The preparation of metal oxygen molecular cluster embedded organic–inorganic nanocomposite and its rectification behaviour

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ABSTRACT

A metal oxygen molecular cluster compound has been utilized for the preparation of organic–inorganic nanocomposite film by a sol–gel method. The entrapment of these cluster compounds in a composite film has been characterized by various physico-chemical techniques. The entrapped metal oxygen cluster stabilizes its energy levels, which is evidenced from the change in redox potential and band gap. The rectification phenomenon of composite films is attributed to the embedded cluster compounds. The rectification behaviour of the composite film, which is due to the charge transfer from molecular cluster and the electrode, has been studied.

1. Introduction

The acidic and redox properties of metal oxygen molecular clusters (polyoxometalates, POMs) have been exploited in catalysis for the past few decades [1–5]. The redox properties of POMs can also be exploited as advanced materials in many fields such as optics, electronics, ionics, mechanics, membranes, protective coatings, sensors and biology. Despite their value adding properties, it is not easy to process these solid polyoxometalate compounds as thin films, due to their highly crystalline nature. Traditionally, thin films of POMs are made by spin coating, Langmuir–Blodgett technique [6,7], electrodeposition [8,9] or by compressing POM solids on indium tin oxide coated glass slides. More recent approaches involve the use of surfactant-encapsulated POM clusters [10] and another method is layer-by-layer self-assembly of POM and charged polyelectrolyte [11–15]. *In situ* controllable synthesis of polyoxometalate nanoparticles in polyeletrolyte multilayers and particle size variation by adjusting the concentration of the POM precursor solution have been described [16].

Organic–inorganic composite materials are a remarkable family of isotropic, amorphous nanocomposite materials [17], which have been investigated extensively for structural materials, biomedical materials, etc. These materials, which have properties of thermal and electrical conductivities, mechanical strength, flexibility, optical density and toughness, can be widely controlled by adjusting the composition, nanophase size and chemical bonding between organic and inorganic components. Recently, a new synthetic route has been developed for organic–inorganic hybrid materials as realistic ionic conducting membranes for electrochemical devices such as fuel cells and batteries. In these materials, the structure of hybrid has been designed to possess a fast proton conducting property mostly through manipulating organic ligands to inorganic surfaces. The composite membrane can be derived by hydrolysis and condensation reactions of polymer precursor consisting of polyethylene oxide encapped with triethoxysilane. The membrane doped with surfactant molecule shows good proton conductivity at high temperatures up to 160 °C and is shown to be flexible as well as thermally stable conducting polymer electrolyte for high temperature electrochemical devices [18]. The structural stability and conductive properties at elevated temperatures with various organic–inorganic as well as doping ratios have been investigated.

The characteristics of a metal–insulator–semiconductor (MIS) device with tunnel thin insulator, for example a solar cell, are mainly defined by the parameters of thin layer and interface states [19,20]. A number of theories have been put forward to explain the decrease in saturation current and the corresponding increase in photovoltage of MIS solar cells (Fonash [21] & Shewchun et al. [22]). These theories invoke a number of governing factors such as barrier height modification and transport control including surface states, fixed charges, traps, tunneling or hopping conduction through the insulator and asymmetrical tunneling probabilities for majority and minority carriers [21,22]. Yao et al. [23] deposited silicotungstic acid as thin film on the surface of silicon based solar cell in order to improve the performance. The short circuit

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current (I_{sc}) and the efficiency have been enhanced by 12.61 and 11.00%, respectively. When considering this type of modification, in comparison to silicon solar cell the anti-reflection coating and texturation are poor. Chaidogiannos et al. [24] have fabricated planar and vertical devices in order to investigate the transport properties of the POM materials. These POMs are embedded into resist systems with the intention to formulate an active molecular material that can be patterned by electron beam lithography. They have used three types of matrices (a) a negative tone resist based on poly(vinyl alcohol) (PVA), (b) a methacrylate copolymer (PHECIMA) and (c) poly(methyl methacrylate) (PMMA). The formulations containing different amount of matrices with $H_3PW_{12}O_{40}$ in water have been deposited using bilayer e-beam lithography. In the present study, we adopted a simple sol–gel method to embed the metal–oxygen molecular cluster compound (phosphotungstic acid) for the preparation of organic–inorganic nanocomposite film. The prepared composite was structurally characterized by various techniques such as UV–vis, Infrared and Transmission electron microscopy (TEM). The electrochemical properties have been evaluated using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The electron diffusion coefficient was determined from the impedance studies. The entrapped metal oxygen cluster compounds stabilized their energy levels, which are evidenced from the change in the redox potential, band gap of active component. Using this composite film, a planar device has been fabricated to study the *I-V* properties of the film. The composite with embedded phosphotungstic acid exhibited rectification behaviour.

