Polyoxmetalates based nano composites: Synthesis and Applications

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CERTIFICATE

This is to certify that **TRUSHA P. KOUTHANKER** of M.Sc.(Analytical Chemistry) has successfully completed dissertation work on the topic ***"POLYOXMETALATES BASED NANO COMPOSITES :SYNTHEIS AND APPLICATIONS"*** in the year 2021-2022, it is further certified that this project is the individual work of the candidate.

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I . Introduction

There been many research work going on, on Polyoxometalates. The recent study says of multifunctional imaging and Photothermal therapy of Polyoxometalates in year 2020[1] (POMs) are a type of inorganic Polyanionic clusters bearing an architecture consisting of oxygen atoms and primary transition metals, such as Ta, Nb, W, V, and Mo in their maximum state of oxidation they significantly consist of different heteroatoms including As, Si, P, and Ge. It is possible to distinguish between the molecular oxides of POMs and most metal Oxides. MO_x coordination polyhedral are called addenda ions structures contain MO_6 octahedral most commonly, but in some cases MO_5 pentahedral and MO_4 tetrahedral elements also exist. One of the p-block elements can be the heteroatom, Xn^+.

Among the basic constructions of POMs, two main forms of POMs are Dawson (X/M =2/18) and Keggin (X/M =1/12).[2] They have electronic application in fields such as gas and chemical sensors, electrochromic displays, capacitors, and electrochemical cells.POMs can be used in different application as biotechnology, medicine, nanotechnology, materials science and catalysis.[3] POMs act like a redox catalyst in many different areas such as analytical chemistry, catalysis and medicine. Such as this methods is adsorption of POM on the electrodes by dip coating, the electrode position of POM on the electrode surface another method involves, trapping the POMs into conducting polymers accumulated on the electrode surface by utilizing the interaction with conducting polymers. Although studies on sensor applications of POM/conducting polymers composite structure in literature are very limited, the constructing of sensors that utilize superior properties of the POM clusters could provide a numerous advantages in term of sensitivity, selectivity and detection limits.

In recent years conductive polymers have been widely used in amperometric sensor applications for determination of some analytes such as glucose, cholesterol, ethanol. For detection of glucose, electroactive monomers containing the free amine functional group such as SNS-NH_2, m(SNS-NH_2),HKCN,(TBT_6-NH_2) have been synthesized and polymerized on the graphite electrode.[4] Nanocomposite materials have received a great deal of attention of the design, fabrication, and functionalities.[4]

In optics, most of POMs are weakly or even not luminescent. However, the incorporation of them into POMs has put some unique optical property for the materials, as the luminescence of rare-earth metal ions is known to be sensitive to the environment. Several special rare-earth atoms have been added in POMs with different structural morphologies.[5]

Due to their properties such as fast, reversible, multi-electron transfer reactions, unique structural and optical properties, Polyoxometalates (POMs) among various electrocatalytic nanoparticles have the ideal characteristic for sensor applications.

A new research area has been made with the excellent performance like high sensitivity, selectivity and low detection limits of glucose sensors obtained by using POM. For the last few years, carbon-based materials have been extensively used as appropriate matrices for POM compounds because of their electrical conductivity, powerful affinity and good chemical stability. Carbon-based material such as MWCNT are intergrated with excellent features originating from the fast redox transitions of the POM compound and are used as supporting material for POM in the development of the sensor.[6]

Polyoxometalates (POMs) were used, together with Chitosan (CS), to obtain hybrid nanoaggregates. Three typical POMs were efficiently assembled into nanoparticles of few hundred nm diameter, featuring entangled ribbons substructure. POMs have been extensively employed as catalysts for the oxidative degradation of pollutants and for the oxidation of organic substrates.

Several different classes of POMs have been reported as efficient antimicrobial agents in a number of different formulations: polyoxotungstates were used to inhibit the growth of *methicillin*-resistant *Staphylococcusaureus*, since they depress the formation of a penicillin-binding protein with low affinity for *b-lactam*[7]

using nanoparticles can lead to better impact and performance.[8]

The building blocks are often very different in terms of their structure, composition, and physical/chemical properties of a nanocomposite.

