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SYNTHESIS, CHARACTERIZATION AND STUDY THEELECTROCHEMICAL BEHAVIOUR OF AG/TIO$_2$THIN FILM

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ABSTRACT

Silver (Ag) nanoparticle assisted titania thin film photoelectrode was prepared using sol-gel method on fluorine doped tin oxide(FTO) substrate. The physico-chemical analyses of the film were investigated using different analytical techniques correlate well with the performance results. The surface plasmon induced local field due to silver nanoparticle enhances the photoelectrochemical performances of the device. The photocurrent density of the silver deposited titania (Ag/TiO$_2$) is observed to be enhanced about 74 fold than the pristine TiO$_2$ under visible light. Moreover, the cyclic voltammograms reveals that the Ag/TiO$_2$ photo-electrode has very good capacitive behavior and an excellent stability with an average 4% drop of the initial capacitances after 5000 voltametric cycles

Keyword: Silver Sensitization, Surface Plasmon Resonance Titania Thin Film.

I. INTRODUCTION

Metal deposited semiconductor oxides have been extensively investigated for energy storage devices in recent decades [1-3]. Titanium dioxide is one of the most widely studied semiconductor oxide electrode for photoelectrochemical water splitting and supercapacitor applicationsbecause of its inherentphysico-chemical stability, suitable bandalignment, high resistance of photocorrosion, and low cost [4-5].However, the large band gap and low quantum yield of unmodified pristine titania (E_g =3.2 eV) limits its applications and usage. Several efforts have been made to overcome these limitations through structural modification [6], doping with metals/non-metals [7] and sensitization with oxides [8].It has been reported thatthe deposition of metals, such as silver (Ag), gold (Au) and cobalt (Co)using differentmethods, improves thephotocatalytic and photo-electrocatalytic performance of the material [9-11]. The surface plasmon resonance (SPR) effect due to noble metals (e.g. Ag and Au) deposition plays an important role in making the catalyst visible light active.The local electric filed generated near the junction of Ag and titaniajunction enhances the charge separation from each other and easily transport to the active surfaces, where the photocatalytic transformation take place [11]. Furthermore, Ag or Au nanoparticles embedded titania system improves the performance of energy storage capacity due to its high redox stability [12]. Based on the charge storage mechanism, supercapacitors can be classified into two categoriessuch asi)electrochemical double layer capacitor (EDLC), where charge is stored through electrostatic charge diffusion and accumulation and ii) pseudocapacitors, where charge is stored through Faradaic reactions on the electrode [5-6].

In the present study, silver deposited titania electrode has been synthesized as a photoanode by sol-gel method to investigate the photoelectrochemical performance as well as charge storage capacity for supercapacitor applications. The performance of the device was tested under constant illumination of visible light in the indoor condition. Moreover, the voltammetry study reveals that the photoelectrode exhibit high capacitive behavior and excellent redox stability.

II. EXPERIMENTAL

2.1 Preparation of TiO_2 and Ag/TiO_2 film

The pristine and Ag deposited titania film were prepared on Fluorine doped tin-oxide (FTO) coated glass slides by dip-coating method. Titanium iso-propoxide ($Ti(OCH(CH_3)_2)_4$) purchased from Sigma-Aldrich ; and isopropyl alcohol ($(CH_3)_2CHOH$) and silver nitrate ($AgNO_3$) purchased from Merck(India) were used to prepare the film. Double distilled water was used throughout the experiment.

Initially, a sol was prepared by mixing of titaniumisopropoxide and isopropoxide alcohol with the ratio 1:10 (v/v) ratioand allowed to stir constantly for 30 min. 0.2 ml nitric acid (HNO_3, 1.0 mM) was added to the solution before coating the film. Afterward, using the dip-coating method the TiO_2 film was prepared and allowed to dry at 80^0 C. To prepare Ag/ TiO_2 film, 1 weight % $AgNO_3$ solution ($AgNO_3$ + 1 ml isopropyl alcohol) was dissolved drop wise before the addition of nitric acid. Later the same process was followed to obtain the film and subsequently the films were calcined at 400^0C for 1 hour. The photographs of the prepared films were shown in Fig.3(b).

