

**SYNOPSIS OF
SOME DEVICE APPLICATIONS OF (EMBEDDED) METAL
OXYGEN CLUSTER COMPOUNDS**

A THESIS

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Introduction

In recent years, chemistry of polyoxometalates has developed rapidly to produce a number of structurally well-defined solid architectures. A variety of polyoxometalates have been used in chemical synthesis as versatile building blocks for the construction of large supramolecular structures and inorganic materials. Soft chemical methods have been employed to explore the polyoxometalates as a constituent of the organic-inorganic composites by combining with organic polymers. Modifying the surface properties of the polyoxometalates opens a new avenue for various applications in science and technology such as catalysis (Okuhara et al 1996), electrochemistry (Sadakne et al 1998) medicine (Rhule et al 1998), nanodevices (Volkmer et al 2000) bleaching of paper pulp and analytical chemistry (Katsoulis et al 1998). Polyoxometalates self-assembly proceeds by the linking of low molecular metal-oxide building blocks of different sizes and shapes. Polyoxometalates are suitable candidates for photochromic/electrochromic devices due to their ability to act as photosensitizer/electron relays. Among the semiconductor nanoparticles and quantum dots, polyoxometalates are desirable because of well-defined metal-oxide cluster at atomic/molecular level (Kozhevnikov et al 1983). It is also possible to tune their acidic/redox behaviour by suitable substitution in the heteroelement and exchange of counter ion with various cations. For realization of such devices with polyoxometalates, organic-inorganic synthetic strategies can be adequate. Despite the potentiality of polyoxometalates, their implementation in advanced materials such as smart windows and nanodevices (nanoreactors/nanosensors) still remained elusive, mainly due to the fact that they are obtained as crystalline solids, which are difficult to process. POMs modified electrodes can be achieved by various techniques like electrodeposition (Keita et al 1988, 1989) adsorption on electrode surface (Dong et al

1987, 1992), doping in conducting (Kuhn et al 1996) and nonconducting matrices (Shiu et al 1991), self-assembly (Kuhn et al 1996), layer-layer deposition (Chen et al 2000) and Langmuir Blodgett () So, embedding of functional inorganic components into a polyelectrolyte matrix permits preparation of flexible films of arbitrary shape with diverse properties.

Motivation and scope of the investigation

So far extensive work was carried out to explore the acidic properties of the polyoxometalates. These polyoxometalates have been employed as alternate solid acid catalysts for various industrial reactions. The strong acidity of these compounds makes them potential candidates for acid catalyzed reactions. The potential redox properties of the polyoxometalates makes them viable candidates in the advanced materials like photochromic/electrochromic devices because these properties can be easily altered by means of potential or photons. The redox behavior can be exploited by suitable modifications of the polyoxometalates. We aimed to explore the acidic and redox properties of Keggin type polyoxometalates for various applications.

1. In the present investigation Keggin polyoxometalates have been employed as solid acid catalysts for Esterification of triethylene glycol with methacrylic acid. The catalytic activity was compared with various conventional acid catalysts. Detailed kinetic studies were carried out the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid.
2. Organic-inorganic nanocomposites were prepared using POMs as active components. Prepared composites were characterized by various physico-chemical techniques.

3. The photochromic behaviour was studied and reduced composites were employed to photobleaching of dyes. The prepared composite has been employed for the metal insulator semiconductor(MIS) devices for the solar energy harnessing.
4. The composites were exploited as modified electrodes for electroreduction of various inorganic species
5. The composite was employed as reducing medium for the preparation of platinum nanoparticles and employed as anode for methanol oxidation.

Experimental techniques

Various Keggin polyoxometalates have been synthesized and characterized. The esterification of methacrylic acid was carried out with various diols (EG, DEG, TEG and PEG) in a three-necked 100 ml flask equipped with a Dean-Stark trap, thermometer and a magnetic stirrer. The temperature was maintained with an oil bath. When the mixture in the flask reached a temperature about 10°C lower than the desired temperature, the catalyst was added quickly. After the addition of catalyst, 1 ml of aliquot was withdrawn immediately and the reaction was arrested by adding 20 ml cold water and titrated with ~0.1 M standard sodium hydroxide solution using phenolphthalein as indicator. For a typical reaction 82.5 mmol of TEG, 171 mmol of MAA and 55.8 mmol of trichloroethylene were employed. The reaction was carried out at 368 K for 5 h. The water formed in the reaction was removed by azeotropic distillation with the solvent TCE and the solvent was reverting back to the reaction vessel. For the equilibrium constant measurements, the reaction was carried out for 15-20 h and the acid concentration was monitored periodically. The products were further confirmed by ^1H and ^{13}C NMR

analyses. For comparison, the same reaction was carried out on various acid catalysts such as amberlyst-15, sulfuric acid and p-toluene sulfonic acid.

