetric responses in 0.1 M phosphate buffer (first cycle) of ITO in the potential range of 0.2 to −1.2 V at (a) pH 2.2, (b) pH 4.2 and (c) pH 6.2 at scan rate of 0.05 V s^{-1}.

cycling the electrode potential from 0.2 to −1.0 V in a phosphate buffer at pH 2 for 0, 10 and 30 cycles, the anodic and cathodic peak currents decrease gradually with the number of pretreatment cycles with simultaneous gradual increase in the ΔE_p value. After 30 cycles of pretreatment, ΔE_p increases to ~90 mV indicating transformation of electron transfer to quasi-reversible nature. The increased redox peak-to-peak separation is due to the physical transformation occurring in the ITO film during electrochemical cycling. This confirms that the surface of ITO glass undergoes changes during the pretreatment cycles. On examination of the pretreated ITO under optical microscope, we detect the development of dark spots whose number increases with pretreatment time (not shown). Resistance of the ITO also increases gradually indicating some irreversible changes, the film undergoes as a result of the pretreatment mentioned above. A systematic variation of pH of the pretreatment bath revealed that the changes occur from below pH 6.2.

Figs. 2(a–c) and 3(a–c) represent the voltammetric response of ITO in a sodium dihydrogen phosphate buffer medium in the electrolytes of pH 2.2, 4.2 and 6.2 during first, and 34th cycles respectively. Ionic strength of the medium is maintained at 0.1 M. From this figure it can be noticed that a deposition/dissolution process is taking place around 0.9 V whose peak heights increase with the cycle number. This deposition/dissolution process is prominent at lower pHs as seen from the magnitude of voltammetric peak currents seen from Figs. 2(a–c) and 3(a–c). The dissolution/deposition peaks become well developed on cycling as evident from the increased peak currents for the redox peak. The increased peak currents during potential cycling from 0.2 to −1.2 V indicate that the ITO film is undergoing some permanent changes in the chemical composition during potential cycling in the cathodic potential range. The reaction products accumulating in the film results in continuous increase in the redox peak currents. The voltammet-
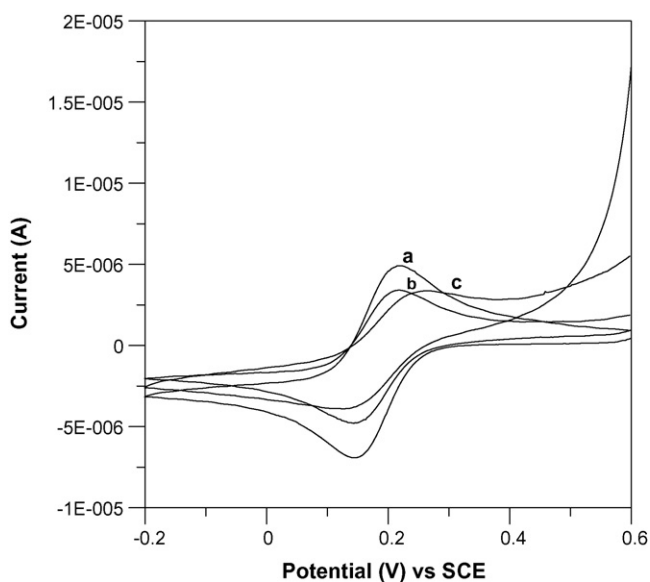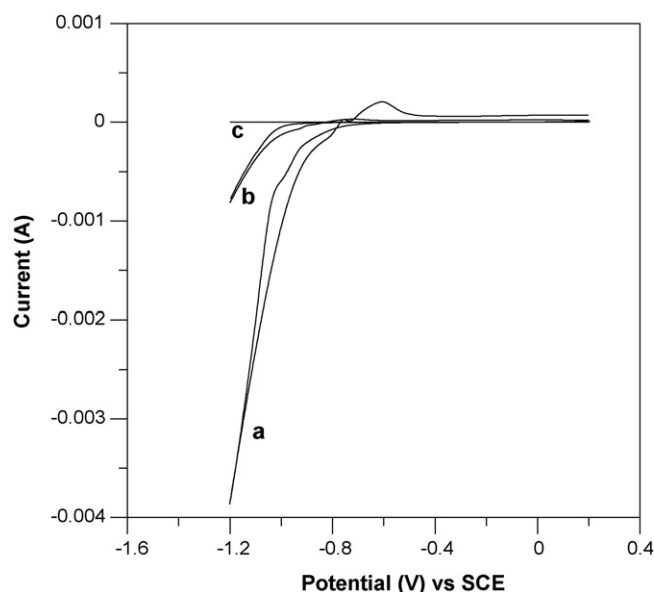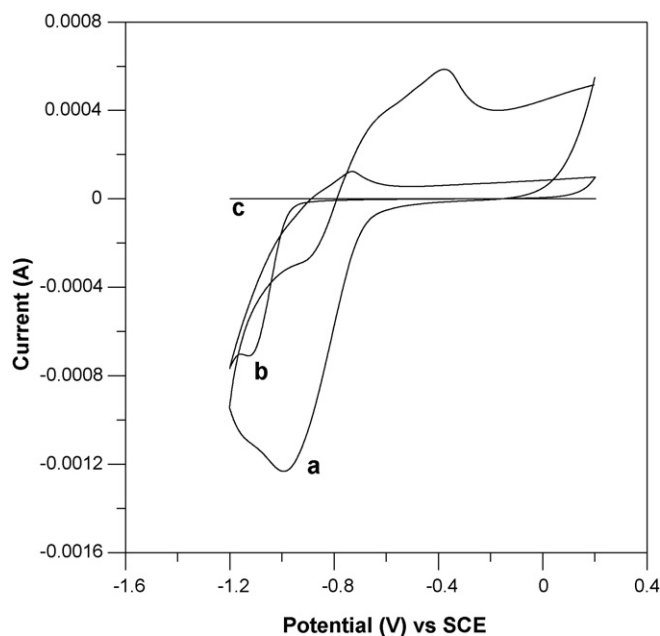