2.2 Characterization

The crystallite phase and crystallinity of the samples were investigated by X-ray diffraction (XRD) diffractometer (Rigaku Mini-flex, Japan) using Cu Kα radiation at 30 kV and 450 W at 0.05 2θ/s scanning rate. Energy dispersive x-ray analysis (EDAX) was done using the EDAX (Oxford Instruments, UK) model Jeol 6390LV, Japan. To study the spectral response of the sample the UV–vis diffuse reflectance spectrophotometer (Shimadzu UV-2200, Japan) was used. The photoluminescence spectrometer (Perkin Elmer LS55, USA) is used to identify the trapping states. The morphology of the samples was investigated using scanning electron microscope (SEM) model Jeol 6390LV, Japan at 15 kV.

III. RESULTS AND DISCUSSION

3.1 XRD spectra

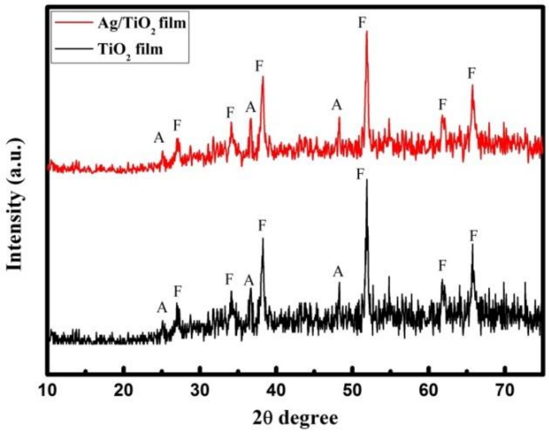

Fig.1: XRD spectra of TiO$_2$ and Ag/TiO$_2$ film (A: anatase phase, F: FTO substrate).

Fig1. Shows the XRD spectrum of pristine and Ag deposited TiO$_2$ in the range of 2θ= 10^{o}to 75^o.Thepeaks at 25.1^o, 36.8^o and 48.2^o(JCPDS File no. 894203) corresponding to the planes [101], [103] and [200], respectively, are attributed to the anatase phase of titania.The particle size of titania (calculated using Scherer's equation) is found to be in the range of 20-25 nm. The rest of the peaks indicated by F in the Fig.1 are due to the FTO substrate [13].

UV-DRS analysis

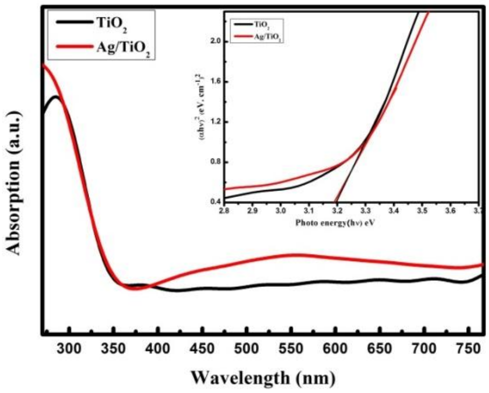

Fig.2: UV-DRS spectrum of TiO$_2$ and Ag/TiO$_2$ film. Band gap calculation using Tauc's relation is shown in the inset.

Diffuse reflection spectra of pristine and Ag deposited TiO$_2$ are shown in Fig. 2. The absorption bands of both the samples are seen in the ultraviolet region.A broad absorption peak at around 550 nmis observed in the Ag/TiO$_2$composite, which is attributed to the surface plasmon resonance (SPR) due to presence ofthe metallic silver (Ag^o) nanoparticles [14-15]. No shift of the absorption edge was observed in Ag/TiO$_2$ composite, which means no impurity is formed during synthesis process and Ag particles deposited only on the titania surface. The bandgap of the samples were calculated using Tauc's equation($\alpha h\nu = A\,(h\nu - E_g)^n$, where A is the absorption constant, α is the absorption coefficient, E_g is the energy gap, hν is the energy of photon and n is a number that depends on the type of transition process. By plotting (hν) vs. $(\alpha h\nu)^2$ as shown in the inset of Fig.2,the estimated band gap of both the pristine TiO$_2$and Ag/TiO$_2$are found to be 3.2 eV.