For a typical synthesis, 1.50 g of polyvinyl alcohol was dissolved in 30 ml distilled water and 2.50 ml of tetraethylorthosilicate was added and the mixture was stirred for 10 minutes, then 0.50 g of polyoxometalates was added and refluxed at 70°C for 6 h. The obtained gel was utilized for the further studies. The thickness of the film has been measured by Gaertner ellipsometer (Model 119 XUV) using He-Ne laser 632.8 nm. Photochromic experiments were carried out in sunlight (sep-oct 2002) by coating the composite on glass plate. UV-Visible spectra were obtained by Perkin-Elmer Lambda 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. Electrochemical impedance studies were carried out by using PARSTAT 2263 electrochemical analyzer in the frequency range of 500 kHz-100 Hz. Composite was coated on glassy carbon (BAS 0.07 cm²) and impedance measurements were done in 1.0 M sulphuric acid.

The reduced composite film was employed to reduce the metal precursors and after certain time, the composite gets reoxidised (colorless) and the metal ions are reduced to the zero valent state. In a typical experiment the composite film was placed in a medium containing 10 ml of 10⁻⁴ M H₂PtCl₆ solution and 50 mg Vulcan XC72 carbon for 30 min Reduction of metal ions and reoxidation of polyoxometalates were monitored through UV-visible spectroscopy. Typical preparation of metal supported carbon is given in scheme 1.

Results and discussion

A systematic study was carried out on esterification of methacrylic acid with various alcohols (Ethylene glycol, diethylene glycol, triethylene glycol and polyethylene glycol 400) with solid acids and conventional catalysts. A detailed kinetic study was carried out for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid and silicotungstic acid and results are compared with conventional acids (Table 1). The effect of catalyst concentration, molar ratio, and temperature were studied. The activation energy and preexponential factor were determined and obtained results are compared with silicotungstic acid (Table 2). The equilibrium constant was calculated at various temperatures and reaction enthalpy and entropy were determined.

Table 1. Comparison of catalytic activity and product selectivity over various acid catalysts

Catalyst	Initial rate (mmol ⁻¹ min ⁻¹)	Conversion of Methacrylic acid (%)	Selectivity (%)	
			Diester	Monoester
H ₃ PW ₁₂ O ₄₀	510	83	64	36
H ₄ SiW ₁₂ O ₄₀	320	62.2	76	24
Amberlyst-15*	291	64.7	41	59
PTSA*	187	21.5	18.6	81.4
H ₂ SO ₄ *	71	41	55	45

Reaction conditions: TEG-82.5 mmol, MAA-171 mmol, TCE-55.8 mmol,
Temperature - 368 K, Reaction duration 5 h, Catalyst -3g,
*200 mg of hydroquinone was added.

Table 2. Kinetic and thermodynamic parameters for the esterification of triethyleneglycol with methacrylic acid over heteropolyacids.

Catalyst	Activation energy (E _a) kJmol ⁻¹	Pre-exponential factor (A) lit mol ⁻¹ min ⁻¹	Reaction enthalpy (Δ H°) kJmol ⁻¹	Reaction entropy (Δ S°) JK ⁻¹ mol ⁻¹
H ₃ PW ₁₂ O ₄₀	124.7	3.19 X 10 ¹⁵	135	383
H ₄ SiW ₁₂ O ₄₀	138.4	1.72 X 10 ¹⁷	128	360

Reaction conditions: Catalyst -3g, Reaction temperature - 353-383 K,
Reaction duration - 15-20 h;

The composites render photochromic behaviour when they were exposed to sunlight. The effect of coloring and bleaching was studied for the composites prepared with polyethylene glycol. Various Keggin type polyoxometalates were employed to prepare organic-inorganic composites and the rate of coloring was also studied. The photochromic behavior was studied and compared with composites containing different POMs. The photochromic behavior was correlated with the first redox potential of the POM present in the composite and with that of the charge transfer resistance and Warburg impedance (Table 3). Metal insulator semiconductor device was fabricated with the prepared composite and current – voltage and capacitance – voltage measurements were carried out.

