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Polyoxometalate Based Organic-Inorganice Nanocomposites

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Abstract

The organic-inorganic nanocomposites were synthesized by sol-gel techniques. The constructed film renders photochromism, which can be tuned by choosing suitable polyoxometalates (POM). The molybdenum POMs show better photochromism than the tungsten POMs, which is well correlated with the first reduction potentials and band gap of the POM.

Introduction

Photochromic materials are receiving attention in recent times because of potential applications in devices, such as high-density optical memory, photochromic switches, energy-conserving coatings, eye protection and privacy shield [1-4]. For example fast transformations are required for optical switches, while slow transformations are useful for optical data-storage. As far as the photochromic devices are concerned, fine tuning between a strong and fast reversible colouration and a very fast thermal fading are needed [5]. These can be achieved by careful adjustment at the interface between the photoactive entities. Polyoxometalates are metal oxide clusters, discrete and well defined at atomic/molecular level with an extensive range of structures and properties [6-10]. POMs are promising candidates due to their ability to act as an electron reservoir, thereby giving rise to colour mixed-valance state without any change in the structure. Utilization of these potentialities of POMs in advanced materials has remained elusive due to their poor film forming and exists as well crystalline solids. Various techniques have been employed to construct POM thin films [11]. However, these composites show poor photochromic response and cannot be employed for practical devices. The challenge lies in the rate of coloration and decoloration of POM containing devices. Photochromic phenomenon in POMs is absorption of photon from UV/Visible light (having $h\nu > E_g$ than of POM), which excites the valence band electron to the conduction band resulting in reduction of the central metal ion. In the present study, various POMs have been employed as active components, silica as inorganic moiety and polyethylene glycol (4000) and polyvinyl alcohol (72000) as organic components.

Experimental

The organic-inorganic composite was prepared by sol-gel method [12-13]. For a typical synthesis, 1.5 g of polyvinyl alcohol was dissolved in 30 mL distilled water and 2.5 mL of tetraethylorthosilicate was added and the mixture was stirred for 10 min, then 0.5 g of polyoxometalates was added and refluxed at 70°C for 6 hrs. The obtained gel was utilized for the further studies. The thickness of the films has been measured by Gaertner ellipsometer (Model 119 XUV) using He-Ne laser 632.8 nm. Photochromic experiments were carried out in sunlight by coating the composite on glass plate. UV-Visible spectra were obtained by Perkin-Elmer Lamda 17. Transmission micrographs were taken in Philips CM12/STEM, Scientific and Analytical Equipment. Cyclic voltammetric measurements were carried out by using BAS Epsilon with three electrodes system. Composite was coated on glassy carbon (BAS 0.07 cm^2) and measurements were done in 1.0 M sulphuric acid.

Results and Discussion

The organic-inorganic composite was coated on a glass plate by spin coating method (initially 2000 rpm for one minute and then 4000 rpm for two minutes) and was employed for all characterization and

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further studies. Figure 1 shows the transmission micrograph of PEG-SiO_2-PW. It is clear from the micrograph that the PW clusters are well dispersed in the polymer matrix and the particle sizes are between 5.0 to 10.0 nm.

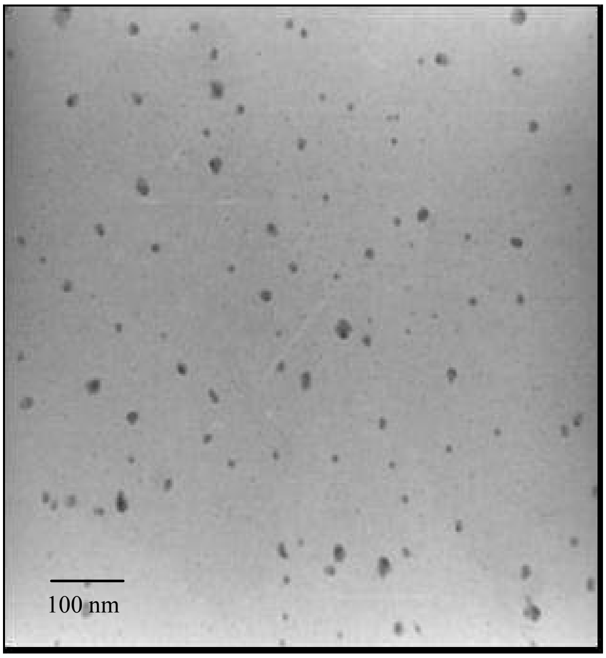

Fig. 1. Transmission electron micrograph of PEG-SiO_2-PW.