Fig. 1. Cyclic voltammetric response of 1 mM ferro/ferricyanide in 1 M KCl on ITO (a) without pretreatment, (b) after pretreatment by cycling ITO between 0.2 and −1.0 V for 10 cycles and (c) for 30 cycles at scan rate of 0.05 V s^{-1}.

Fig. 3. Cyclic voltammetric response in 0.1 M phosphate buffer (34th cycle) of ITO in the potential range of 0.2 to −1.2 V at (a) pH 2.2, (b) pH 4.2 and (c) pH 6.2 at scan rate of 0.05 V s^{-1}.
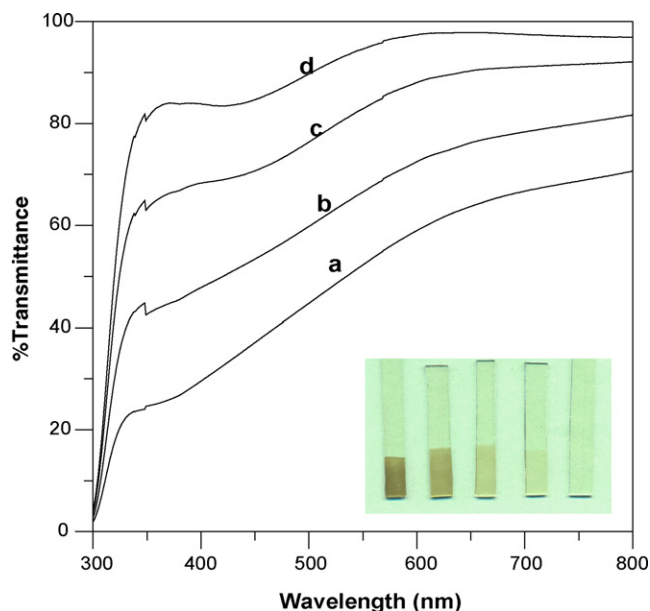

Fig. 4. The transmittance spectra of ITO substrate pretreated by potential cycling in phosphate buffer of pH 2.2 in the range of 0.2 to −1.0 V for (a) 30, (b) 20, (c) 10 and (d) 5 cycles (inset photograph of the ITO pretreated for 30 min, 20 min, 10 min, 5 min and 0 min, from left to right, the opaqueness increases with number of potential cycles).