Potential synergies deriving from their combinations yields multi-functional composite materials with extraordinary versatility and a wide range of potential applications are combined with the diversity of the constituents. Polyoxometalates (POMs), a huge class of metal oxygen clusters of the early transition elements, are some of the most promising building blocks for nanocomposite materials. POMs have an unmatched range of physical and chemical properties that arise from their seemingly endless variety of molecular structures and Sizes. There are additional properties or functionalities of these molecules have been reported including super acidity, photo or electrochromism , magnetism , and ionic conductivity . However, one of the main properties of polyoxometalates and the one most relevant to this review is their unique electrochemical redox behavior. These molecules shows high stability of their oxidation and reduction states and can participate in fast reversible electron transfer reactions.[4]

Polyoxometalates (POMs) have been found to be good end-capping ligands for gold nanoparticles (AuNPs). Polyoxometalates (POMs) are discrete negatively charged inorganic metal oxide clusters with fascinating properties and applications in various research areas ranging from catalysis to medicine and biology. This is because POM clusters represent a great family of compounds which exhibit a wide range of shapes, sizes and topologies. Due to their polyanionic nature, structural diversity and redox properties, POMs also have been used as end-capping ligands for nanoparticle Synthesis.[9]

In recent decades, increasing interest has been devoted to design and fabrication of novel intercalation composite materials with a variety of desirable physical and chemical properties.[10]

At a molecular level with complementary properties nanocomposite hybrid materials represent an excellent approach to disperse two different compounds, and put them to work for a specific application.[11]

II .Table for synthetic details and application of polyoxometalate based nano composites.

Sr. no.	compounds	Synthesis details/ conditions	applications	Reference
1	fCNFs-POM Cs, P, Mo, and O that form the POM, and C from fCNFs. $Cs_3PMo_{12}O_{40}$ (POM)	Reflux2.5MHNO_3/ dry 100◦C 2 h. malic acid(POM) / solid-state method. nanocomposite CNFs 50%w of POM salt/fCNFs sonicated in DMF (dimethyl formamide) 20 min ultrasound bath, of POM and sonicated /20 min/vacuum-fifiltered/ Millipore filter, dried at 100◦C/1 hr.	Hybrid material to work for a specific application	[11]
2	Lcys-SiW_{12} microtubes	----------	Enhancing the redox process between L-cysteine and Alkaline gas chemical sensors developed using Lays-SiW_{12} microtubes.	[4]
3	Hexagonal boron nitride (2D-hBN) nanosheets	------------	Electrochemical behavior of electrodes was studied	[12]
4	f Na_3 $PW_{12}O_{40}$ on TiO_2	$Na_3PW_{12}O_{40}$ on TiO_2 /Keggin type of PW_{11}	Increased the sensor film detection sensitivity and response time photo-induced electron-hole separation,	[2]
5	H_3 $PW_{12}O_{40}$ (PTA) and graphene oxide (GO) nanosheets	---------	The composition of PTA/ rGO film/ excellent electrocatalytic activity for	[2]

			the oxidized dopamine DA,	
6	($H_3PW_{12}O_{40}$, POM)	Synthesized by electro-polymerizing 100 mM pyrrole	Functionalized multi-walled carbon nanotubes (MWCNs) sheets	[6]
7	Hybrid POMs ($(APy)_6[H_2W_{12}O_{40}]$)/carboxylic acid -synthesized SWCNT-based	----------	Amperometric sensor for hydrogen peroxide sensing	[2]
8	Only transition-metal-functionalized Dawson anions (M = Fe^{3+}, Cu^{2+}, Co^{2+}) ($[P_2W_{17}O_{61}M]^{n-}$)	----------	Detection of H_2O_2 . Fe3+ and Cu2+ substituted in POM-doped polypyrrole films	[2]
9	Composition of POM/CP for gas sensing, demonstrating that the nanostructured composition of POM/PPy	------------	Detection of NOx	[2]
10	Dawson anion P_2Mo_{18}	---------	Oxidant to polymerize pyrrole in situ	[2]
11	Keggin type $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]$.$15H_2O$ (Co-POM)	MWCNT synthesized by chemical vapor deposition.	Detection of glucose	[6]
12	POM/$CaCO_3$ nanocomposites	---------	Elastic modulus and tensile strength	[8]
13	$[H_3PW_{12}O_{40}]$	Impregnation	Photosensing of acetone	[13]
14	$[H_3PMo_{12}O_{40}]$	Impregnation	Hydrodeoxygenatioand alkylation of phenolics	[13]
15	$Na_7[PW_{11}O_{39}]$, $K_6Na_2[SiW_{11}O_{39}]$, $K_6Na_2[GeW_{11}O_{39}]$ and $K_6Na[HBW_{11}O_{39}]$	In situ templated sol–gel synthesis	Photocatalytic degradation of malic acid	[13]
16	$[\{Ru^{IV}_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{34})_2]$	Fe_2O_3/FTO Impregnation onto a silylated electrode	Photoanode for water splitting	[13]
17	$[H_3PW_{12}O_{40}]$ and $K_6[CoW_{12}O_{40}]$	$BiVO_4$/FTO Impregnation	Photoanode for water splitting	[13]
18	$[H_3PW_{12}O_{40}$	$BiVO_4$/FTO Impregnation	Photoanode for water splitting	[13]
19	$(C_4H_{10}ON)_{23}[HN(CH_2CH_2OH)_3]_{10}$	SnO_2 (nanorods)/ITO Impregnation	Photoelectrochemical gas sensing of formaldehyde and	[13]

