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Short communication

Aerobic photoxidation of sulfides using unique hybrid polyoxometalate under visible light

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Keywords: Polyoxometalate Hybrid compounds Photocatalyst Aerobic oxidation Sulfide oxidation	A unique hybrid Polyoxometalate was synthesized, which can absorb visible light and perform photocatalytic activity. This Organic-Inorganic hybrid material was synthesized through attaching the organotin compound to the vacant polyoxometalate. Interestingly, this hybridization brought an outstanding decrement in the polyoxometalate band gap and turned this hybrid polyoxometalate to a photocatalytic compound, which can conduct catalytic reactions under visible light. In this line, we devised photoxidation of sulfides using this photocatalyst and under O ₂ atmosphere as a sustainable and environmental friendly oxidant. Various kinds of sulfides were investigated under optimum reaction conditions and the corresponding sulfoxide products were synthesized in good to high yields.

1. Introduction

Polyoxometalates (POMs) are a large class of metal-oxygen clusters, which have shown great potential to be utilized in many applications. These nanoscale inorganic compounds have interesting structures and unique properties, which have been put them under vast attention. Having outstanding characteristics, bring diverse applications for these compounds in many fields such as catalysis, materials science, life science, solar cells, medicine, molecular magnetism and polymers [1–5].

Besides the diversity in the parent structures of POMs, these compounds are capable to be attached to the various organic moieties to make hybrid-POM structures. Hybridization of POMs with different organic groups and structures through covalent bond can boost the characteristics of POMs in efficient way. Following this route, it is achieved functionalized-POMs that are more capable to be used in many applications [6–8].

Among these characteristics, photonic behavior of POMs has been under more consideration in recent years [9,10]. Interestingly, this behavior can vastly be influenced by hybridization. Therefore, with sensitizing POMs through hybridization we can improve and enhance the photonic properties of these compounds.

One of these improvements can be monitored through the ability of light absorption. As POMs can absorb specific wavelengths in the UV

region, there is a need to expand this range of absorption and shift it to visible region to have POMs with more efficient photonic behavior. This improvement can be operated with making hybrid-POM structures. Introducing an appropriate organic moiety to the POMs structure allows us to obtain hybrid-POMs, which have the lower band gap and ability of absorbing visible light that cause to show photonic behavior under higher wavelengths. Attractively, this modification can provide lots of enchanting capabilities for these compounds and impressively be utilized in the POMs photocatalytic applications [11,12].

Sulfoxides are the important and vast-used fragments in organic synthesis. These compounds can be obtained by oxidation of Sulfides and have shown that can be utilized in various fields such as medicine, polymer sciences, catalysis, synthesis, as well as many pharmaceuticals and antiseptics products [13,14]. Moreover, as sulfides are considered as one of the major air pollutants, desulfurization of fuels is a high demand and necessary process, which is so important from environmental and health aspects. Oxidation of sulfides proposes an effective and benign method that desulfurizes fuels along with removal of the potential of polluting in these compounds [15,16].

For achieving this aim, one of the effective and promising methods for desulfurization that is called oxidative desulfurization has been vastly utilized [17]. Interestingly, Oxidation of Sulfides Using photoxidation pathways would be a mild and useful method for producing

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desired oxidized organic products. Furthermore, in the sulfide oxidation process, the mild photoxidation path allows us to convert the sulfide compounds to the sulfoxides, which are important intermediates in synthesis of many organic compounds. Applying photoxidation has been attracted much attention recently and various efforts have been done to improve and modify this system of desulfurization [18–20].

As an operating sustainable and useful route for photoxidation, Utilizing visible light and molecular oxygen in the role of oxidant is so worthwhile and important. This efficient path not only provides a benign and cost-effective procedure for the reaction but also doesn't bring any harmful effect to the environment.

Incorporating of oxygen into the organic substrate can be proceeded by two pathways: by singlet oxygen or by electron transfer mechanism [21]. The oxidative desulfurization process has been done using different catalysts and various procedures. However, some drawbacks such as having environmentally harmful waste, production of byproducts, low yields, and high cost have revealed in these systems [22–24]. These systems show that there is a need to employ more environmental friendly and useful methods for oxidation of sulfides.