3.2 Transmittance

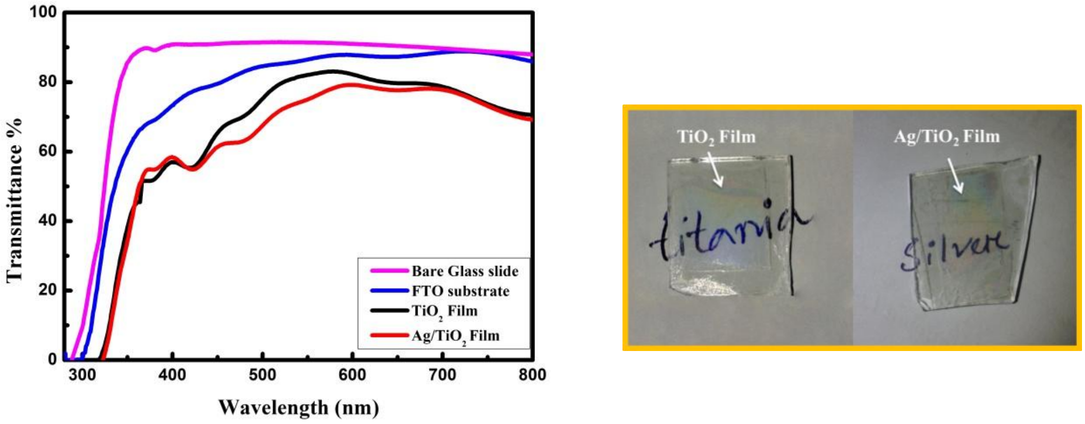

Fig.3: (a) UV-vis transmittance spectrum of bare Glass slide, FTO, TiO2 and Ag/TiO2 film. (b) Digital photographof pristine TiO_2 and Ag/TiO_2 film.

The transmission spectra of pristine TiO_2 and Ag/TiO_2composite prepared on FTO wererecorded using UV-vis spectrophotometer (shown in Fig.3(a)).The bare Glass slide and FTO substrate are used as reference for comparison. The transparency of bare Glass and FTO substrate shows about 90% (air baseline) and 88 %, respectively, in the range of 400 to 800 nm. Both the filmsTiO$_2$ and Ag/TiO_2 show excellent transparency in the range of 400-800 nm with their maximumtransmittance 83% at 587 and79% at 597 nm, respectively. This property may lead to new applications in the field of optoelectronics and solar photovoltaic devices. It is observed that the transmittance of Ag/TiO_2 composite decreased mostly in the range of 425 to 702 nm compared to pristine TiO_2, where the composite showsbroad absorption peak in this range due to SPR effect (shown in Fig.2). A digital photograph of pristine TiO_2 and Ag/TiO_2 composite film are shown in the Fig.3(b).

3.3 Photoluminscence spectra analysis

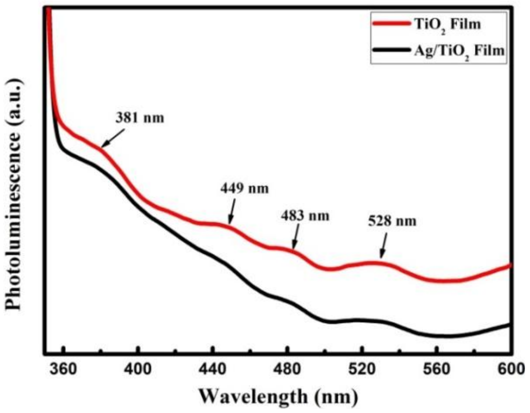

Fig.4: Photoluminscence spectra of pristine TiO_2 and Ag/TiO_2 film at an excitation wavelength 330 nm.