	$[H_2FeIII(CN)_6(\alpha^2\text{-}P_2W_{17}O_{61}CoII)_4]\cdot27H_2O$		methylbenzene detection	
20	$[H_5PMo_{10}V_2O_{40}]$	ZnO (within a MOF) Impregnation	Photoelectrochemical gas sensing devices for formaldehyde	[13]
21	$[H_3PMo_{12}O_{40}]$, $[H_3PW_{12}O_{40}]$, $(NH_4)_3[PMo_{12}O_{40}]$, $(NH_4)_3[PW_{12}O_{40}]$	g-C_3N_4 (mesoporous), graphitic carbon (N-doped) and activated carbon Impregnation	Methanol oxidation	[13]
22	$Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$	g-C_3N_4/FTO Hydrothermal Interaction-Hydroen bonding	Photoelectrochemical CO_2 reduction	[13]
23	$[H_4SiW_{12}O_{40}]$	C_3N_4 (KOH-modified, functionalized) Impregnation Interact-Covalent	Photocatalytic N_2 fixation	[13]
24	CNF and MWCNT	refluxing for 7 h / 2M HNO3 + 0.5 M H2SO4, /sonicated / 50 or 75 wt% /Keggin POM $PMo_{12}O_{40}$ 3(PMo_{12}).	-----------	[4]
25	POMs $(NH_4)_6V_{10}O_{28}$, $H_5PMo_{10}V_2O_{40}$ and $Na_4W_{10}O_{32}$	, NH_4VO_3 for $(NH_4)_6V_{10}O_{28}$, Na_2MoO_4 $2H_2O$ and Na_2HPO_4 $12H_2O$ for $H_5PV_2Mo_{10}O_{40}$, Na_2WO_4 $2H_2O$ for $Na_4W_{10}O_{32}$, sodium hydroxide and glacial acetic acid./Deionized water.	Antimicrobial agent	[7]
26	$TiO_2/PW_{11}Ti$	------------	Excellent acetone gas sensing capabilities	[2]
27	2D-hBN	ultra-violet light +$H_3PW_{12}O_{40}$ (1 mL, 1.0 mM) /2DhBN nanosheets /reduced POM (1: 1)/ mixed for 3.5 h./1.0 mM H_2PtCl_6 /sonicated stirred -45 min dried at 80 °C for 3 h.	Electroanalytical sensor	[12]
28	Au/POM composites	Impregnation	Catalyst	[14]