In the following context, the novel and effective hybrid-POM was synthesized in which the photosensitive organic moiety is covalently attached to the POM. This hybrid POM was demonstrated the outstanding photonic behavior and therefore was utilized in photoxidation reaction. Accordingly, sulfide oxidation reaction was operated in the presence of this hybrid-POM as a photocatalyst. Aerobic Oxidation of sulfide under visible light was carried out and the remarkable results indicate the capability of this photocatalyst in this oxidation reaction.

2. Experimental

The utilized materials and chemicals were provided from Merck and Sigma chemical companies. The precursor monovacant POM K₈[SiW₁₁O₃₉].13H₂O, which is used for the hybrid POM synthesis, was prepared according to the literature [25]. The used light source for photocatalytic reaction was 150 watt Superior SQP-SX1501 Xenon lamp. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker, D8 ADVANCE, Germany, Wavelength: 1.5406 Å (Cu K α), Voltage: 40 kV, Current: 40 mA in the 2 θ range from 4 to 80.Gas chromatography (GC) analysis was performed on a Varian CP 3800 instrument with a flame-ionization detector using silicon DC-200 or carbowax 20-M columns. Infrared spectra were recorded on a JASCO 6300 spectrophotometer. UV–vis and Diffuse Reflectance Spectroscopy (DRS) spectra were recorded on JASCO V-670 spectrophotometer. HPLC analysis was based on Ecom system quipped with UV–Vis detector. NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer.

2.1. Synthesis of photocatalyst

2.1.1. Synthesis of Cl₃Sn(CH₂)₂CHO

For the synthesis of first part of photocatalyst, we followed a literature procedure [26]: 0.12 mol of Acrolein was added dropwise and slowly to the flask of prepared-solution of $HSnCl_3.2C_2H_5O$ (0.1 mol). After stirring of the reaction mixture for 12 h, the rotary evaporated was used to remove the by-product and some excess reactants. The residue was dissolved in chloroform and filtered. After evaporation of filtrate, the white solid product was obtained and collected.

2.1.2. Synthesis of Cl₃Sn(CH₂)₂HCNC₁₆H₉

For synthesizing the organic moiety of the hybrid compound, we followed the imine formation reaction using Aminopyrene. Accordingly, 0.8 mmol Cl₃Sn(CH₂)₂CHO was dissolved in 25 mL of ethanol and next, 1 mmol of 1-aminopyrene added to this solution. The reaction mixture was stirred for 6 h at room temperature. Then the solvent was evaporated under vacuum and the residue was collected for the next part of synthesis.

Table 1

Photocatalytic oxidation of thioanisol on the presence of different catalyst amounts^a.

Entry	Amount of catalyst (mg)	Yield ^b (%)
1	60	85
2	30	82
3	20	64
4	10	41
5	5	26
6	2	14
7 ^c	30	11
8 ^d	30	17
9	No catalyst	6
10	30	87 ^e

^a Reaction condition: thioanisol (1 mmol), acetonitrile (5 mL), time (4 h) and photocatalyst.

^b Yields are GC yield.

^c (2) was utilized as catalyst.

^d Reaction was done in dark.

^e Yield is achieved in acetonitrile/water (95:5, ν/ν).