2. Experimental

2.1. Materials

Phosphotungstic acid (PW) and polyvinylalcohol (PVA) (72000) were purchased from Sisco Research Laboratories Pvt. Ltd., and Tetraethylorthosilicate was purchased from E-Merck. All other chemicals were reagent grades and were used as received. The glassy carbon (GC) disc (Ø 3 mm and Ø 1 mm.) and the polishing kit were purchased from Bio Analytical System (BAS USA). Indium tin oxide (ITO) glass plates were purchased from Delta technologies, Germany.

2.2. Instrumentation

UV–vis spectra were obtained by PerkinElmer Lambda 17 spectrophotometer. Transmission electron microscopy (TEM) images were taken using Philips CM12/STEM, scientific and analytical equipment. TEM sampling grids were prepared by placing 2 µl of the solution on a carbon-coated grid and the solution was evaporated at room temperature. Infrared spectra of the composite samples were in the range 4000–400 cm^{-1}, on Shimadzu spectrophotometer. The thicknesses of the films were measured by Gaertner ellipsometer (Model 119 XUV) using He–Ne laser 632.8 nm. Cyclic voltammetric measurements were carried out by using BAS Epsilon potentiostat with three electrodes system. All measurements were carried out with Ag/AgCl (satd KCl) as reference electrode and Pt as counter electrode (1.5 cm^2 area). Electrochemical impedance measurements were carried out by using PARSTAT 2263 and spectra were recorded in the frequency range of 100 kHz–100 mHz by using a sinusoidal excitation signal (single sine) with excitation amplitude of 5 mV. The cell was purged with nitrogen for 15 min prior to electrochemical measurements.

The glassy carbon was first polished with alumina paste (procured from BAS, USA) followed by ultrasonication in water for 5 min and then polished with diamond paste (3 µm) and again ultrasonicated for 10 min in water. The composite was coated onto the glassy carbon electrode by taking 10 µl of PVA–SiO$_2$–PW composite and dried in an oven at 80 °C for 2 min to create a thin film on the glassy carbon electrode (PVA–SiO$_2$–PW/GC). This was employed as working electrode for further studies.

2.3. Synthesis of composite

The organic–inorganic composite was prepared by sol–gel method. Polyvinyl alcohol (PVA) dissolved in deionized water was stirred at 353 K for 10 min, to which tetraethyl orthosilicate and phosphotungstic acid were slowly added and refluxed at K for 6 h. For a typical synthesis, to a solution of PVA (30 wt% in water) was added a solution containing 20 wt% tetraethyl orthosilicate and 50 wt% phosphotungstic acid. The resultant solution was refluxed at 353 K for 6 h, to obtain a clear viscous gel. The final transparent solution was used to make films for further studies. The polyoxometalate is entrapped in the polymer matrix by interacting with the

hydroxyl groups of polymer. The polyoxometalate ($H_3PW_{12}O_{40}$) acts as acid catalyst for hydrolysis and promotes the condensation of the tetraethyl orthosilicate present in the precursor. The crosslinking between the silica matrix and polyvinyl alcohol takes place in presence of POM.

2.4. Fabrication of device

The indium tin oxide (ITO) coated glass plate was pretreated by washing with trichloroethylene to remove grease and subsequently ultrasonicated in acetone and water and dried in air. The composite was spin coated on the pretreated ITO glass plate with a speed of 2000 rpm for 1 min and 4000 rpm for another 2 min. The coated composite was dried in an oven at 60 °C for 12 h. The thickness of the composite film was about 180 nm. The contacts were formed by evaporating Al as dots by thermal evaporation method. The current-voltage and charge trapping characteristics were studied by using an automated Keithley 238 high current source measure unit (SMU). The dark *I–V* measurements of the samples were performed at room temperature. For the photosensitivity measurements, light was irradiated from the ITO side.

