Crystal Engineering of nano-architecture from Giant Polyoxometalate: Synthesis and its characterization

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Abstract

Polyoxometalate cluster anions (POMs) control formation and morphology, and serve as protecting ligands, for structurally and compositionally diverse nanostructures. Utilizing new experimental approaches and gradual understanding of the underlying chemical processes, a great advancement is recorded in the self-assembly of inorganic and metal–organic compounds at a very fast pace over the last decades. Exploitation of unveiled information originating from initial experimental observations has sparked the development of new families of compounds with unique structural characteristics and functionalities. The first part of this research article summarizes the one pot-synthetic procedure of 3d transition metal incorporated Keggin hetero polyacid using basic chemicals without using any other derived POM as starting material. In the second part of the script, we represent use of POMs as protecting ligands for stabilizing metal nanoparticles, as well as their use as templates for the preparation of new inorganic materials. Not only that, new information concerning the structure of POM-protected metal nanoparticles is systematically developed. This detailed information is obtained by the combined use of scanning and transmission electron microscopy (SEM &TEM), FTIR spectroscopy along with thermogravimetric analysis which provides a new perspective on the formation and structure of POM-decorated nanoparticles. The purpose of this research article is not the exhaustive discussion of the broad field of inorganic and metal–organic chemical systems, but to focus on a novel representative example which demonstrates the implementation of new synthetic approach and design.

Keywords

Polyoxometalates, Keggin, Solvothermal synthesis, POM motivated nano particles

Introduction

Polyoxometalates or POMs are metal–oxygen cluster-anions [1] which constitute a large and rapidly growing class of discrete molecular structures with applications ranging from catalysis [2–3] to functional materials. [4] These are formed by metals (addenda atoms) such as tungsten, molybdenum and vanadium in their higher oxidation state. POMs are composed of condensed metal-oxygen $\{MO_x\}$ polyhedral (x = 4 to 7). POMs can be formed mainly by vanadium, molybdenum and tungsten due to their appropriate ionic size and their ability to act as good acceptors of oxygen's electrons. The fundamental requirements for a transition metal to serve as addenda are the ability to adopt a variety of

coordination modes (mainly 4 to 6) in response to acidification, have high positive charge, and are capable of p–d interactions. However, there are a few examples that deviate from this set of rules, as reported by Kortz et al (2010), where the authors demonstrated the preparation and characterization of metal oxides made of noble metals [5,6] in the presence of supporting organic or inorganic ligands. The most commonly studied POM is the heteropolyacid (HPA) best represented by Keggin. [7] The arrangement of twelve metal atoms (e.g. M = V, Mo, W) around one single heteroatom (e.g. X= Si, P, As etc.) forms a Keggin based POM, where X/M=1/12. In the Keggin structure, the heteroatom X is bonded to four oxygen atoms to form a tetrahedron and each metal atom is linked to six oxygen atoms to form octahedral. The assembly of three octahedra yields a trimetallic group M_3O_{13} which are connected to others and the common site of M_3O_{13} is linked to the central heteroatom X. In summary, there are four M_3O_{13} gathered around the central heteroatom X to form $(XO_4)M_{12}O_{36}$. In this paper, the synthesis of a mixed addenda Keggin type heteropolyacid (HPA) will be described and characterized. HPA typically has low surface area and high solubility, which makes it challenging to use them as catalytic materials in aqueous media. The cooperative chemistry of polyoxometalates (POMs) and metal nanoparticles (NPs) still remains a relatively unexplored area of nano science despite showing remarkable potential and application in fields as diverse as catalysis and medicine. Titanium dioxide (TiO_2) nanoparticles (NPs) are manufactured worldwide in large quantities for use in a wide range of applications. To make it more economically viable, different strategies are adopted. Keeping in mind the recent developments in the synthesis of nanoparticles using polyoxometalates (POMs), we have tried to bring a new synthetic line for producing TiO_2 - nanoparticles. Many procedures can be foreseen to fabricate POM-based nanostructures, but solvothermal synthesis of nano oxides is a novel method till date. Not only this, numerous examples of POM-protected metal nanoparticles syntheses and reactions can now be found in the literature, [8] but the use of Keggin POMs to prepare nano-scale analogs of binary inorganic materials like metal-oxides is completely a new pathway which can be considered as the latest development. In short, solvothermal synthetic method of nano materials from gigantic POMs is undoubtedly a pioneer work when nano synthesis is concerned.