2.1.3. Synthesis of $((n-C_4H_9)_4N)_5[SiW_{11}(Sn(CH_2)_2HCNC_{16}H_9)O_{39}]$ (1)

A the last part, for synthesizing the photocatalyst we used this procedure: 3 mmol Cl₃Sn(CH₂)₂HCNC₁₆H₉ was dissolved in 60 mL of DMF and then 1.5 mmol of K₈[SiW₁₁O₃₉] was added to the solution and the mixture was stirred overnight at the room temprature. In the next step, 0.08 mol tetrabutylammonium bromide was added to the reaction mixture and stirred for a while. After adding Et₂O to the mixture, the dark orange precipitation was obtained and collected on a fine frit. The precipitation was washed with ethanol and dried for 12 h in the vacuum oven. IR (KBr, cm-1): 3454 (m), 2958 (m), 2932 (m), 2869 (m), 1643 (s), 1551 (m), 1489 (m), 1381 (w), 1254 (w), 1036 (vw), 960 (vs), 884 (vs), 809 (vs), 745 (s), 538 (m). Calcd elemental analysis for ((n-C₄H₉)₄N)₅[SiW₁₁(Sn(CH₂)₂HCNC₁₆H₉)O₃₉] (%): C 27.90, H 4.59, N 1.97. Found: C 27.86, H 4.53, N 1.95.

2.1.4. Synthesis of $((n-C_4H_9)_4N)_5[SiW_{11}(SnCl)O_{39}]$ (2)

For comparing the result of our hybridization on the POM, we synthesized a hybrid-POM without a sensitizing organic moiety. The solution of 3 mmol SnCl₄ in the 50 mL of DMF/H₂O mixed solvent was prepared. Then 1.3 mmol of K_8 [SiW₁₁O₃₉] was added to the solution and the mixture was stirred overnight in the room temprature. In the next step, 0.075 mol tetrabutylammonium bromide was added to the reaction mixture and stirred for a couple of minutes. After adding 100 mL of ethanol to the mixture, the white precipitation was obtained and filtered. The precipitation was washed with water and dried overnight in the vacuum oven. IR (KBr, cm-1): 3451 (w), 2964 (m), 2934 (m), 2873 (m), 1471 (m), 1371 (w), 1108 (w), 964 (vs), 886 (vs), 805 (vs), 743 (s), 534 (s). Calcd elemental analysis for ((*n*-C₄H₉)₄N)₅[SiW₁₁(Sn (CH₂)₂CHO)O₃₉] (%): C 23.78, H 4.49, N 1.73. Found: C 23.75, H 4.47, N 1.71.

2.2. General oxidation procedure

A quartz reaction tube with 10 mm diameter, containing solution of sulfide (1 mmol) in 5 mL of mixture of solvents acetonitrile/water (95:5, ν/ν) was prepared. Then, 0.007 mmol (0.030 g) of catalyst were added and the O₂ molecules purged to the solution before irradiation. The power of the lamp was set and the lamp equipped with UV filter to remove any irradiation in UV region. The light intensity at the sample position was determined utilizing a genetic power meter and photocell technology. The reaction temperature was kept around 25 °C by circulation of water through an external cooling coil. After stirring the reaction for couple of hours, the progress of the reaction was monitored by GC. At the end of reaction, the product was extracted by chloroform from reaction mixture, and sulfoxide products were obtained by flash chromatography on a silica-gel plate with *n*-C₆H₆/EtOAc as eluent. After

Table 2

Using different kinds of solvent in photocatalytic oxidation of thioanisol^a.

Entry	Solvent	Yields (%) ^b
1	CH ₃ CN / H ₂ O (95:5, v/v)	87 ^c
2	CH ₃ CN	82
3	C ₂ H ₅ OH	31
4	H ₂ O	51
5	CH ₃ OH	48
6	CH ₂ Cl ₂	24

^a Reaction condition: thioanisol (1 mmol), photocatalyst (30 mg), time (4 h) and solvent (5 mL).

^b Yields are GC vield.

^c The yield is achieved in 3 h.

gaining the products, they were qualified by IR and HNMR spectroscopy methods.

For recycling the catalyst, after extraction of the product by silica-gel plate, the remaining of the reaction mixture was evaporated under the vacuum and the catalyst was collected at the end of the flask. The catalyst was washed three times with methanol and then dried under vacuum.

Tables 1–3 show the results for optimized reaction conditions and the oxidation of various sulfides under optimum conditions.