The reduced composites were employed to reduce the methylene blue to leucomethylene blue and activities were compared. Various composites containing different POMs have been employed to reduce the methylene blue and results are given in Table 4 and the rate constant was correlated with first redox potential of POM.

Table 3. 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 M⁶⁺/M⁵⁺ b-taken from literature, c- calculated from optical absorption spectra, d- Maximum absorption IVCT band for 30 min irradiation in sunlight

*- Reduction of V⁵⁺/V⁴⁺

Composite	1st redox potential (V)		k_{obs} M ⁻¹ S ⁻¹
	Reported	observed	
PVA-SiO ₂ -SiW	-0.187	-0.248	456
PVA-SiO ₂ -PW	-0.023	-0.127	228
PVA-SiO ₂ -PMo	0.429	0.351	24

The systematic electrochemical studies were performed over the composite prepared with phosphomolybdic acid. Cyclic Voltammetry studies were carried out at various scan rates and are shown in Fig.1. As the scan rate increases the cathodic and anodic peak currents increase and as well as the cathodic peak potentials shift towards the negative direction and the corresponding anodic peak potentials towards the positive direction. At higher scan rates (>100 mV) the first two anodic peaks are merging together giving rise to a broad peak centered at 320 mV. As the scan rate increases, the peak currents increase indicating that the redox process is surface confined. The cathodic current is found to be proportional to the square root of the scan rate. This shows that the process is a surface phenomenon. This is also further demonstrated by rotating disc experiments, i.e. the rotation speed (10,20,100 and 1000 rpm) has no effect on the peak currents. 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. The electrochemical activities were carried out for the reduction of hydrogen peroxide, nitrite, bromate and iodate with cyclic voltammetry. An amperometric bromate sensor was developed based on phosphomolybdic acid composite. Fig. 2 shows chronoamperograms of bromate sensing on PVA-PMo-SiO₂ of different concentrations range (8.4 X 10⁻³ M to

45.6 X10⁻³ M) at -50 mV in 1 M H₂SO₄. The current increases proportional to the concentration of bromate with sensitivity of 4.5 μA mM⁻¹. The electrode response was linear for BrO₃⁻ within the concentration range of 8.4 X 10⁻⁵ M to 160 X10⁻³ M. The detection limit was 10 X 10⁻⁶ M (signal to noise ratio =2) and the standard deviation of the current to seven repeated cycles were 0.3 and the percentage standard deviation is 3.6%. Glassy carbon electrode freshly coated with the PVA-PMO-SiO₂ has been employed to determine the concentration of bromate species. Interference study was performed by testing the response of the modified electrode to Br⁻ and for a typical experiment 50 fold excess in concentration of Br⁻ was taken and did not interfere in the detection of bromate concentration. For a typical experiment an unknown concentration was determined with an error of less than 3%. This demonstrates that the modified electrode can be employed as disposal bromate sensor.

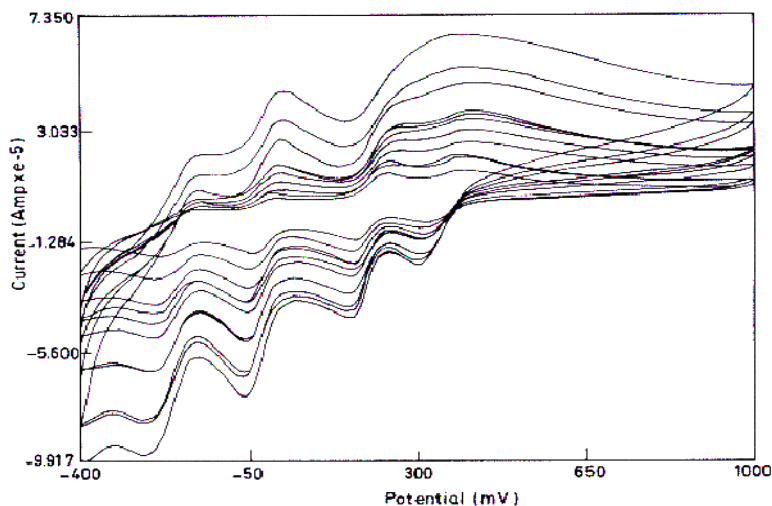


Fig.1. Cyclic voltammograms of PMo-PVA-SiO₂/GC in 1 M sulfuric acid, at different scan rates (from inner to outer: 10, 20, 40, 50, 60, 80, 100, 200, 300 mV s⁻¹, respectively).