The coated composite was transparent and upon exposure to sunlight it turned blue. Figure 2 shows the UV-Visible spectra of PEG-SiO_2-PW irradiated under sunlight at different time intervals. As the irradiation time increases the absorbance increases and reaches a maximum value around 750 nm. The inset in Figure 2 illustrates that the rate of colouring is 4 times faster (at 20 min) than that of the film prepared with polyvinyl alcohol as organic component. This envisages that the surrounding environment of the POM also plays a vital role in photochromic response. The composite prepared with PEG shows reversible photochromism, while the composite containing PVA retains its colour for a minimum of three months when stored in dark [13]. This demonstrates that the charge separation is important for the photochromism. It is well known that the charge separation occurs at the conduction and valence bands depending upon the depth of the trapping centres.

The decolouring process has been studied on composite prepared with PEG. It showed reversible photochromism. The composite film exposed to sunlight for 30 min and decolouring process was monitored by measuring the change in absorbance at 750 nm. The coloured film is completely bleached within 2 min when exposed to atmospheric air. Similarly, the colouring and bleaching processes have been carried out to see the efficiency of the photochromism and obtained results are presented in Fig. 3.

The hole present in the valence band is utilized for the oxidation of polymer functional groups and electron is trapped at trapping centres [14,15]. Depen-

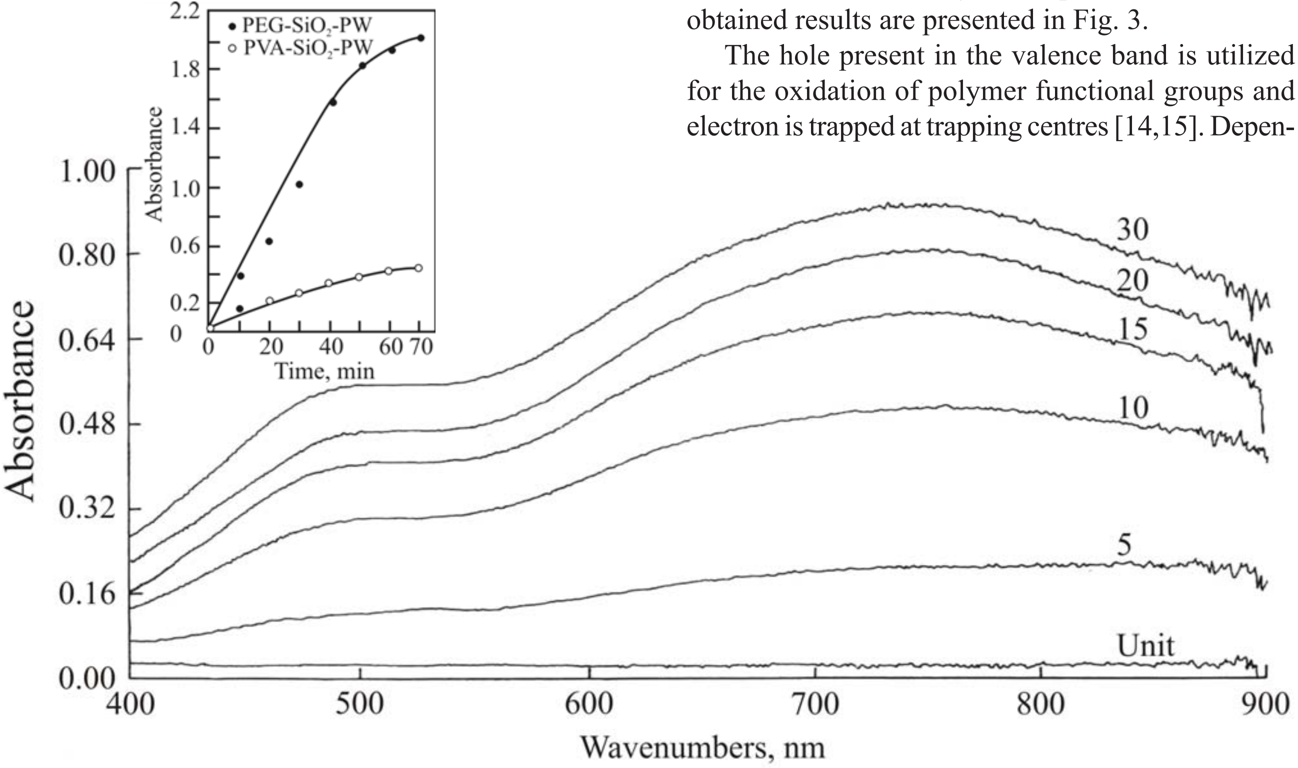

Fig. 2. UV-Visible spectra of PEG-SiO_2-PW upon irradiation under sunlight. Inset shows rate of colouring.