3. Results and discussion

Hybridization of POM is a unique and useful way to synthesize more efficient polyoxometalates, which can be exploited in many fields like photochemical applications. Utilizing hybridization, the highly capable polyoxometalates containing new and modified characteristics are achieved. It is known that photoactivity is one of the most important characteristics of POMs. However, the activity range of simple polyoxometalates is in UV region, which limits the applicability and efficiency of these valuable compounds. Interestingly, hybridization of the POMs can be useful arsenal to make more efficient and valuable polyoxometalates and enhance the applications of these compounds. In this regard, we devise a hybridization system, which can work greatly as a photocatalyst for oxidation of sulfides. During this hybridization, the band gap of the final compound is decreased more than 1 ev and the absorption range of polyoxometalate is spread from UV to visible region.

For this synthesis, we started from $[SiW_{11}O_{39}]$ lacunary polyoxometalate that followed by reaction with organotin derivatives and aminopyrene to conclude the hybrid compound (1).

Following the synthesis route, first, we synthesized lacunary polyoxometalate [SiW₁₁O₃₉]. Then the synthesis of complete organic part is proceeded through forming the imine bond between photosensitizer Pyrene molecule and 3-(trichlorostannyl)propanal. In the last part, the synthesized organotin molecule was attached to monovacant POM in order to gain the final hybrid product (1).

For the aim of showing the formation of new bonds in the hybrid compound, the FT-IR spectroscopy was utilized to monitoring the bonds before and after hybridization.

As Fig. 1 shows, besides the characteristic peaks of polyoxometalate that have appeared around 960, 984, 809 cm⁻¹, the spectrum of hybrid compound (1) show the strong peak at 1634 cm^{-1} , which is related to the formation of imine bond. Moreover, the characteristic peaks of polyoxometalate are observable in both spectra of (2,1) that indicate the intact remaining of POM structure during hybridization.

Employing XRD patterns also revealed that POM structure has not changed in the hybridization process. According to the fig. S2 (Supporting Information), the peak around 7.5° shows the (111) plane of Keggin structure crystalline phase. As both spectra depict this orientation along (111) direction, it indicates intact structure of POM after hybridization. This comparison has done on the basis of reported XRD pattern analysis [27].

Observing the ¹HNMR and ¹³CNMR spectrums of compound (1) was

Table 3

Aerobic oxidation of sulfides in the presence of hybrid POM (1) photocatalyst^a.

^aReaction conditions: sulfide (1 mmol), photocatalyst (30 mg), acetonitrile/water (95:5, ν/ν) (5 mL). ^bGC yield.



Fig. 1. The FT-IR of **(2)** (red line) and **(1)** (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. UV–vis spectra for **(2)** (green line) and **(1)** (dark red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also indicated that during functionalization, the organic moiety remains intact and attachment to the POM was properly carried on (supporting information, Fig. S4 and S5).

The unique changes in POM properties that come from hybridization are in optical properties. The UV–vis study of both (2, 1) demonstrate that after hybridization, two strong peaks at 399 and 562 nm appear in the spectrum (Fig. 2). These new peaks arise from expanding the absorption range of hybrid compound to visible region. This expansion provides the remarkable photoactive behavior for hybrid POM in comparison to bare POM.

Employing the Kubelka-Munk equation, $F(R) = \alpha = (1-R)2/2R$, (R is the percentage of reflected light and α is absorption coefficient) and transformed Kubelka-Munk function, $[F(R)h\nu]p = A(h\nu - E_g)$ where $h\nu$ is incident photon energy, E_g is optical band gap energy, A is the related constant to transition probability and p is the power index according to optical absorption process [28], the band gap study was carried out. Regarding to DRS analysis and mentioned calculations, the band gap

Entry Sulfide Produc Time (h) Yield⁶ (%)
1
$$\int_{c} \int_{c} \int_{c}$$



Fig. 3. Transformed UV–vis spectra for **(2)** (green line) and **(1)** (dark red line), based on Kubelka-Munk equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

energy for (2) and (1) was obtained. Comparison between these two evaluated band gaps, clearly demonstrate that after hybridization the POM shows the significant decrease in band gap from 3.78 eV to 2.35 eV (Fig. 3).