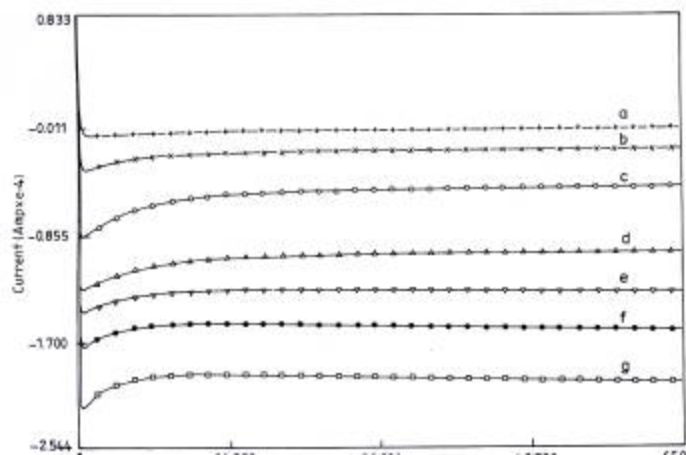


Fig.2. Chronoamperograms for different concentration of bromate ion

The prepared PMo-PVA-SiO₂ organic-inorganic composite was employed for the reduction of nitrite in acidic medium. Fig. 3 shows cyclic voltammograms for the electroreduction of nitrite on PMo-PVA-SiO₂/GC in 1M H₂SO₄ aqueous solutions. On the addition of nitrite, the third reduction peak current increases while the oxidation peak current decreases whereas the first two redox peaks are unchanged, suggesting that the nitrite is reduced by the four and six electron reduced species. The catalytic currents were taken at -150 mV and plotted versus concentration of nitrite. The catalytic efficiency of electroreduction can be expressed as $CAT = [I_{(HPA+NO_2^-)} - I_{HPA}^d / I_{HPA}^d] \times 100$ where $I_{(HPA+NO_2^-)}$ is the peak current for reduction of nitrite with composite and I_{HPA}^d is the corresponding diffusion peak current for the HPA alone.