29	$K_6[P_2W_{17}O_{61}-(PO_2C_{17}H_{26}SH)_2]$	4-((11-(thio)-undecyl)oxy)phenylphosphonic acid and the monolacunary precursor $K_{10}[P_2W_{17}O_{61}]$ were combined by an acid-mediated condensation reaction in acetonitrile	Capping ligand	[15]
30	Ni-CoWO4 (NCW-NPs)	$Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ was dissolved /water /heated at 50 ◦C for 30 min $Na_2WO_4.2H_2O$ /heated/ 30 min centrifuged and washed / product air calcined at 600 ◦C with a heating rate of 10 ◦C/min for 5 h.	------------	[16]
31	Gold nanoparticles (AuNPs)	-----------	Excellent catalytic properties for nitrite oxidation	[17]
32	AuNPs and graphene sulfide (SG) nanocomposites	Graphene sulfide was deposition on the glassy carbon electrode and then AuNPs were adsorbed on the electrode by electrostatic attraction	Detect nitrite concentration	[17]
33	Nano composites ($Ag-Fe_2O_3$)		Catalysis for water oxidation and for the oxidation of carbon monoxide	[18]
34	Keggin-type polyoxometalates (POMs) $[PW_{12}O_{40}]^{3-}$, $[TiW_{11}CoO_{40}]^{7-}$, and $[Ti_2PW_{10}O_{40}]^{7-}$	In virto synthesis	Anticancer treatment	[19]
35	$K_6CoW_{12}O_{40}$	Anchored on TiO2 through immobilizing in MIL-101	Prevent agglomeration and calcining	[20]

III . Brief about the synthesis and applications mentioned above

1.Hybrid material of nano composites

They prepared nanocomposite hybrid materials based on previously oxidized carbon nanofibers (fCNFs) and polyoxometalates (POM) in year 2007. They analyzed fCNFs by XRD and TEM where observed that the presence of carbon nanocoils, and the removal of amorphous carbon and thinfibers. The nanocomposite hybrid sample (fCNFs-POM) microstructure was observed and analyses revealed the presence of Cs, P, Mo, and O that form the POM, and C from fCNFs. Confirmation shows the intact presence of both components that conform the hybrid, where their interaction was not evident, so the presume a chemisorption of POM onto fCNFs through carbonyl groups. Finally, solid-state symmetric super capacitor cells were assembled, showing higher capacitance values (120mF/g) for the cell with hybrid electrodes, revealing the pseudocapacitive contribution of POM aside from the double layer of CNFs.CNFs were functionalized in order to oxidize the surface and create carbonyl groups by means of a reflux procedure. $Cs_3PMo_{12}O_{40}$ (POM) was synthesized using a solid-state [11]

2.Nano composite based sensors(Keggin type $K_7[CoIIICoII(H_2O)W_{11}O_{39}].15H_2O$ (Co-POM))

They have studied analytical performance of ($K_7[CoIIICoII(H_2O)W_{11}O_{39}].15H_2O$)/MWCNT composite for detection of glucose. Co-POM compound consisting of specific mixed-valence Co (III) and Co (II) structures is an influential for non-enzymatic sensor with high electrocatalytic activity toward the detection of glucose,there are many glucose sensor application studies have been published. However no paper has been reported on glucose sensing, using mixed-valence Co(III) and Co(II)$K_7[CoIIICoII(H_2O)W_{11}O39].15H_2O$.

When the structural properties of Co-POM are examined, it is manifests that, the oxidation process of central CoIII and the presence of the environmental CoII are the two main components that enables Co-POM to have considerable stability and catalytic activity. Accordingly, CoPOM as active sensing materials is appropriate to carbon based prodused electrochemical non-enzymatic glucose sensor. Due to synergistic effect of Co-POM and MWCNT, obtained novel sensor platform demonstrated short response time, good performance, high sensitivity and selectivity with linear range.[6]

3.**Antimicrobial agent [** $(NH_4)_6V_{10}O_{28}$, $H_5PMo_{10}V_2O_{40}$ and $NA_4W_{10}O_{32}$ **]**

Polyoxometalates (POMs) were used, together with chitosan (CS), to obtain hybrid nanoaggregates. Three representative POMs were efficiently assembled into nanoparticles of few hundred nm diameter, featuring entangled ribbons substructure. The assemblies were characterized in solution by UV–Vis spectroscopy in order to establish suitable preparation and stability conditions, dynamic light scattering and f-potential. The nanoparticles were tested against *E. coli* in aqueous solution, showing a synergic activity of the heteropolyacid$H_5PMo_{10}V_2O_{40}$ and CS. For such components, a highly porous and antibacterial film was obtained upon lyophilisation of the colloidal mixture.