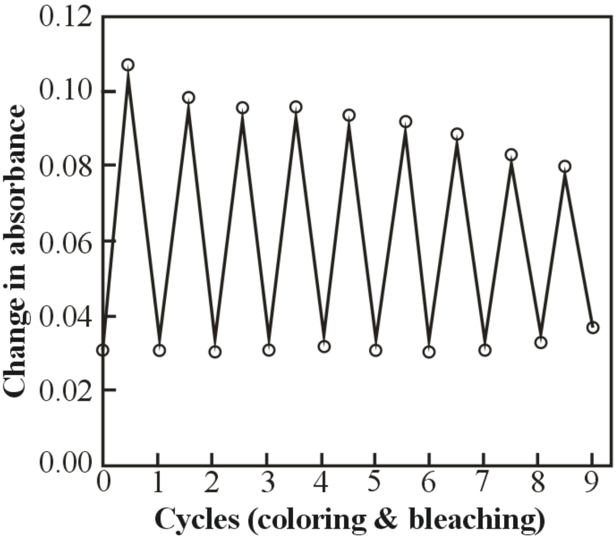

Fig. 3. Colouring and bleaching cycles of PEG-SiO_2-PW irradiated in sunlight and bleached in the air.

ding upon the environment of POM, they can be employed as electron reservoirs or energy reservoirs. The trapped electrons can be utilized for reduction of various organic compounds at later stages depending upon the environment of the polyoxometalate. In order to rationalize the photochromic response of organic-inorganic composite, so further experiments are restricted to PVA composite containing four different POMs (vanadophosphomolybdic acid (PMoV), Phosophomolybdic acid (PMo), Phosphotungstic acid (PW) and Silicotungstic acid (SiW)). It is known that the phenomenon of photochromism in POM is due to the reduction of central metal M^{6+} to M^{5+} [16,17]. The photochromic response is related to the first redox potential of POM and as well as to the band gap (Table 1). The change in absorbance is 0.656 at around 750 nm for the film containing PMoV, while it is 0.249 for film prepared with SiW (650 nm), for 30 min irradiation under sunlight. In order to envisage the photochromic response, impedance studies were performed on the prepared composites. These studies will help in understanding how the charge transfer is taking place between the electrode and the composite and the diffusion of electron from the electrode to the active component. Figure 4 shows the complex impedance plot for the composites prepared with different POMs. There is a semicircle part at high frequency region and a straight line part at low frequency region, which is due to the diffusion (Warburg impedance) of electron transport. The values of charge transfer resistance and Warburg impedance were extracted from Fig. 4 and are shown in Fig. 5. Figure 5 shows the charge transfer resistance is low for molybdenum-based polyoxometaletes than the tungsten based POM. This demonstrates that the electron transfer (reduction of POM) is facile in the case of molybdenum POM than the tungsten based POM. The molybdenum POM shows less Warburg impedance than the tungstates, which is due to the electron transverse (hopping from one POM to another POM), which is facile in molybdenum containing POM than in the tungsten POM. This can be further attributed to the higher value of first reduction potential of PMoV compared to that of the SiW. More the positive potential of the polyoxometalates they will get easily reduced. This is further supported by calculating the band gap of the POMs present in the composite (Table 1). PMoV has a lower band gap than that of SiW demonstrating that PMoV could absorb more visible light than SiW. Figure 6 shows photograph of PVA-SiO_2-PW composite coated on glass plate that was partially exposed to sunlight for 15 min. The exposed parts turned blue and the colour was stable for a minimum of three months if stored in dark or inert atmosphere. This shows the potential application of polyoxometalates containing organic-inorganic composite.

Table 1

Physico-chemical data of POM containing organic-inorganic composites

Composite	Redox potential of POM (V)[a]		O→M, (nm)	Band gap[c], (eV)	Change in absorbance[d]	Film thickness, (nm)
	Parent[b]	Obtained				
PVA-SiO_2-PMoV*	0.501	0.41	330	2.44	0.656	188
PVA-SiO_2-PMo	0.429	0.351	341	2.73	0.470	192
PVA-SiO_2-PW	-0.023	-0.127	293	3.32	0.280	181
PVA-SiO_2-SiW	-0.187	-0.248	285	3.50	0.249	186

a – First reduction potential M^{6+}/M^{5+}; b – Taken from reference [17]; c – Calculated from optical absorption spectra; d – Maximum absorption IVCT band for 30 min irradiation in sunlight; * – reduction of V^{5+}/V^{4+}

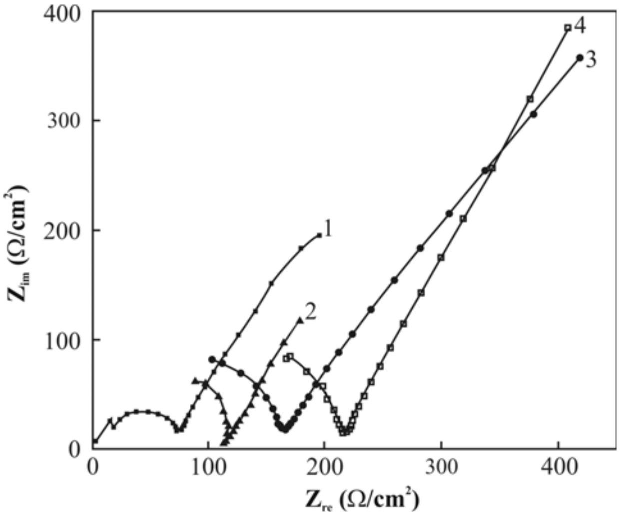

Fig. 4. Nyquist plot of composite containing different POM (1– PMoV, 2 – PMo, 3 – PW, 4 – SiW).