Table 1
Composition of the ITO film before and after electrochemical treatment as measured using XRF

Conditions	Compositions (%)
Simple ITO	In:Sn, 86.5:13.5
pH 4.2 (10 min)	In:Sn, 85.9:14.1
pH 4.2 (30 min)	In:Sn, 66.0:33.0
pH 2.2 (30 min)	In:Sn, 97.9:2.1

ric response obtained on cycling at pH 2.2 is very broad and show additional peaks implying that there is more than one process responsible for deterioration. The cross-over observed in the high cathodic region also vouch for electrochemical phase formation [16]. The electrochemical reactions, which can occur during this potential range during cycling, are obviously either the reduction of Sn^{4+}, or In^{3+} in the ITO film [12] to lower oxidation states. On visual examination, an opaque film was found to form on the surface. In XRF measurements (Table 1), the composition of the ITO film was found to change from In:Sn ratio of 86:14 to 97:3 after cycling of the ITO for 30 min in a bath of pH 2.25 indicating (i) segregation of indium on the sur-

face either by diffusion or (ii) by preferential dissolution of Sn from the film. It should be borne in mind that both oxides of In and Sn constitute to make the glass surface electrically conducting. As a consequence of these changes, the resistance of the ITO also increases with pretreatment time as observed from Table 2.

Further, pretreatment of ITO in a phosphate buffer of pH 2.25 for 30 min from 0.2 to −1.2 V was found to increase the

Table 2
Resistance of ITO surface before and after electrochemical treatment

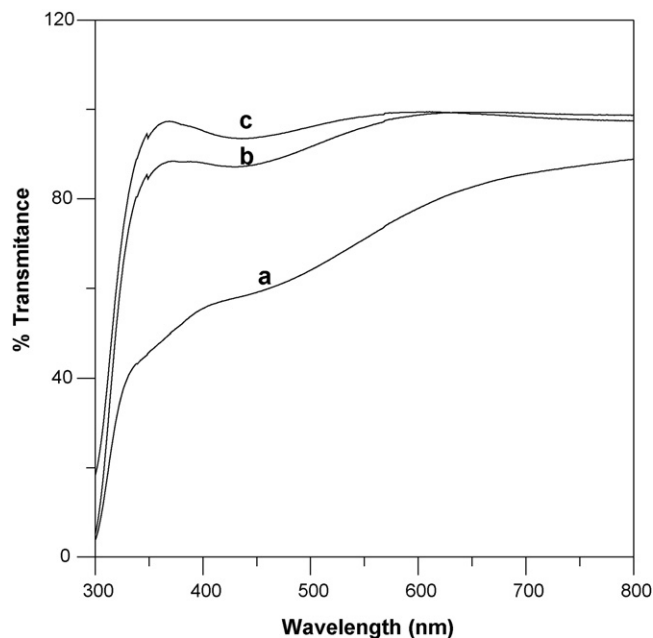| Potential cycling conditions as in Fig. 2	Resistance of coating (Ω cm^{-1})	Resistance of coating (after pretreatment) (Ω cm^{-1})
pH 4 (10 min)	29.4	34.0
(30 min)	193.4	47.0
pH 2 (30 min)	277.5	Very high
Simple ITO (0 min)	22.6	22.0

Fig. 5. The transmittance spectra of ITO pretreated in the phosphate buffer in the potential range from 0.2 to −1.2 V for one cycle at (a) pH 2.2, (b) pH 4.2 and (c) pH 6.2.

resistance of the substrate from 22 to 400 Ω cm^{-1} and lead to total loss of conductivity when the opaque film was removed by dissolving in 0.1 M HCl solution. These results can throw light on the observations of Stotter et al. [14] who reported total loss of electrical conductivity on electrochemical pretreatment of ITO involving cycling between +1.0 and −1.0 V in more aggressive media like 1 M NaOH or 1N HNO$_3$.