3. Results and discussion

3.1. UV–vis studies

It is well known that POMs exhibit oxygen-to-metal ($O \rightarrow M$) charge transfer band in ultraviolet region [25]. The composite gel was coated on a quartz plate and UV–vis spectra were recorded (Fig. 1). When the POM is embedded in the composite, the oxygen-to-metal charge band is red shifted. This can be attributed to the interaction of polyoxometalate terminal M–O bond with the polymer hydroxyl groups as well as with silica matrix. Parent phosphotungstic acid has a characteristic oxygen metal charge transfer band at 265 nm. This charge transfer band is red shifted to 298 nm when PW is present in the composite film environment.

3.2. Infrared studies

The positions of vibration modes of all types of W–O bonds are strongly affected by the interaction of phosphotungstic acid with the polymer and silica network [26]. Therefore, the spectra of parent PW and composite film with PW have been compared. It is found that the frequencies of PW in the composite film are blue shifted. A detailed inspection of the band of W=O$_t$ bond of PW in the composite is red shifted from 964 to 956.2 cm^{-1} and the band of W–O$_c$–W from 871.6 to 856.6 cm^{-1} (Fig. 2). The band of W–O$_b$–W has a blue shift from 776.1 to 800.5 cm^{-1}. This may be due to the coulombic interaction between the hydroxyl groups of the polyvinyl alcohol donor and the polyoxometalate. IR absorption bands at 1122.4 cm^{-1} (Si–O–C) and (Si–O–Si), 1650.7 cm^{-1} and 796 cm^{-1} indicate the development of an organic–inorganic hybrid network during the gel formation. In addition, there are several strong bands below 1100 cm^{-1} due to polyoxometalates. The vibrations of the central tetrahedron XO$_4$ could not be identified because of the overlapping of the silica matrix vibrational bands. It is found that the frequencies of PW in the hybrid film are shifted from those of pure PW by only a few cm^{-1}, which indicates that the Keggin geometry of PW is still preserved inside the gel.
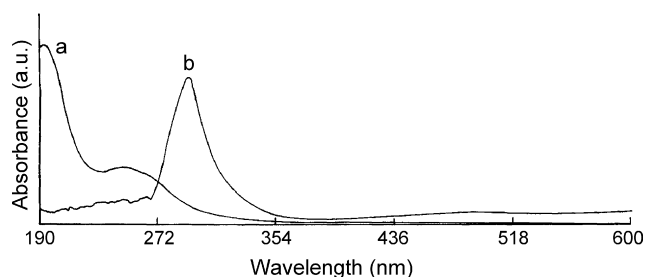

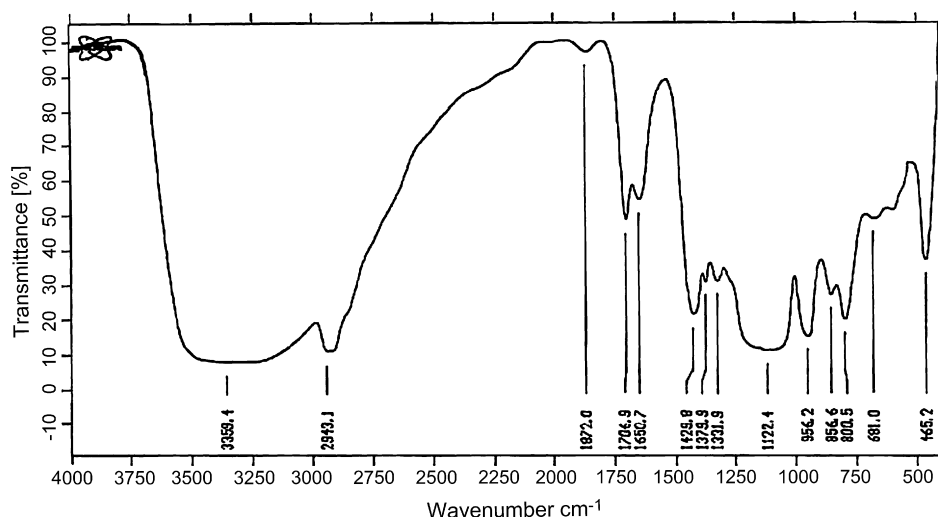**Fig. 1.** UV–vis absorption spectra of composite (a) PW and (b) PVA–SiO$_2$–PW.