Experimental

Materials and methods

Chemicals were readily available from commercial sources and were used as received without further purification. Disodium hydrogen phosphate (Na_2HPO_4), sodium vanadate ($NaVO_3$), sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$), titanium tetraisopropoxide Ti $[OCH (Me)_2]_4$ were purchased from Sigma-Aldrich and were used as received. Deionized water was used as the solvent.

Synthesis of (PVMA) phosphovanado molybdic acid $H_4[PVMo_{11}O_{40}]$ (1)

$NaVO_3$ (6.1 g, 0.050 mol) was dissolved in boiling water (100 mL) and then mixed with another 100 mL aqueous solution of Na_2HPO_4 (7.1 g, 0.050 mol). The mixture was cooled prior acidification by 5 mL concentrated sulfuric acid H_2SO_4 (5 mL) which   gives rise to a red color solution. A solution of $Na_2MoO_4 \cdot 2H_2O$ (133 g, 0.55 mol) was dissolved in 200 mL water in a different beaker and was added to the mixture. 85 mL conc. H_2SO_4 was then added drop-wise with vigorous stirring of the solution. Solution color transited from dark red to lighter red upon addition of the acid. The aqueous mixture was allowed to cool before being extracted with diethyl ether (400 mL). The heteropoly etherate was

present in the middle layer. After separation was achieved, a stream of air was passed through the heteropoly etherate layer to free it of diethyl ether. The orange solid residue was dissolved in appropriate amount of water to obtain a saturated solution. The solution was further concentrated in a vacuum desiccator over concentrated sulfuric acid to allow for crystallization of the product. The orange crystals of phosphovanado molybdic acid (PVMA) were filtered, collected and left to air dry.

Solvothermal synthesis of $H_4[PVMo_{11}O_{40}]$ stabilized TiO_2 nano particles (TiO_2-PVMA)

The synthesis of POM modified nano TiO_2 was carried out as follows: 0.2 g of $H_4[PVMo_{11}O_{40}]$ (PVMA) was dissolved in 1 mL ultrapure water. 9 mL of concentrated HCl (37%, 12M) was added and charged to a 45 mL Teflon sleeve. 0.6 mL of titanium tetra isopropoxide $Ti[OCH(Me)_2]_4$ (TTIP) was mixed with 19.4 mL of hexane and this mixture was carefully added into the Teflon without mixing with the aqueous layer. The Teflon was then sealed in a stainless-steel autoclave and heated at 170 °C for 24 h. The resulting TiO_2 was collected after cooling and washed 3 times with a mixture of 10 mL of water and ethanol (50% v/v) and dried in a vacuum oven at 40 °C for 24 h. This customized TiO_2 was dispersed into an absolute ethanol solution containing 3-Aminopropyl triethoxysilane (APTES) (1.5 % v/v) and magnetically stirred for 24 h for surface aminization. APTES is used here for covalent attaching of organic films to metal oxide titania TiO_2. It is then centrifuged and washed with 10 mL ethanol 3 times before being dried in a freeze dryer for 24h. The surface-aminated $TiO_2$was then dispersed into 15 mL absolute ethanol containing 0.2 g of $H_4[PVMo_{11}O_{40}]$ and stirred for 24 h. The resulting POM based TiO_2 was washed until the yellowish coloration of $H_4[PVMo_{11}O_{40}]$ was no longer observable and then freeze dried for 24 h before used for further application.

Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Spectral measurements were made in a Varian Cary 1E UV-visible spectrophotometer with 1.00 cm glass cells. IR (400–4000 cm^{-1}) was recorded in KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. The morphology and elemental analysis of the as-synthesized TiO_2 and PVMA modified material was analyzed by a field emission scanning electron microscope (FESEM JEOL-7600F). Powder XRD patterns were obtained by Bruker D8 advance diffractometer with monochromatic CuKα (λ = 1.5418 Å) with step size of 0.02° s^{-1}. Thermo gravimetric analysis (TGA) was performed using TA instrument TGA Q500. Temperature was ramped up from room temperature to 100 °C at a rate of 5 °C min^{-1}, held isothermally at 100 °C for 15 mins, ramped up to 200 °C at a rate of 10 °C min^{-1}. It is then finally and ramped up to 500 °C at 10 °C min^{-1}.). Sample was dispersed in ethanol and dripped onto a copper grid with holey carbon support to study the local structure using a transmission electron microscope (TEM JEOL-2100F) at an accelerating voltage of 200 kV with a point to point resolution of 1.9 Å.