This decrement in band gap interestingly depicts that through hybridization, POM is sensitized and absorb higher wavelength in visible region. This attracting characteristic allows the hybrid POM to behave as a good photocatalyst, which can catalyze substrates to desired products using visible light. Also, many organic reactions can be photocatalyzed utilizing this hybrid POM. In this regard, in this paper we investigated the aerobic oxidation of sulfides to corresponding oxidized compounds using hybrid POM photocatalyst and under visible light.

In the second part of this paper, we investigated the photocatalytic activity of this hybrid POM on various sulfides in aerobic oxidation reaction. For modeling the oxidation reaction and find optimum reaction condition, we utilized thioanisol through following typical route: 1 mmol of sulfide was dissolved in 5 mL solvent, the O2 purged to the reaction tube, the photocatalyst added and irradiated at room temperature. Using various amount of photocatalyst, we gained the optimum usage of hybrid POM (1) (Table 1). As it is shown in this table, the conversion yields increase with higher amount of photocatalyst. But for the reactions using more than 30 mg of photocatalyst, no significant increasing in yield was observed. Therefore, the 30 mg of photocatalyst selected as an optimum amount that should be used in oxidation reactions (Table 1, entry 2). In order to monitor the capability of photocatalyst in oxidation of sulfides, the reaction was done with (2) as a catalyst (Table 1, entry 7). As the results show, it is observable that running the reaction in the presence of (1) as a catalyst cause to get much more yield than using (2), and powerfully shows the effect of hybridization on increasing the photoactivity of POM. Also, the oxidation reaction, in the presence of (1) and in dark, proceeds only by 17% of sulfide conversion (Table 1, entry 8).

In the same line, the optimization for catalyst was repeated in the mixed solvent (acetonitrile/water 95:5, ν/ν) and the results indicated that the 30 mg of catalyst is the efficient amount of catalyst for proceeding the reaction with good yield (Table 1, entry 10).

The next optimization was carried out on the solvent. As the studies have depicted, the photoxidation reactions of sulfides are affected by the nature of solvent [29,30]. Depending on the mechanism of the reaction, various kinds of protic and aprotic solvents can demonstrate their potency and efficiency by influencing on the yield and time of the reaction [31].

In this regard, different kinds of solvent were operated in the reaction

and the results recorded. Among these solvents, acetonitrile exhibits the better yield for this oxidation reaction (Table 2). Since acetonitrile have shown photoinert behavior [32], it would be predictable to observe this result. Moreover, it brings in mind that the reaction probably following the electron transfer (ET) mechanism.

We found that adding a little amount of water as a co-solvent can affect on the speed of the reaction. For shedding more lights on this issue, the reaction in acetonitrile and mixed solvents (acetonitrile/ water) was operated. Using different ratios of acetonitrile and water, the photoxidation reaction was done and the results are monitored in fig. S3. According to results, the best ratio as a solvent is 95:5 for acetonitrile and water respectively. Applying this ratio, the yield of the reaction is nearly the same in comparison with the solely acetonitrile, but the reaction is expedited and proceed in the lower time. However, adding more amount of water as a co-solvent cause to decrease the yield of the reaction.

Regarding to the obtained optimum conditions for oxidation reaction, the various kinds of sulfides such as aliphatic and aromatic ones was employed in the aerobic oxidation reaction in the presence of hybrid POM photocatalyst (Table 3). It is shown that all of the sulfides were oxidized to the corresponding sulfoxide products in good to high yields.

As Table 3 monitors, various kinds of sulfides were examined in the photocatalytic oxidation reaction. Interestingly, these sulfides are oxidized effectively up to the corresponding sulfoxide compounds and the substrates didn't overoxidized to the sulfone products, although, in some cases the sulfones were detected in very low yields as a side product. The thioanisol and its derivatives were converted to the sulfoxide. The results show that for thioanisol derivatives, both kinds include electron-releasing and electron-withdrawing ones have shown good conversion yields under the reaction condition (Table 3, entries 1–3). However, the derivatives with high electron deficiency didn't sufficiently progress the reaction and demonstrated lower yields even in the longer reaction time (Table 3, entry 4).