Fig. 2. Infrared spectra of PVA–SiO$_2$–PW composite film.

3.3. Electron microscopic studies

The surface of the composite was examined with scanning electron microscopy. It is evident from the image that the organic–inorganic composite structure is highly homogeneous in nature. The SEM images of the composite prepared with polyvinyl alcohol gave good films and the active entities are embedded. The dispersed phosphotungstic acid can be seen from the high resolution SEM image (not shown). The microstructure of composite film can be visualized through the transmission electron microscopy. A few microliters of PVA–SiO$_2$–PW viscous gel were dropped on to the carbon-coated copper grid and dried at room temperature. The embedded molecular clusters are spherical in shape and have a size in the range of 10–50 nm which is evidenced from transmission micrograph (Fig. 3). Thus, one could effectively disperse the active components in controlled manner through organic-inorganic synthetic strategies.
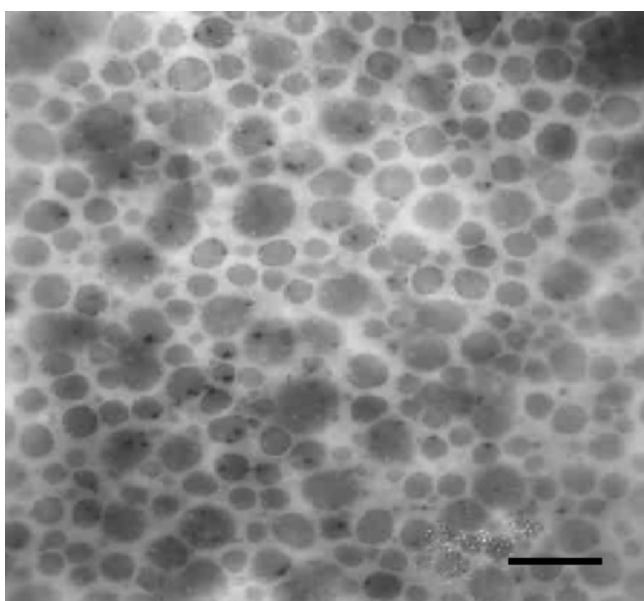
3.4. Electrochemical studies of composite

The electrochemical behaviours of the parent and embedded PW were characterized by cyclic voltammetric studies. Fig. 4a presents the cyclic voltammogram of PVA–SiO$_2$–PW, which exhibits four anodic peaks (E_{pa} at −89, −358, −518 and −614 mV)

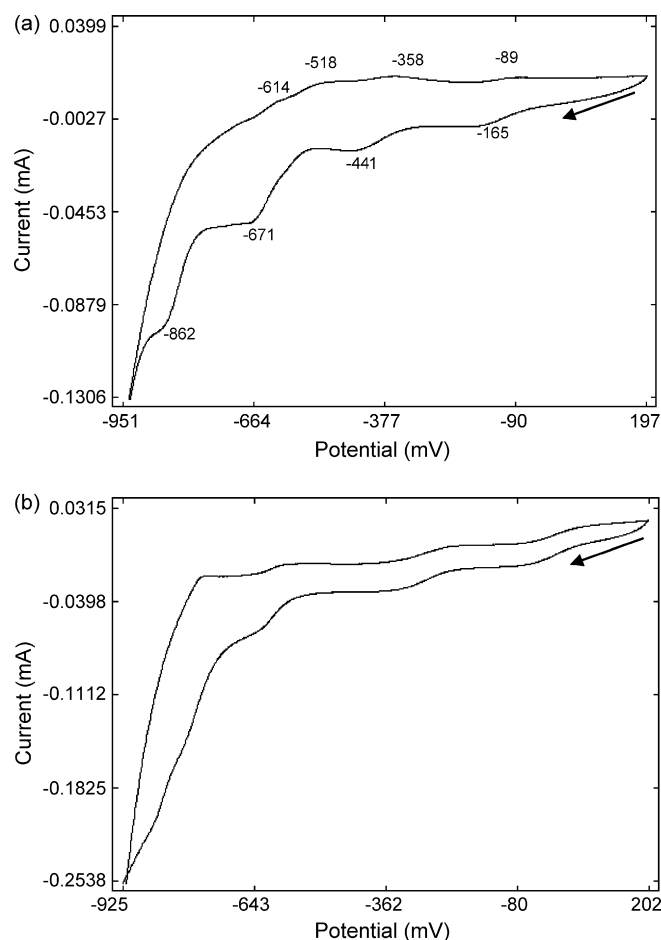**Fig. 3.** Transmission electron micrograph of PVA–SiO$_2$–PW. Scale bar -50 nm.