Results and discussion

Vibrational and UV-vis- spectra

The synthesis of Keggin type phosphovanadomolybdic acid (PVMA) lays the foundation for the preparation and modification of materials. Using FTIR spectroscopy, the characteristic bonding in the PVMA were identified and presented in Figure 1. The characteristic peaks of the Keggin structure can be found in the range of 1100 – 700 $cm^{-1.}$.

The main features are from P–O_a bonding of the centre tetrahedral, M–O_b–M corner sharing bridging oxygen, M–O_c–M edge sharing bridging oxygen and M=O_t terminal oxygen (where M = Mo or V). The characteristic bands of P–O_a, M=O_d and M–O_b–M in PVMA undergoes red shift with increase in vanadium substitution, which likely originate from the weaker metal oxygen bond due to vanadium (+5) being in a lower oxidation state that molybdenum (+6). Detailed study is illustrated below.
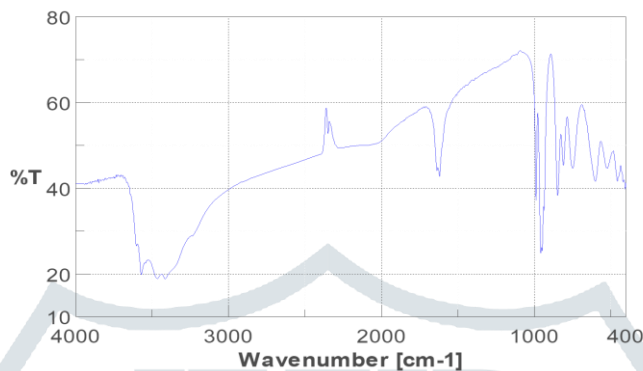

Fig-1: FTIR spectrum of complex 1, taken as KBr pellet

The IR spectra of compound (1) display the characteristic features of a Keggin-type structure as shown in Fig.1. Five strong vibration bands are indeed observed for, ν (V=O), and ν (V–O–V) at 1104.8, 1060, 957, 889, and 796.5 cm^{-1}. Apart from these, the IR spectrum of the title compound has some characteristic bands for the polyoxoanion at 510, 940, 878, 770 and 1320 cm^{-1} which are attributed to ν (V=O_t terminal), ν (V–O_b-V) octahedral edge sharing) and ν (V–O_c-V octahedral corner sharing) respectively. [9] In addition, a strong broad peak observed at 3350 cm^{-1} is assigned to ν (−OH) absorption along with the hydrogen bonds which proves the presence of lattice water. Again, from the UV-visible spectral point of view, it has been observed that the formation of POM stabilized TiO$_2$ nano-composites resulted in a red-shift as shown in UV-vis diffuse reflectance spectra of TiO$_2$, H$_4$ [PVMo$_{11}$O$_{40}$] (PVMA) and TiO$_2$-PVMA composite.
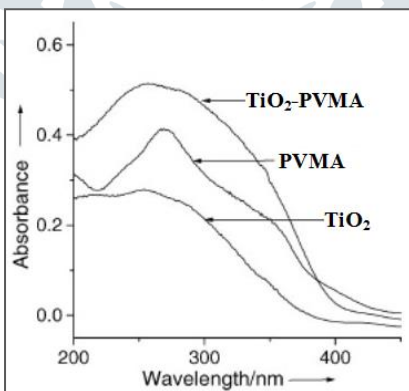