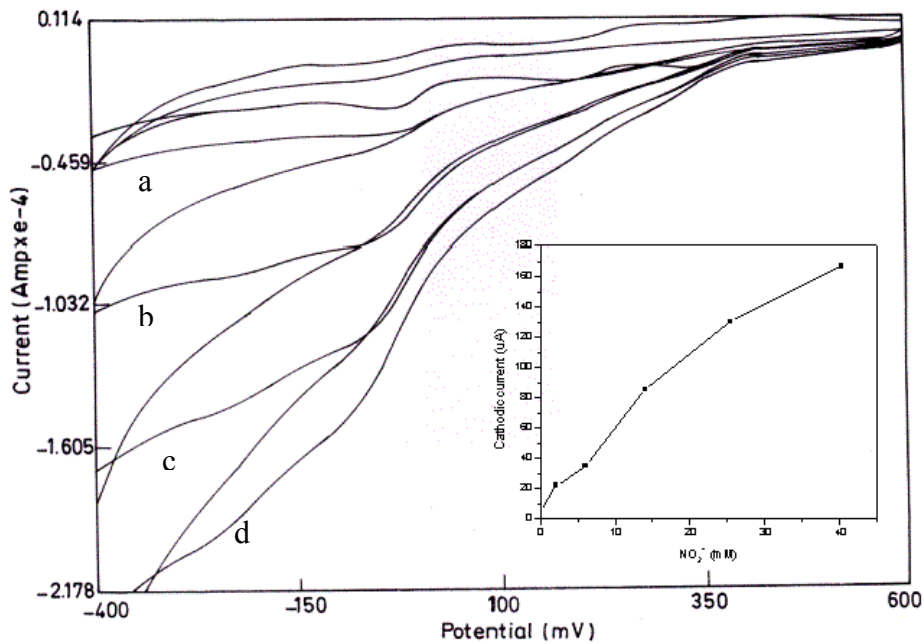


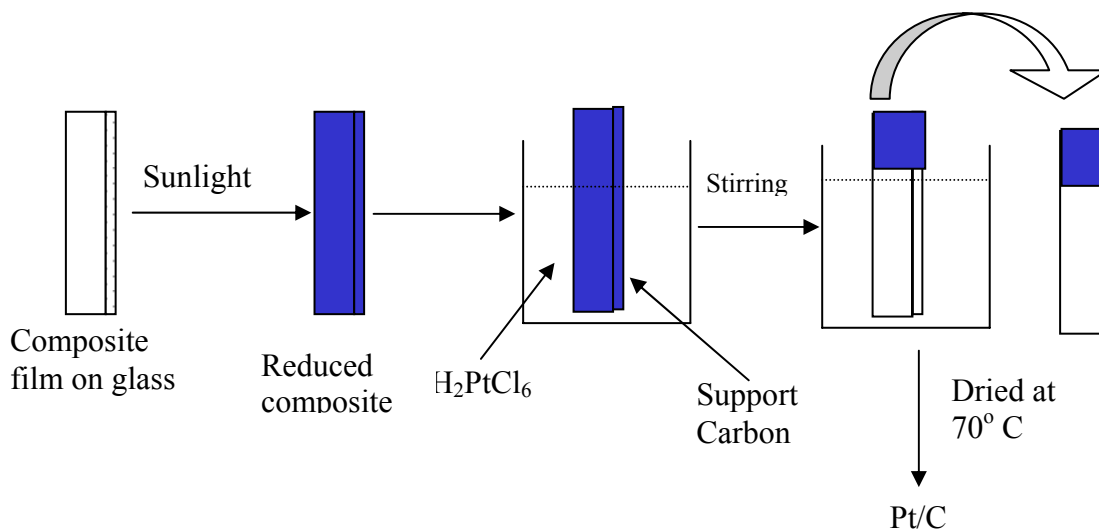
Fig.3. Cyclic voltammograms of PMo-PVA-SiO₂/GC in 1 M sulfuric acid solutions containing a) 2.02, b) 6.05, c) 13.98, d) 25.4 mmol l⁻¹ of NaNO₂. Inset shows the plot of catalytic current at – 150 mV vs. nitrite concentration.

Electrochemical impedance studies were carried out over the composites prepared with different POMs. Dependence of potential and pH of the electrolyte can be evaluated from the EIS study and it alters some features of the impedance data on the electrode surface, e.g., the double layer capacitance, charge transfer resistance and ohmic resistance. The complex impedance can be represented as a sum of real and imaginary impedance components, which are mainly contributed from the resistance and capacitance of the cell. Nyquist plot of composite coated on GC in 1.0 M sulfuric acid shows a depressed 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. The effect of temperature on the charge transfer resistance was evaluated for the composite prepared with silicotungstic acid.

The reduced composite was employed as a nanoreactor to prepare noble metal nanoparticles. The composite film after reduction (blue) was employed to reduce the metal precursors and after certain time, the composite gets reoxidised (colorless) and the metal ions are reduced to the zero valent state. In a typical experiment the reduced composite film was dipped in a medium of 10 ml of 10⁻⁴ M H₂PtCl₆ and 50 mg Vulcan XC72 carbon for 30 min. Reduction of metal ions and reoxidation of polyoxometalates were monitored through UV-visible spectroscopy (Fig.4). Typical preparation of metal supported carbon is given in scheme 1.

Composite	DC potential	R _s (Ω)	R _{ct} (Ω)	C _{dl} (μF)
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PVA-SiO ₂ -MoV	300	112	19.1	43.3
	100	107	16.8	44.5
	-50	100	4.1	137
	-200	96.5	3.4	257
	-250	93.0	1.2	513
PVA-SiO ₂ -PMo	309	153	39.9	19
	400	130	27.9	14.6
	-16	127	11.9	36
	-197	117	2.4	112.7