Fig. 4. Cyclic voltammogram of (a) PVA–SiO$_2$–PW/GC and (b) PW at 25 °C in 1 M H$_2$SO$_4$. Scan rate: 25 mV S^{-1}. Arrow indicates initiation of voltammogram.

and four cathodic peaks (E_{pc} at −165, −441, −671, and −862 mV). One electron half wave potential for phosphotungstic acid in 1.0 M sulphuric acid was observed at −23 mV by Pope et al. [27]. The peak potentials shifted towards more negative when POM was present in composite environment when compared to the parent compound. This might be due to the stabilization of energy levels of polyoxometalate upon embedding. POM present in the composite is strongly interacting with the functional groups of the polymer as well as with that of the silica matrix. There was no appreciable decrease in the cathodic or anodic current upon cycling. The first reduction potential of phosphotungstic acid present in the composites is shifted cathodically (104 mV) indicating the stabilization of the energy levels of the POM.

The cyclic voltammograms of the PVA–SiO$_2$–PW at different scan rates (25, 50, 75, 100, 200, and 300 mV) were recorded. The cathodic and anodic peak currents increase with increase in scan rate with the cathodic peak potentials shifting towards the negative direction and the corresponding anodic peak potentials towards the positive direction. As the scan rate increases, the peak current increases indicating that the redox process is surface confined. It was observed that the cathodic current is proportional to the square root of the scan rate. This shows that the process is a surface phenomenon. The cyclic voltammetric studies of the PVA–SiO$_2$–PW have been studied in H_2SO_4 + Na_2SO_4 aqueous solutions at different pH values (0.79, 1.01, 1.48, 2.05, 2.48, and 3.0). As the pH increases, the peak potentials shift towards more negative values and the peak currents gradually decrease. When the pH increases (that is replacement of H$^+$ by bulky cations), the slower penetration of larger cations into the active component is immobilized in the composite, which is evidenced from the decrease in the peak current as well as the shift in the reduction potentials towards more negative values. Similar trend was observed by Song et al. [28]. As the individual POM cluster is reduced, evolution of protons from the solution results in maintaining the charge neutrality. The electrochemical stability of the composite film was tested by cycling in 1 M H_2SO_4 in the potential window of −1000 to 200 mV for 3 h. We observed a marginal current decrease in both anodic and cathodic peaks indicating that the PW cluster compounds are firmly embedded in the composite.

Electrochemical impedance spectroscopy is an effective method to study the interfacial properties of modified electrodes [29,30]. The complex plot Z_{re} vs Z_{im} shows a semicircle at high frequency region and a straight line having slope of 45° at low frequency region, which is a characteristic plot for polymer modified electrode. The ohmic and charge transfer resistances were extracted from the complex plot. Fig. 5. shows the Nyquist plot of the composite coated on GC in 1.0 M sulfuric acid. It exhibited a semicircle at high frequency region and a spike boost at low frequency region. The high frequency impedance is contributed from the charge transfer resistance along with the ohmic resistance and the low frequency impedance is due to the diffusion of the electron from the active species present in the composite. All the experimental data were interpolated using the equivalent circuit, which was able to fit all the spectra, giving χ^2 values of the order of 10^{-4} to -10^{-3}. The charge transport diffusion coefficient was calculated from impedance measurements [31,32]. The effective electron diffusion coefficient can be extracted from the impedance data through equation: $D_e = d^2/R_e C_{low}$, where d is the film thickness and C_{low} is the low frequency capacitance, which can be obtained as the inverse slope of a plot of imaginary impedance Z'' against reciprocal frequency (in rad S^{-1}) [33–36]. The electron diffusion coefficient in the composite film was measured in 1 M sulphuric acid in the frequency range of 100 mHz−100 kHz and is found to be 2.2×10^{-10} cm^2 s^{-1}.
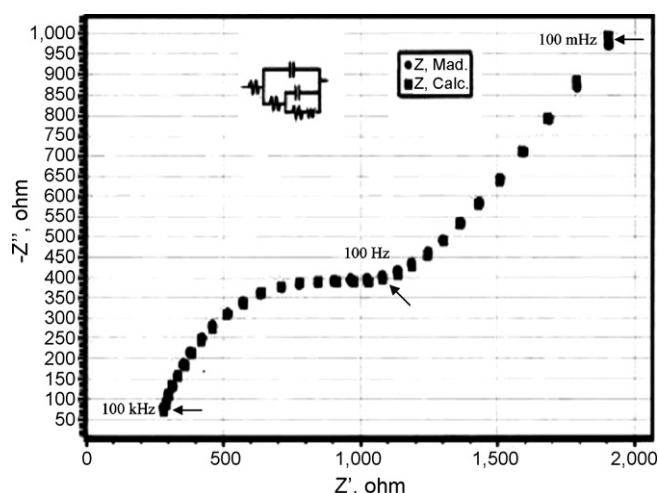