Fig-2: Comparative study of UV-vis spectra of TiO₂, PVMA and TiO₂-PVMA composite

Crystal structure

Polyoxometalates generally form ionic crystals [10] which can accommodate lattice water of crystallization and counteraction within the large interstices formed due to the size of the heteropolyanion and the requirement due to their huge ionic charge. The removal of water is easy and reversible by simple increment of temperature up to 150°C. Thus lattice water plays an important part in the crystal structure and packing of the heteropolyanion. A good example will

be the different crystallographic space groups exhibited by 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$). In the most highly hydrated state $H_3PW_{12}O_{40} \cdot 29H_2O$, the crystal structure has a cubic Fd3m space group. Further decrease in lattice water gives $H_3PW_{12}O_{40} \cdot 21H_2O$ with orthorhombic Pcca space group. [11] Therefore, variation in the structure of polyoxometalate makes it difficult to obtain highly reproducible X-ray crystallographic information especially when powdered material is used instead of single crystal samples. That is why we prepared XRD sample mainly from single crystals. The powder XRD patterns of PVMA exhibits the diffraction peaks which show that the PVMA prepared consist of mainly a single crystalline phase. The lattice parameters of the crystals are close in values with $H_4[PVMo_{11}O_{40}]$ having a=12.862Å and c=18.292 Å, with the incorporation of increasing number of vanadium atoms in place of molybdenum, the influence on the XRD peak position and intensity is minute. The small reflection peaks appearing in the diffraction patterns of PVMA are common, especially in powdered samples due to loss of water molecules which easily influence the crystal structure of PVMA. Our aim was to attain morphological control along with PVMA incorporation in the TiO_2 crystals. The combined XRD diffractogram given below indicates that desired incorporation of PVMA in the TiO_2 crystal lattice via electrostatic interaction.
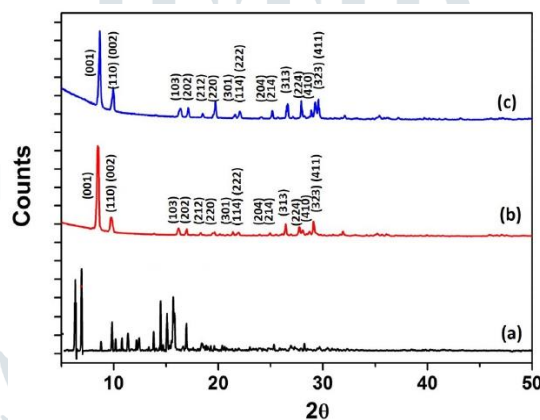

Fig-3: XRD diffractogram of (a) TiO₂, (b) PVMA and (c) TiO₂–PVMA with the characteristic reflection peaks of the Keggin structure labeled.

Thermo gravimetric analysis

Figure 2 shows the thermo gravimetric weight loss profile of PVMA. The crystal effloresces slowly even at room temperature and the large amount of water of crystallization which are loosely attached are easily lost as temperature increases. It can be seen that the sample experiences major weight loss as the temperature increases up to 100 °C. The temperature setting for the analysis was made to hold at 100°C and 200°C so as to remove the water of crystallization completely. The 2nd derivative weight loss peak appearing around 300°C is associated with the removal of the structural water molecules holding the secondary structure of the PVMAs. The calculation from the overall weight loss reveals that water of crystallization and chemical formula of the PVM prepared to be $H_4[PMo_{11}VO_{40}] \cdot 32H_2O$.
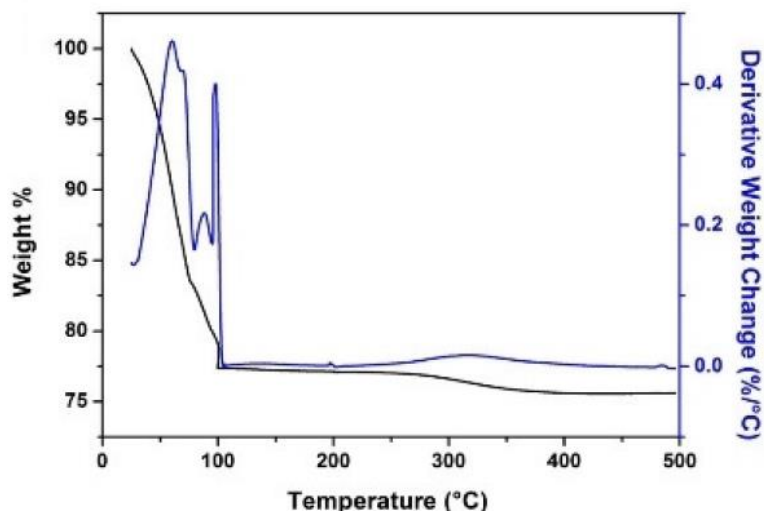
Fig-4: Thermo gravimetric analysis weight loss profile of complex 1