Photoluminescence (PL) spectrum of TiO_2 and Ag/TiO_2 film has been studied to investigate the trapping, separation and migration of the photo-induced charge carrier's photoluminescence. Fig.4 shows the recorded PL spectra of pristine TiO_2 and Ag/TiO_2 film using the excitation wavelength of 330 nm. Thepeak at 381 nm for both the pristine $TiO_2$and Ag/TiO_2 is due to the main band transitions peak corresponding to the band gap value 3.2 eV. The quenching of the PL peaks of Ag/TiO_2 film is mainly due to the lessening the recombination rate of photogenerated charge carriers due to Ag particle at the TiO_2 surface [16]. The Ag particles on the titania surface act as an electron traps centers to capture the photo-generated electrons and consequently obstruct the recombination of electron-hole pairs [17-18]. The PL peaks at 449and 483 nm of both TiO_2 and Ag/TiO_2 film, equivalent to 2.76 and 2.56 eV, respectively, are mainly due to the surface oxygen vacancies of titania[17]. The peak due the defect states in the surface region is appeared at 528 eV and no additional creation of the defect stares is observed after Ag deposition, which is well agreed with the UV-DRS result (Fig.3) and confirms that the Ag particles are sensitized/deposited only on the surface of titania.

3.4 Scanning Electron Microscope analysis

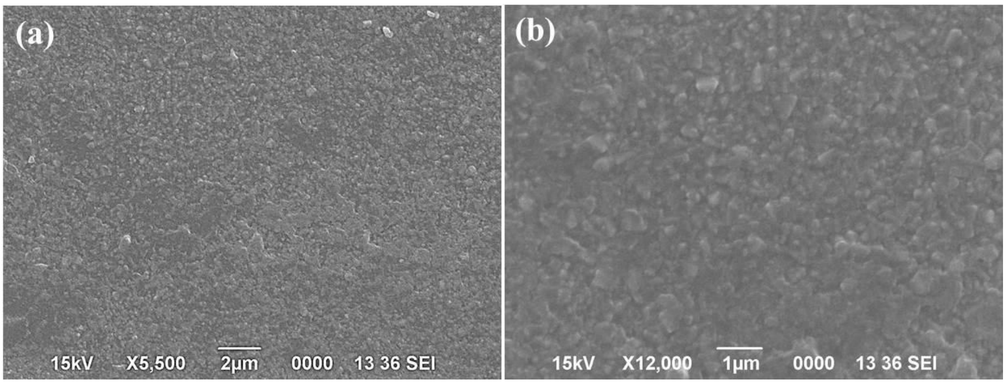

Fig.5: Scanning electron micrograph of Ag/TiO_2 film (a, b) at different magnification.

Fig. 5(a, b) depicts the SEM micrograph of Ag/TiO_2 film at different magnifications. The micrograph does not give clear morphology of the composites but the agglomeration of the particles can be seen in Fig. 5(b). For further morphological analysis TEM microscope has been studied.

3.5 Cyclic Voltammetry

The evaluation of electrochemical performance of TiO_2 and Ag/TiO_2sample was further studied by collected cyclic voltammetry curve in the electrochemical cell described above.