Fig. 5. A typical complex impedance plot of the PVA–SiO$_2$–PW on GC at 25 °C in 1 M H$_2$SO$_4$, Potential: OCV; frequency range: 100 kHz–100 mHz. Inset shows equivalent circuit which was used to fit the experimental data.

3.5. Rectification behaviour of composite film

The configurations of device with PW embedded composite film and without PW composites, are shown in Fig. 6a and b. For both devices, the thickness of the film is about 180 nm. The current –voltage curve for the ohmic contact is shown in Fig. 7a. The thin composite film coated on ITO device designed with POM containing composite film has the characteristics of a rectifier (Fig. 7b), behaviour. In order to understand this phenomena, the device was fabricated with the composite without any active entities (without POM). It showed similar behaviour like ohmic contacts (Fig. 7c). This clearly showed that the rectification process is originated from the active compounds which are embedded in the composite film. We have also varied the concentration of active component in the composite film and observed similar results with different current response. The reverse current shown in the Fig. 7b corresponds to the tunneling from the aluminum metal electrode to the semicon-
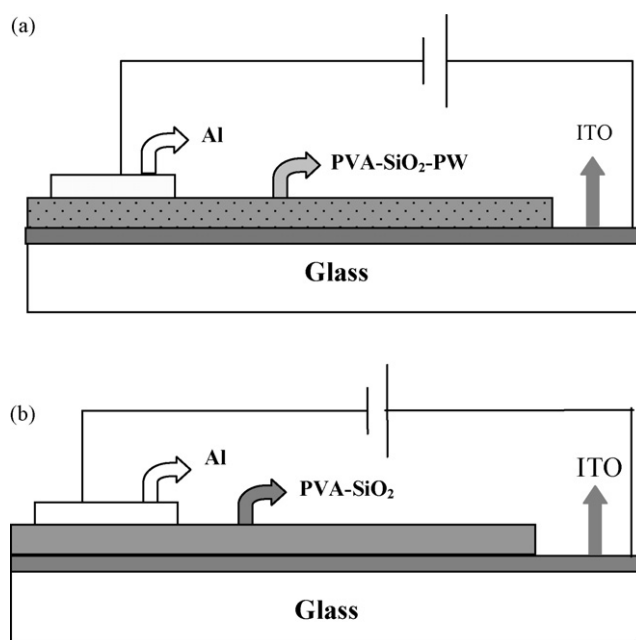