Scheme 1. Preparation of platinum supported on carbon

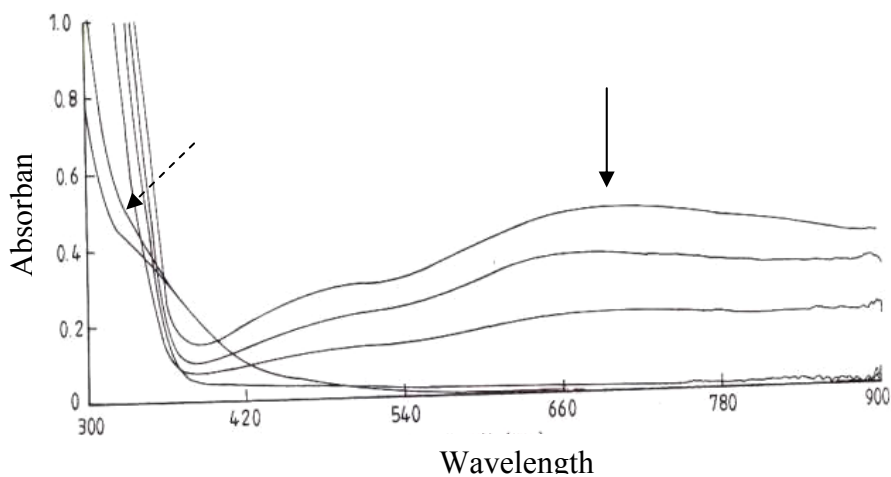


Fig. 4. UV-Visible spectra of the reoxidation of reduced composite and metal particles formation. A broken arrow shows formation of platinum colloids, solid arrows indicates reoxidation of $[SiW_{12}O_{40}]^{6-}$.

In order to assess the shape and size of the metallic particles, electron micrograph was recorded and this is shown in Fig.5. It is clear from the micrographs that the formations of platinum nanoparticles are very facile in the initial stages and the individual particles aggregate into bigger cluster leading to anisotropic structures. The formation of anisotropic platinum nanocrystal at the solid-liquid interface indicates that growth is highly localized, thus leading to considerable growth of the crystals away from the interface forming nanoparticles of triangular, hexagonal, pentagonal, square, fused pentagonal and star like particles as evidenced from the TEM image.

The noble metal supported on carbon was used as the electrode and tested for the oxidation of methanol (relevant for the use as anodes in DMFC) was tested. The data extracted from the cyclic voltametric results are given in Table.2. The points to be noted are a) The oxidation onset potential for methanol is shifted to lower values (80 mV) for electrode prepared with composite reduction method showing that the metallic particles have appropriate shape and symmetry so as to alter the redox behavior of the active component. b) These metallic particles prepared by the composite reduction method show slightly higher activity and also higher electrochemical active surface area as compared to the catalyst prepared by the conventional method.

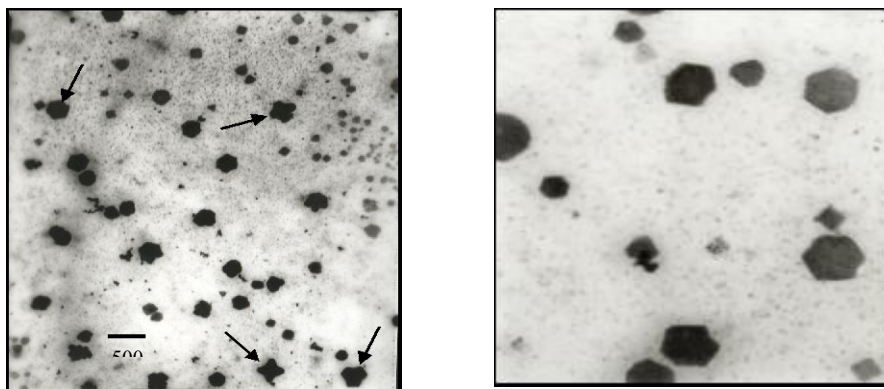


Fig.5 Transmission electron micrographs of platinum nanocrystals prepared by composite reduction method.