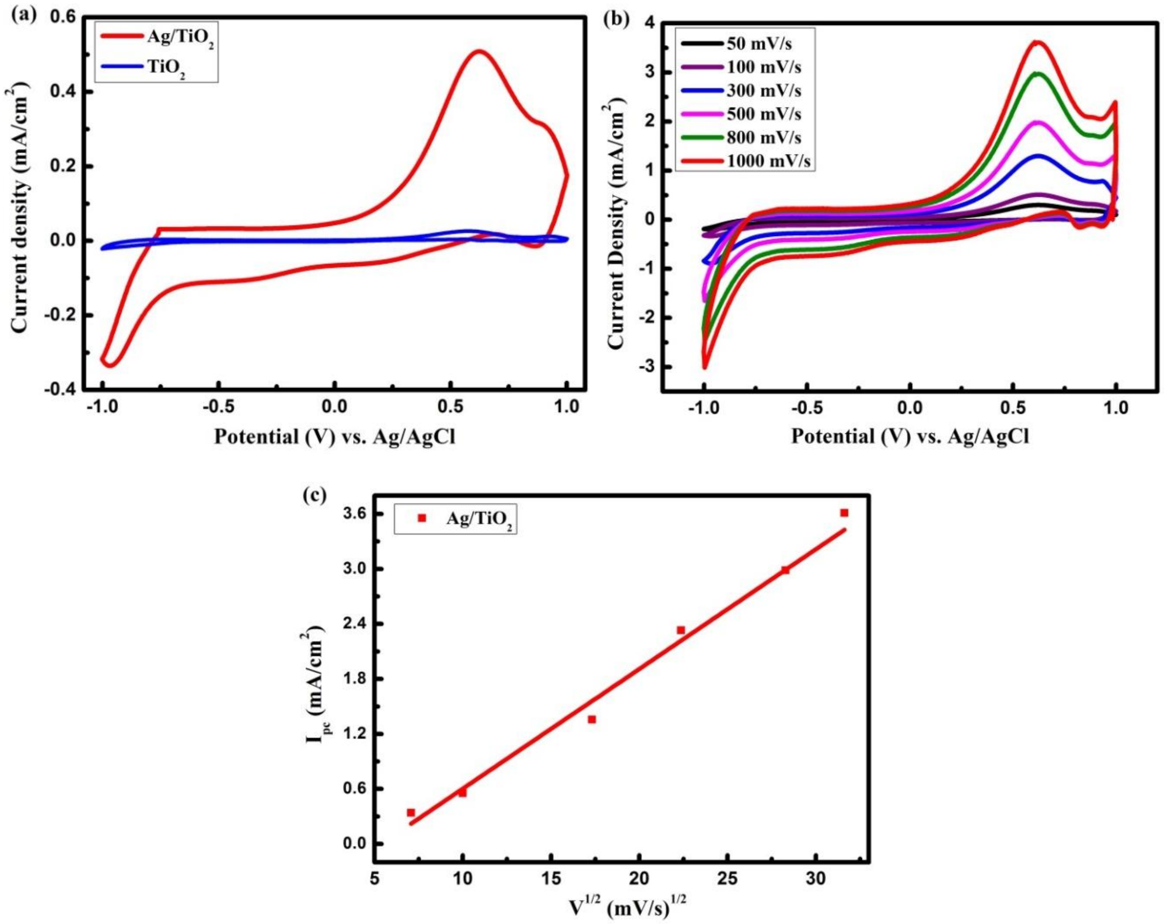

Fig.6: Cyclic voltammetry curve of (a) pristine TiO_2 and Ag/TiO_2at 100 mV/s, (b) CV curve of Ag/TiO_2 at different scan rate and (c) The square root of the scan rate vs. the anodic peak current.

Fig. 6(a) shows the cyclic voltammetry curves (CV) of the pristine TiO_2 and Ag/TiO_2 samples/electrodesin 1 M KOH electrolyte solution at 1000 mV/s.Both the samples TiO_2 and Ag/TiO_2 show pseudocapacitive CV curve. The observed oxidation peak at 0.61 V is attributed to the reduction of surface hydroxyl group [9]. Furthermore, it is observed that the area under CV curve of Ag/TiO_2sample/electrode increases with the increasing scan rate (50 mV/s to 1000 mV/s) (shown in Fig. 6 (b)) and the shapes of CV curve remain unchanged, which impliesthe good capacitive behavior of the sample/electrode[9]. Thecathodic peak current at 0.61 V is observed to be increase linearly with the square root of the scan rate (Fig. 6 (c)),indicating that the rate of ion diffusion is increased and the process is a diffusion-controlled process [20].