Low molecular weight CS (40–90 kDa), TPP, hydroquinone (HQ) and b-nicotinamide adenine dinucleotide. POMs $(NH_4)_6V_{10}O_{28}$, $H_5PMo_{10}V_2O_{40}$ and $Na_4W_{10}O_{32}$ were synthesized. Starting materials for POMs synthesis, NH_4VO_3 for $(NH_4)_6V_{10}O_{28}$, $Na_2MoO_42H_2O$ and $Na_2HPO_412H_2O$ for $H_5PV_2Mo_{10}O_{40}$, $Na_2WO_42H_2O$ for $Na_4W_{10}O_{32}$, sodium hydroxide and glacial acetic acid . Mueller–Hinton broth (OXOID), *agar–agar*

(Sigma–Aldrich) and bacteriological peptone (OXOID) were used to carry out the antibacterial activity[7] tests. *E. coli* (ATCC 25922) was chosen as the test microorganism. Deionized water was produced by a Sartorius Arium water purification system.

4. Short review of gold nanoparticle

The role of polyoxometalates (POMs) in the synthesis and stabilization of gold nanoparticles (Au NPs)
is reviewed in light of many of the recent developments. The vitality of these hybrid materials is discussed with many examples of POMs and different synthesis techniques. Also, applications of these newly emerging hybrid materials in many different fields such as electrocatalysis, photocatalysis, biomass catalysis, oxidation of alkenes, bio-sensing, and medicinal use are highlighted. Limitations in these applications are indicated, and areas of future applications that could be explored in these wide ranging hybrid materials are described.

In recent years, the study of nanoparticles (NPs) has been a vast area of research owing to size-dependent chemical and physical properties which allow tuning of NP properties. Techniques for the synthesis of nanomaterials with a preset size, shape, and chemistry are the focus of many research groups. Metal NPs possess many interesting spectroscopic, electronic, optical, magnetic, catalytic, and chemical characteristics that result from their small size and high surface/volume ratio. In addition, the control of NP size and composition influences electronic structure and catalytic properties.

NPs are prepared through self-assembly into ordered and stable organizations mediated by surfactants, ligands, and other different factors that are not always intuitive but are critical to reproducibility. Different hydrophobic compounds like alkylamines, alkanethiols, and cationic surfactants have been employed to induce NPs toward self organization, and different geometrical forms of gold nanoparticles (Au NPs) have been synthesized that have numerous applications for devices such as optical gratings, antireflective surface coatings, sensing, biodiagnostics, surface-enhanced Raman spectroscopy, and DNA detection .

The different forms of Au NPs are acknowledged as effective catalysts for industrially vital reactions including oxidations and hydrogenations and also different biological and biomedical applications. Capability of the Au NPs as oxidation catalysts highly depends upon size with smaller NPs as better catalysts. This observation makes the inhibition of sintering or aggregation of NPs an important objective, and much work has been devoted to NP supports as well as the support's influence on activity and recyclability. Polyoxometalates (POMs) possess high potential as supports for NPs as their stability is enhanced by high charge, as well as avoiding sintering of the NPs . However, there is little research to the point of mechanism for anions (especially POMs) in stabilizing and tuning the properties of Au NPs are concerned .[1]

5. Synthesis procedure of polyoxymethylene(POM)Silver (Ag) nanocomposites.

Materials

Polyoxymethylene (POM) was obtained by Yunnan, Yuntianhua Co., Ltd., Shanghai, China. The melt flow index of POM is 2.5 g/10 min at 230 ◦C with a standard weight of 2.16 kg, and the density of POM is 1.40 g/cm3. Silver nitrate (99.8%), oleic acid (99%), anhydrous ethanol (99.7%), n-propylamine (98%), and ascorbic acid (99.7%) .

6. **Synthesis of Ag Nanoparticles**

The silver nitrate was reduced by ascorbic acid to prepare Ag nanoparticles, under the stability of oleic acid and n-propylamine. Therefore, the as-synthesized Ag nanoparticles were coated with a monolayer of surfactants consisting of oleic acid and the n-propylamine. The detailed preparation process and characterization of the Ag nanoparticles can be found in a previously published papers.

Preparation of POM/Ag Nanocomposites

By melting processing method in a torque rheometer POM/Ag nanocomposites were prepared.

The mixing process has continued for 10 min at 190 ◦C, and the roller speed was 60 rpm. In addition,

POM and Ag nanoparticles were both dried in vacuum oven overnight at 80 ◦C before melt processing to

get rid of moisture.