Table 2. Comparison of methanol oxidation on Pt/C prepared by different methods

Catalyst	Onset potential (mV)	Anodic peak Potential (mV)	Activity (mA/cm ²)	[Pt] (mg/cm ²)	EAS (m ² /g)
Pt/C (composite)	468	819	16.71	0.071	115
Pt/C (H ₂)	551	892	14.7	0.062	79

EAS- Electrochemical active surface area

Conclusion:

- Environmentally green process was developed for esterification reaction where Keggin polyoxometalates have been used as solid acid catalysts. Among the studied catalysts, phosphotungstic acid exhibits a better catalytic activity for esterification. The developed process is advantageous over conventional processes.
- Tungsten and molybdenum based Keggin POMs have been employed as active components for the preparation of organic-inorganic composites. The prepared composites were characterized by various physico-chemical techniques.
- The composites were found to exhibit photochromism and the studies show that molybdenum based composites exhibit faster photochromic response compared to tungsten based composites. During photochromism, composites undergo reduction and the reduced composites have been employed to bleach the organic dyes. Attempts were made to harness the solar energy through metal insulator semiconductor (MIS) devices, where the composites are active component.
- To understand the interfacial properties of the composites, systematic electrochemical studies were carried out with varying potential, pH and temperature.
- Electrochemical reduction of various inorganic species were done using composites and this reduction was studied by electrochemical studies. Based on this electrochemical reduction, an amperometric sensor was developed for bromate ions.

- An unconventional method for the preparation of platinum nanoparticles using the composites has been developed. These nanoparticles were employed as catalyst for methanol oxidation and it has been found that they show a higher activity than the catalyst prepared by conventional method.

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Proposed contents of thesis

Chapter 1. Introduction

- Chapter 2. Experimental methods
- Chapter 3. Keggin polyoxometalates catalyzed Esterification of Methacrylic acid with various diols and detailed kinetic studies
- Chapter 4. Preparation and characterization of organic-inorganic composite consisting of polyoxometalates
- Chapter 5. Evaluation of photochemical reduction of composite and
- Chapter 6. Electrochemical impedance studies of composites
- Chapter 7. Electrochemical reduction of inorganic species
- Chapter 8. Preparation of platinum nanoparticles/nanorods and exploitation as anodes for methanol oxidation.
- Chapter 9. Summary and conclusion

Visible research output:

1. Esterification using solid acid catalysts, **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, Bull. Catal. Soc. India, 1(1) 2002.
2. Esterification of Triethylene glycol with methacrylic acid over phosphotungstic acid, **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, Bull. Catal. Soc. India, 116 (1) 2002.
3. Esterification by solid acid catalysts - a comparison, **S. Shanmugam**, B. Viswanathan, T.K. Varadarajan, Communicated to J. Mol. Catal: A (2003).
4. Preparation of noble metal supported carbon electrodes using photochemically reduced heteropolyanions in composite films, **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, Communicated to J. Phys. Chem.B. (2003).
5. Electrochemical sensor for nitrite ions based on polyoxometalate containing composites, **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, communicated to J. Electroanalytical Chemistry. (2003).

Conferences attended

1. Synthesis and characterization of transition metal incorporated MCM-48, Subrahmanyam Challapalli, **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, paper presented in CATSYMP-15 & IPCAT-2, National Chemical Laboratory, Pune, January 2001.

2. Polyoxometalate thin film device with Photo/electro chromic effects, **S.Shanmugam**, B. Viswanathan and T.K. Varadarajan, paper presented in the Chemists' Meet, Dec 7-8, IIT madras 2002.
3. Esterification by solid acid catalysts - a comparison, **S.Shanmugam**, B. Viswanathan and T.K. Varadarajan, paper presented in the Catsym-16, Indo-German conference on catalysis at ICT, Hyderabad, Feb 6-8 2003.
4. Inorganic (polyoxometalate) – organic composite – their exploitation as device materials. B. Viswanathan, **S.Shanmugam** and T.K. Varadarajan, Invited talk to be presented in 3rd National symposium & conference on solid-state chemistry and allied areas to be held in IIT Delhi, Dec 4-6, 2003.
5. Nanocrystalline supported noble metal electrocatalysts – An unconventional reduction method. **S. Shanmugam**, B. Viswanathan and T.K. Varadarajan, to be presented in 13th International congress on catalysis, July 11-16, 2004 Paris, France.

Patents filed

1. Nanocomposite for harnessing solar energy, B. Viswanathan, T.K. Varadarajan and **S. Shanmugam**, Indian patent filed, No: 222/MAS/2003.
2. Polyoxometalate based organic-inorganic composite membrane. B.Viswanathan, **S. Shanmugam**, T.K. Varadarajan, Indian Patent (2003) under revision.
3. Bromate sensitive electrode, B.Viswanathan, **S. Shanmugam**, T.K.Varadarajan, under consideration by IC&SR, Dean for Indian patent 2003.