Another feature that distinguishes ITO glass substrates from the other electrode materials is changes in optical transmittance

and the changes that occur during the cathodic treatment in a range of pH values is presented in the discussion given below. Fig. 4(a–d) shows changes in the optical transmittance after potential cycling of ITO in solutions of pH 2.2 in the potential
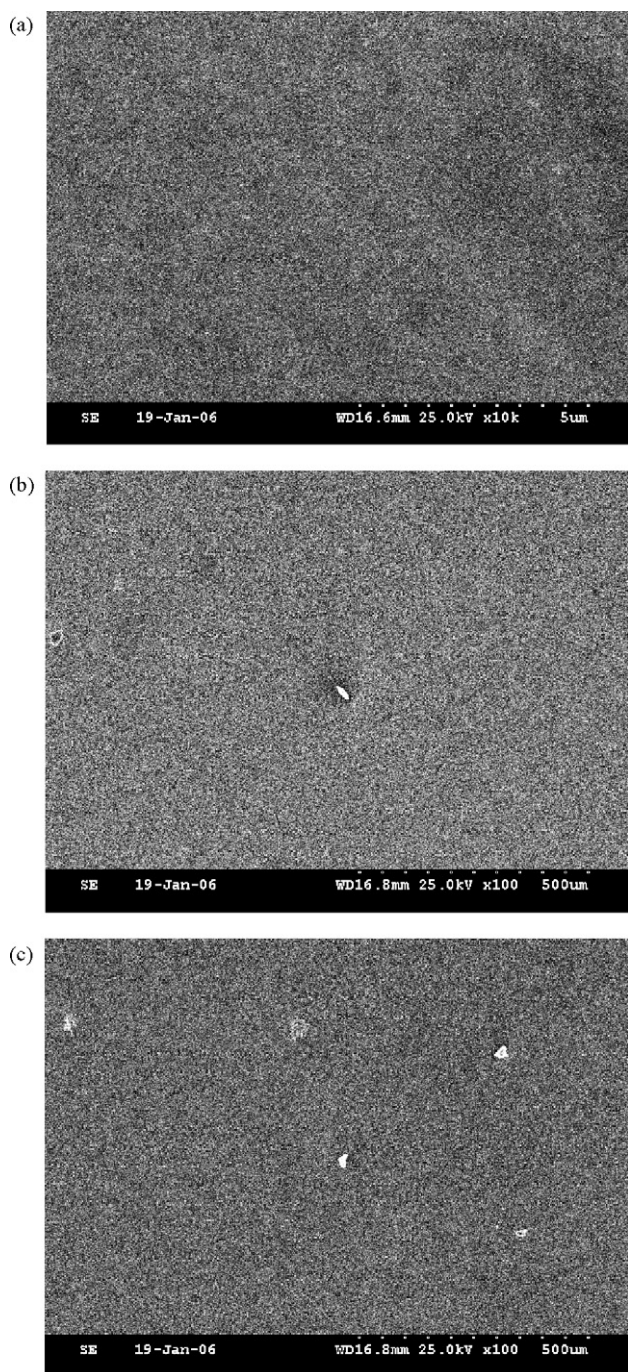