In the same line, various kinds of aliphatic sulfides were treated under this photoxidation reaction. The obtained results exhibited that yield of the reaction for these sulfides are good and near to the aryl sulfides, however, reaction for cyclic aliphatic sulfides were shown lower yields in some measure, and there was need to run the reaction in longer times for these sulfides (Table 3, entries 9–11). Conversion of benzyl phenyl sulfide to corresponding sulfoxide was proceeded in appropriate time and good yields, however, around 14% of benzaldehyde which is a known side product of photoxidation of benzyl sulfides [33] was detected (Table 3, entry 6). Also, it is observed that conversion of sulfides to sulfoxide was proceeded without affecting and overoxidation of C=C double bond side functional group (Table 3, entries 5, 11). Moreover, thiophene and benzothiophene were efficiently oxidized into the corresponding sufoxide products (Table 3, entries 7, 8).

In order to examine the recyclability of this hybrid POM photocatalyst, the oxidation reaction of thioanisol was repeatedly operated at the same condition. The results showed that after four times running the reaction and reusing the photocatalyst, good yield is still observable for the reaction (55%). This capability of catalytic activity shows that the photocatalyst didn't have critical changes during recycling and reusing, which is also observed in characterization investigation for reused catalyst.

In order to investigate the quantum yield for this photoxidation reaction, the thioanisol as a representative of sulfide compounds was selected. According to the presented equation [34], the quantum yield was calculated using the equation $\Phi = \Delta n / \Delta l$. where Δn is number of converted substrate molecules and Δl is number of absorbed photons by the reaction mixture. In this regard, the Δn was obtained from the HPLC analysis of reaction mixture and the Δl was calculated through standard ferrioxalate actinometer. After determination of incident light intensity, calculation was carried on at the wavelength of 562 nm as a selected wavelength, in which the catalyst has intense absorption. Accordingly, the quantum yield was obtained from the linear kinetic part of the



Scheme 1. Proposed mechanism for Photocatalytic aerobic oxidation of sulfides by Hybrid POM.

sulfoxide formation using ferrioxalate actinometer. The result showed the good quantum yield for this photocatalytic reaction ($\Phi = 0.38$).

In regard to suggest a mechanism for this photoxidation process, based on reported studies that utilized quenching experiments and conducted further investigations indicate [16,35], we think that the oxidation reaction dominantly carried out through the ET mechanism, although, for some substrates the contribution of singlet oxygen process should be taken into account. Regarding, the mentioned process in Scheme 1 could be suggesting mechanism for this photoxidation reaction. As scheme 1 depicts, irradiation to the hybrid POM generates exciton in the valence band. The created hole is transferred to the sulfide and makes sulfide radical cation. The excited electron transferred to the oxidant and make superoxide radical anion. Consequently, the hybrid POM regenerates to the ground state and anion react with sulfide radical cation to make final oxidized product.

It should be noted that the mentioned path is our suggested mechanism for this reaction, however for presenting and proving an exact path and mechanism of the reaction there would be a need to run more basic and fundamental studies, which are not in the scope of this paper and will be investigated in future studies by the authors.

According to all mentioned above, enhancing the photoactivity of POMs could be carried out through hybridization process. This increment allows POMs using lower energies to catalyze the oxidation reactions.

4. Conclusion

It was demonstrated a unique Hybrid POM, in which the pyrene molecule was attached to the vacant POM structure. This hybridization sensitized POM and decreased band gap, which provided the outstanding photonic properties for the hybrid compound and allowed to absorb visible light. Utilizing this capability, we operated photoxidation of sulfides under the treatment of this photocatalyst. Accordingly, this catalyst succeeded to aerobically oxidize various kinds of sulfides to sulfoxides in very good yields. Moreover, the simple work up, low cost and being environmental friendly are the other attracting features of this photocatalytic system. In this line, developing more efficient photocatalytic systems using broad spectrum of hybrid POMs is under investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interestsor personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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