Characterization of TiO₂-PVMA

With the aim of heterogenizing PVMA via immobilization, one-pot solvothermal synthesis was designed to incorporate H_4 [$PVMo_{11}O_{40}$] into the crystal lattice of TiO_2. The desired outcome was to attain morphological control along with PVMA incorporation in the TiO_2 crystals for the final product which shows nano-plate morphology. In order to improve the coupling of PVMA with the TiO_2 surface, 3-Aminopropyl triethoxysilane APTES was employed as a coupling agent. The immobilization of PVMA on TiO_2 using a coupling agent increases the relevant elements of PVMA detected, but does not lead to formation of detectable PVMA crystalline phase. Nisar et al [12] showed that the main influence on post-modification was a decrease in the reflection intensity, which can be attributed to the reduction in reflected X-ray due to the surface modification. Further attempts to reduce the number of steps required in synthesis by introducing APTES in the organic phase during synthesis for surface modification proved to be futile and resulted in poor morphological control. This reveals that polyoxometalates are capable of stabilizing and protecting metal nanoparticles (NP) during their formation. [13] Figure 3(a) shows the SEM micrograph and (b) shows the TEM images of TiO_2 NP. Figure 3(b) also shows that the nano-plate is highly crystalline with clearly observable lattice.
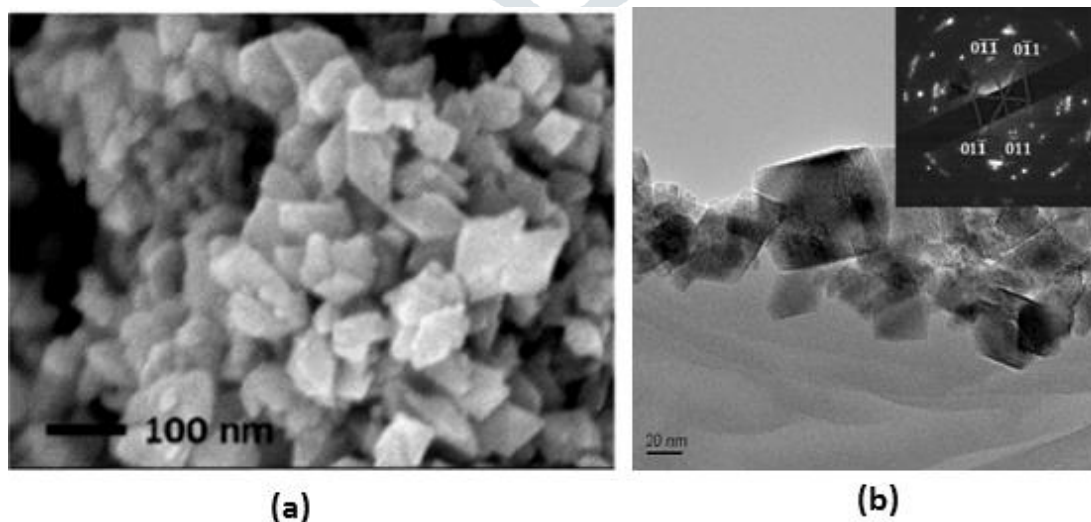

Fig-5: a) SEM micrograph of PVMA modified TiO₂ b) TEM micrograph of TiO₂ nanoparticles

Conclusion

There is increasing interest and need to develop a deeper understanding of the nature and behavior of nanoparticles in the environment. This is driven by the increased use of engineered nanoparticles and the increased pressure to commercialize this growing technology. Banerjee et al [14] in this regard tried a new doped nano crystal synthesis in accordance to green chemistry. Keeping in mind the greener side of technology, in this review we want to emphasize on a new synthetic methodology of nanoparticles from gigantic polyoxometalates. It sounds weird but we have used POM as a precursor for making nano through a solvothermal synthesis. The basic one-pot synthesis of polyoxometalate via acid condensation reaction followed by etherate extraction is neatly described. The immobilization of PVMA on TiO_2 NP described in this article establishes foundation knowledge and understanding of such surface modification process which also allows better consideration of the parameters in the preparation of this kind of nano-architecture. [15] In short, we have penned our investigation which is done to optimize the surface modification using high surface area titanium oxide as solid support for effective immobilization of PVMA.

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