It was found that Ag nanoparticles easily aggregated in POM. In addition, when the content of Ag nanoparticles was low (≤1 wt%), it was difficult to observe larger-size clusters of Ag nanoparticles, and most of

the clusters of Ag nanoparticles were smaller than 200 nm. Simultaneously, the clusters of Ag nanoparticles separated from each other. However, when the content of Ag nanoparticles increased to 2 wt%, it easily formed the larger-size clusters of Ag nanoparticles (≥200 nm). This result proved that when the content of Ag nanoparticles was low (≤1 wt%), the monolayer surfactants on the surface of Ag nanoparticles had a strong effect and passivated the surface of Ag nanoparticles, which effectively inhibited the large-scale agglomeration of

Ag nanoparticles. However, when the content of Ag nanoparticles reached 2 wt%, they would be easily aggregated together due to monolayer surfactants of Ag nanoparticles with weak effect, which resulted in poor dispersion of Ag nanoparticles in POM. This result was consistent with the analysis result of SEM images of POM/Ag nanocomposites in theprevious paper [13]. Synthetic procedure is given in te figure 1. Below.

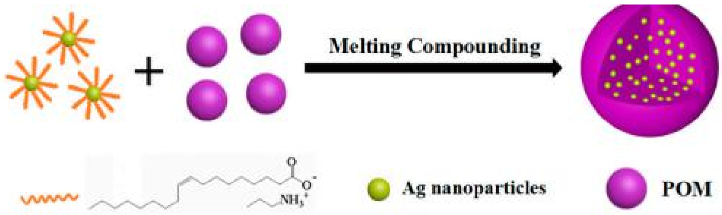

Figure 1. Synthesis procedure of polyoxymethylene (POM)/silver (Ag) nanocomposites.

7. Sensor based on platinum Nanoparticle

In this study, a novel electrochemical method as a conductive voltammetric sensor for determination of N-hy-droxysuccinimide was developed The N-hydroxysuccinimide sensor was achieved by carbon paste electrode (CPE) amplified with tri-component nanohybrid composite (Platinum nanoparticle/Polyoxometalate /Two dimensional hexagonal boron nitride nanosheets) (PtNPs/POM/2D-hBN) and 1-hexyl-3-methylimidazolium chloride (HMICl) as conductive mediators. A significant decrease (110mV) in the oxidation over voltage and significant increased (2.4times) in the current of the N-hydroxysuccinimide were observed using HMICl-PtNPs/POM/2D-hBN/POMBNS/CPE. Further more, the HMICl-PtNPs/POM/2D-hBN/POMBNS/CPE exhibited a good linearity from 0.1 to 300 µM and detection limit 60 nM for determination of N-hydroxysuccinimide. The capability to promote the electron exchange between N-hydroxysuccinimide and the HMICl-PtNPs/POM/2D-hBN/POMBNS/CPE exhibited a novel analytical strategy for fabrication of water pollutant sensor..[12]

Polymer-dispersed liquid crystals (PDLCs) are widely used in electrically switchable windows. Their valuable advantages such as low operating voltage, high contrast ratio, requiring no extra optical elements (i.e. polarizer), quick electro optical response, no leakage of materials, simple fabrication, low-cost production and ease of processing make them more popular over other display technologies.[21]

IV. Discussion and Conclusion

The developments in nanostructured particles and nanocomposite materials have a large impact on our day today life applications, the present study provide overview of nanocomposite applications and method of synthesis. In this review, we have briefly described some of the previous studies, which provided different types of nanoparticles with advantages therein to prepare the nanostructured particles.

From the above data we can say that there are more application of sensors of nanocomposite materials. The hybrid materials are also can be the topic of discussion, there could be many applications. This review shows there is wide applications for the use of POM-based composites as sensors. The future growth of POM/nanocarbon compositions is not limited. It is also seen that nanocoposites are widely utilized in the fabrication of biomaterials and nanomaterials of which many applications have been explored and developed in fields such as material science, biology, medicine and nanotechnology. finally we conclude that by this review, detection sensors are most studied in nanocomposite of POMs and has a wide application and different methods ; Impregnation , deposition, electro polymerization, Pyrolysis ,sol-gel etc .and more applications to add.

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