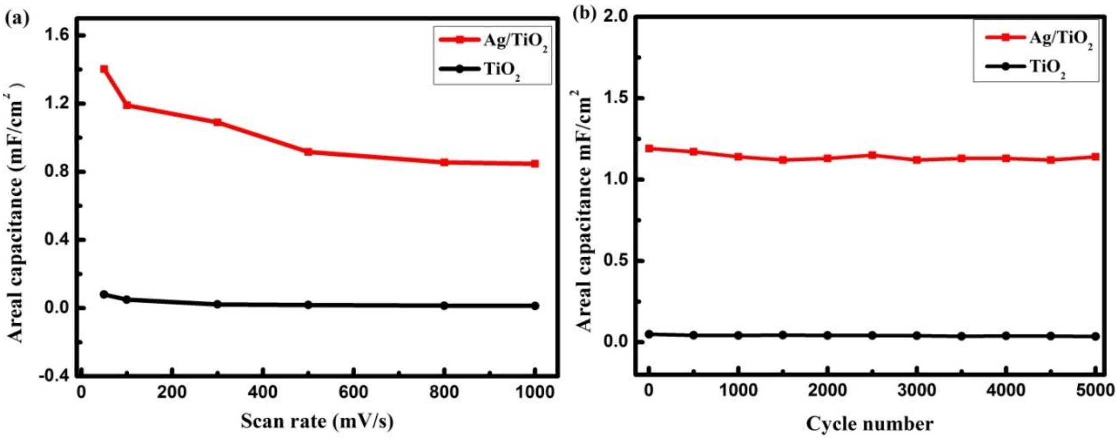

Fig.7: (a) The areal capacitance of pristine TiO_2 and Ag/TiO_2 electrode as a function of scan rate (b) Retention of areal capacitance vs. cyclic number for pristine TiO_2 and Ag/TiO_2at a scan rate 100 mV/s.

The areal capacitance of the pristine TiO_2 and Ag/TiO_2 are calculated from the CV curves using the following equation [9].

$$C_a = \frac{Q}{\Delta V.S} \quad (1)$$

where, C_a is the areal capacitance (mF/cm^2), Q is the average charge during the charging and discharging process (C), ΔV is the potential window (Volt) and S is the surface area (cm^2) of the working electrode.

Fig.7 (a) shows the calculated areal capacitance of pristine TiO_2 and Ag/TiO_2 electrode as a function of scan rate. A significant improvement in the areal capacitance is observed in Ag/TiO_2 electrode compared to the pristine TiO_2. The Ag/TiO_2electrode shows about 42 times higher areal capacitance than the pristine TiO_2 at the scan rate 100 mV/s. The areal capacitance of pristine TiO_2 and Ag/TiO_2 are shown in Table1.The improvement in the electrochemical performance of Ag/TiO_2sample is may be attributed to the increaseof the carrier densitydue to the Ag nanoparticles.The areal capacitance values are well comparable with the earlier workreported by Lu et al.[9].It is observed that the areal capacitance Ag/TiO_2 show about 60% retention of the initial capacitance when scan rate increase from 100 to 1000 mV/s, while the pristine TiO_2 shows only 16% retention of the initial capacitance. This improvement in the capacitance in Ag/TiO_2 sample is mainly due to the enhanced electrical conductivity of electrode.The redox stabilityof pristine TiO_2 and Ag/TiO_2 electrode forlong term charge-discharge cycling has been performedup to 5000 cycles at a scan rate 100mV/s(shown in Fig.8 (b)).The TiO_2 and Ag/TiO_2 electrode showan average drop of 28 and 4% of the initial capacitance, respectively,after 5000 cycles. This result demonstrates an excellent stability of Ag/TiO_2 electrode and very worthwhile for charge storage applications.

IV. CONCLUSION

In summary, we have demonstrated an enhanced photoelectrochemical performance of high transparent Ag deposited TiO_2 thin film (photoelectrode) under visible light. High areal capacitance of Ag/TiO_2 electrode is observed at a scan rate of 100 mV/s. The voltammetry study reveals that the photoelectrode exhibit good capacitive behavior and excellent redox stability with only 4% reduction in the initial capacitance after 5000 cycles. Such photoelectrode with high capacity and stability may be very useful for the charge storage and solar cell applications.

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