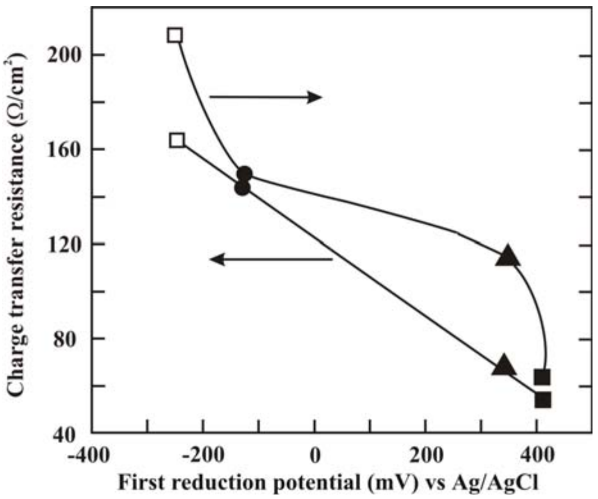

Fig. 5. Effect of first redox potential on charge transfer resistance and warburg impedance for different composites containing POM (■ – PMoV, ▲ – PMo, ● – PW, □ – SiW).

Fig. 6. Photograph of PVA-SiO_2-PW composite coated on glass plate and irradiate under sunlight for 15 min.

The photochromic response of PVA-SiO_2-PMoV is shown in Fig. 7 (0-60 min). Upon irradiation under sunlight the brown film turned to blue colour. The vanadium present in the PMoV is easily reducible than molybdenum [18]. Upon irradiation, valence electrons of oxygen 2*p* orbital will be transferred to the conduction band (mainly contributed by metal *d* orbitals) resulting in the reduction of the central metal ion. Simultaneously, the protons from alcohol groups would have been transferred to POM octahedra to form charge – transfer complex [19]. The reduction of vanadium (^{51}V, I=7/2) can be examined by low temperature (77 K) ESR (8 lines hyperfine splitting) [20]. Among the studied composites, PMoV shows fast photochromic response, which can be correlated with of the reduction potential and band gap of the POM present in the composite. The photochromic response of composite follows the order PMoV>PMo>PW>SiW, which corresponds to the order of first reduction potential (M^{6+}/M^{5+}) as well as to that of the band gap of the POMs present in the composites.

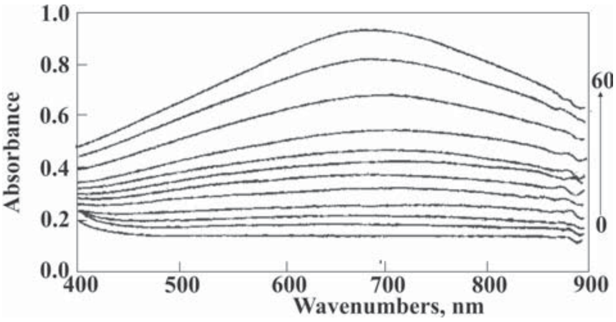

Fig. 7. UV-Visible spectrum of PVA-SiO_2-PMoV irradiated in sunlight.

This is further supported by the electrochemical measurements of composites which revealed that the 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 polyoxometalates present in the composites is shifted cathodically (PW for 104 mV) indicating the stabilization of the energy levels of the POM. Bardin *et al.* [21] calculated proton affinities for molybdenum and tungsten Keggin ions by density functional theory. They reported that the molybdenum polyoxometalates have higher proton affinities (1126 kJ/mole) than tungsten polyoxometalates (1088 kJ/mole). This shows that molybdenum POMs are easily reducible than tungstates. This is further supported by the present study. The composites prepared with molybdenum POMs show better photochromic response than the tungsten counterparts.

Conclusions

Organic-inorganic nanocomposites based on polyoxometalates were synthesized by adopting sol-gel techniques. Among the studied composites, molybdenum POM showed better photochromic response than the tungsten counterparts. The photochromic response was correlated with the charge transfer resistance of the composite, first reduction potential of POM and as well as with that of the band gap of POMs present in the composite. Better photochromic response of molybdenum POM composite is attributed to its lower band gap. Photochromic properties can be fine tuned by selecting the individual components of the composites.

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