Fig. 6. Scanning electron micrographs of (a) untreated ITO and the ITO pretreated in the potential range of 0.2 to −1.2 V for 30 min in (b) pH 4.2 and (c) at pH 2.2.
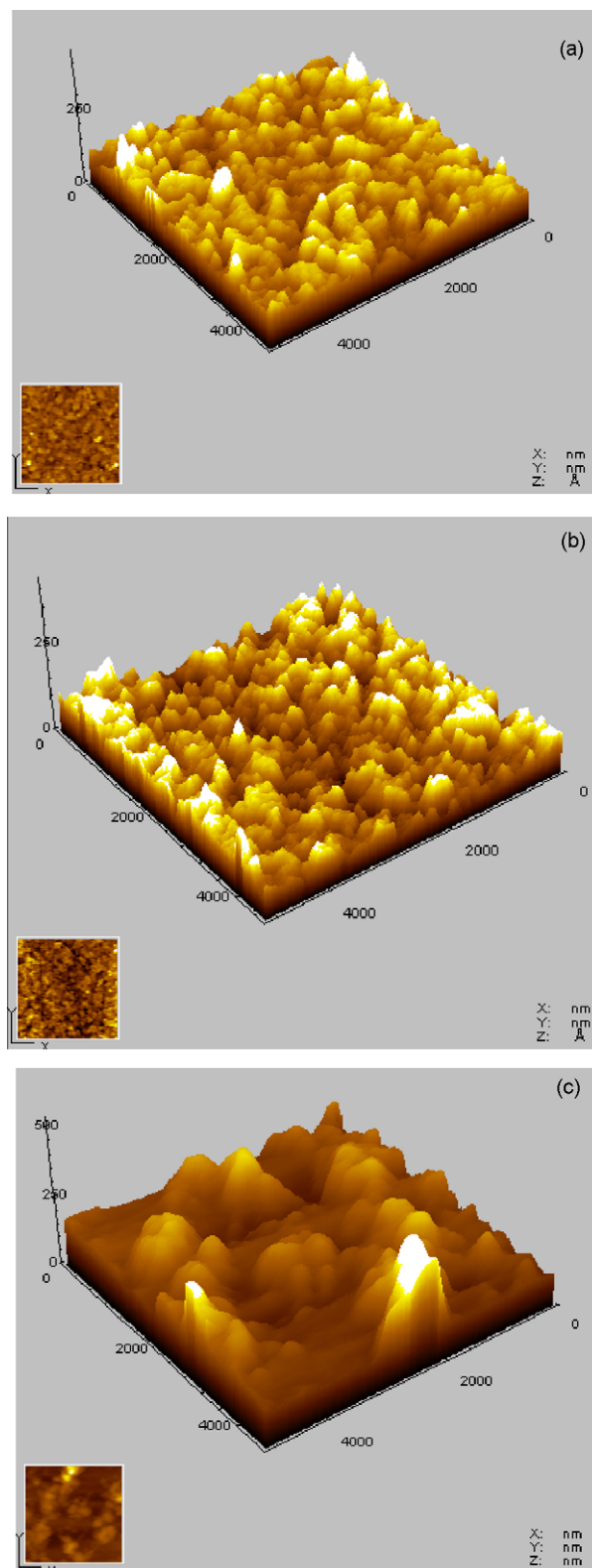

Fig. 7. Atomic force micrographs of the (a) untreated ITO, (b) the ITO pretreated in the pH range of 0.2 to −1.2 V for 30 min in pH 4.2 and (c) at pH 2.2.

range of 0.2 to −1.0 V at 0, 10, 20 and 30 potential cycles. Fig. 4 shows a gradual reduction in the light transmittance from 80% to 40% at a wavelength of 500 nm on 30 min of potential cycling. It should be noted that the transparent ITO becomes opaque when cycled in a medium of pH 2 bath for one cycle itself when the potential limit for cycling is extended up to −1.2 V instead of −1.0 V (Fig. 4, inset). Similarly, the effect of pH on the optical transmittance of ITO was studied by potential cycling of the substrate in phosphate buffer of different pH values in the potential range between 0.2 and −1.20 V for one cycle each at a scan rate of 0.05 V s^{-1}. The loss of transmittance is maximum at pH 2.2 and minimum at pH 6.2 as seen from Fig. 5(a–c). It is obvious that the deterioration of optical properties is maximum at lower pH values. The powder XRD of these pretreated ITO substrates at different pH values showed distinct structural changes (not shown).

Fig. 6(a–c) shows the scanning electron micrographs of ITO cycled for 30 min in pH 2.2 and 4.2 bath. Fig. 6(b and c) shows spots that indicate localized corrosion during cycling of the ITO film. On increased building up during cathodic treatment, the opaque film tends to peel off from the glass surface. AFM of the same films (Fig. 7a–c) indicate that the deterioration of the surface of ITO increases with pH and is maximum at pH 2.2, as shown by surface roughness. It is clear from Fig. 6 that the initial topology of ITO is very smooth and the roughness caused during cycling in pH 4.2 buffer for 30 min is not very high. However, the roughness of the film increases enormously on cycling in buffer of pH 2.2, as evident from the 3D view (Fig. 7c).

After analyzing the data, it can be concluded that potential limit plays a vital role apart from the solution pH and the duration of potential cycling in the electrochemical stability of the ITO. We wish to state that the ITO surface is free from the damages of the kind described above when the cathodic potential is limited to −0.8 V and pH > 6. Since it has become a practice to pretreat the ITO electrode surface before attempting to electrodeposit material of interest, the issues highlighted in this work should be borne in mind while performing electrochemical experimentation. It is emphasized here that the ITO glass substrates show electrochemical instability during cathodic cycling which result in gradual decay in its optical and electrical properties. One should be aware of the above deteriorating factors to judge the suitability of these substrates for the electrochemical experiments and device fabrication.

Conflict of interest

None.

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