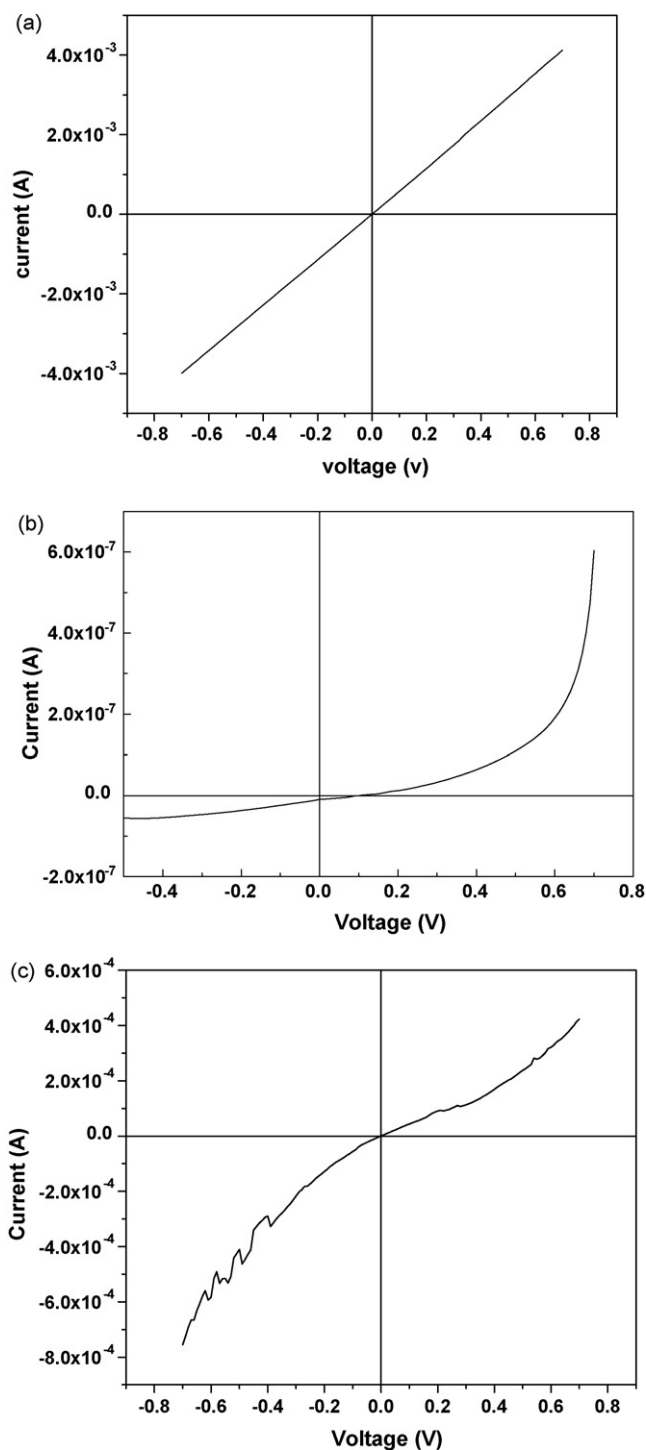**Fig. 6.** Configuration of device (a) ITO/PVA–SiO$_2$–PW/Al and (b) ITO/PVA–SiO$_2$/Al.

Fig. 7. I–V plots for (a) ohmic contact, (b) ITO/PVA–SiO$_2$–PW/Al and (c) ITO/PVA–SiO$_2$/Al.

cation is due to the embedded active molecular clusters, which are present in the composite, and not due to any other component present in the system. The device (Fig. 6a) when irradiated with UV lamp (354 nm) shows I–V curve which is characteristic of a solar cell. The various parameters such as the open circuit potential, short circuit current and fill factor were evaluated and found to be 360 mV, 9.1 nA and 25%, respectively. However, the tungsten-based polyoxometalate absorbs only in near IR radiation from the solar spectrum. It is possible to fine tune the absorption characteristics of the polyoxometaltes by suitable substitution in the appropriate places (for instance, substitution in addenda atoms). The molybdenum and vanadium substituted polyoxometalates absorb in near visible radiation. Since a variety of heteropoly acids based on either W or Mo or V, together with their insoluble salts can be utilized, composites with tailor made properties appear to be a feasible proposition.

4. Conclusions

An organic–inorganic nanocomposite film consisting of a metal oxygen molecular clusters compound (polyoxometalate) has been synthesized by a sol–gel synthesis. The presence of these cluster compounds in composite film has been characterized by various physico-chemical techniques. The entrapped metal oxygen cluster compounds stabilized their energy levels, which is evidenced from the change in redox potential and band gap. The electron diffusion coefficient was determined from the electrochemical impedance studies and was found to be 2.2×10^{-10} cm^2 s^{-1}. The entrapped cluster compounds are responsible for the retification behaviour of the composite film.

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ductor ITO substrate through the thin composite film consisting of active components. The charge carriers could be transferred from the top electrode to the active components, which are embedded in composite film. The charge could transfer by tunneling from one molecular cluster (PW) to another by hopping mechanism. Recently, Chaidogiannos et al. [24] have demonstrated similar effects in polymer/POM composite materials. It is well known that the charge transfer can be possible through hopping mechanism in these cluster compounds. This demonstrates that the rectifi-

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