Application of nano molybdenum trioxide in thermal storage and photocatalysis

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Abstract. The thermal energy storage (TES) in phase change materials (PCMs) plays an important role in energy management systems. Paraffin has found wide range of applications as a PCM due to its unique thermal and physical properties. The present study reports about the synthesis of MoO$_3$ nanomaterials using chemical method. MoO$_3$ nanomaterial was diffused into paraffin wax in 0.5, 1, 1.5, and 2 weight percentages and thermal analysis was conducted. It was observed that 1.5 wt % doped PCM showed best enhancement in thermal performance with 20.28% and 35.71% improvement in heating and cooling cycles. The photocatalytic activity of synthesized nanocomposite was also evaluated by degradation of methylene dye under visible light irradiation. The photocatalytic degradation effectiveness of as synthesized nanocomposites has showed high photodegradation efficiency (93.83%) of methylene blue under visible light radiation.

Keywords: Thermal Energy Storage, Phase Change Materials, Nano MoO$_3$, Photocatalyst, Paraffin

1. Introduction

The crisis of Energy management has put the world in turmoil with fewer supplies available to generate energy. Excessive usage and consequent depletion of existing resources has led to massive energy shortages and if required steps not taken will only increase in the coming years. The traditional methods of conserving energy are failing to power the current needs. Usage of Solar energy, abundant in nature can significantly reduce energy issues and this can be done using Phase change materials. Phase Change Materials or better known as PCM’s are a trending research matter capable of storing thermal energy and thereby improving energy utilization. This thermal energy storage technology absorbs and releases the latent heat stored during its phase transition at a constant temperature [1]. Nanostructured transition metal oxides have been widely researched upon for their thermal properties and incorporation in phase change materials. Numerous studies have focused on metal oxides such as TiO$_2$ [2,3], Fe$_3$O$_4$ [4,5], ZnO [6], MnO$_2$ [7], Co$_3$O$_4$ [8] and CuO [9] as thermal energy storage devices. However, their present usage is restricted due to their expensive prices and unavailability.

Nano-dimensional Molybdenum Trioxide is an n-type semiconductor with a wide but tuneable bandgap for diverse applications. This transition metal oxide synthesizable via various techniques, shows a layered-structure with high surface area, large dielectric constant and high aspect ratio. Synthesized crystalline MoO$_3$ nanomaterials exist primarily in two phases: orthorhombic $\alpha$-phase and monoclinic $\beta$-
phase. They are a readily available, stable and non-toxic chemical compound. Their unique size-dependent physical, chemical and electronic properties enable them to be used in lubrication, optics, catalysis, gas sensing, batteries and electronic devices [10-14]. MoO$_3$ has already exhibited an excellent performance in thermochemical energy storage devices such as supercapacitors and lithium-ion batteries but excessive heat generation by these thermal systems has led to issues of its safety and efficiency and hence low-cost MoO$_3$ phase change system has been proposed as a promising alternative. Additionally, these inorganic oxides are highly efficient photocatalysts [15-19]. Its photo-destructive capabilities have been extensively studied and proven. Traditional wastewater dye treatment approaches only convert pollutants from one form to another which ends up producing more refractory pollutants. Nano photocatalysis transforms pollutants into harmless products, such as CO$_2$ and H$_2$O [21]. The large surface area, high adsorption properties of nano sized MoO$_3$ results in faster rates of degradation. Liang et.al. synthesized α-MoO$_3$ nanoribbons that exhibited complete photodegradation activity against Rhodamine-B dye under visible light [11]. Ahmed et.al. successfully degraded organic dyes via synthesized MoO$_3$ nanosheets [20]. Here, in the present study we are using nanostructured MoO$_3$ as a novel and promising candidate for harvesting thermal energy and photocatalysis.

2. Materials and Methods

2.1 Preparation of Nano MoO$_3$-Paraffin mixtures

Fully refined paraffin wax used was of analytical grade and all chemicals were used directly without any further purification. The synthesis of MoO$_3$ was performed using ammonium heptamolybdate tetrahydrate (AHM) (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O and strong nitric acid HNO$_3$. 5 mL of HNO$_3$ was added to 15 mL of 0.05 M AHM which was heated to 50°C. The solution was stirred for 15 minutes, after which the reaction solution temperature was elevated to 70°C. White colored MoO$_3$ precipitate was observed after the reaction was maintained at 70°C for half an hour. The precipitated MoO$_3$ was collected and washed using distilled water and dehydrated [22]. As synthesized samples were characterized using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), UV visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR) and dynamic light scattering technique (DLS).

MoO$_3$-Paraffin composite was prepared by mixing the MoO$_3$ into melted paraffin at various mass fractions 0.5, 1, 1.5, & 2 wt% respectively. Sonication of the final mixtures was done to avoid agglomeration and ensure uniform dispersion. These mixtures was heated and cooled to record the heating and cooling curves for thermal study. Heating cycles were done by placing the prepared test tubes in a controlled heating water bath and heating the samples up to 75°C. Cooling cycles were studied by cooling the samples back to room temperature. The temperature changes of the nano enhanced PCMs was recorded every 30 seconds using a digital thermometer.

2.2 Photocatalytic tests

Photocatalytic reaction is initiated from the interaction between light and MoO$_3$ nanomaterials. Photocatalytic activity of the synthesized nano MoO$_3$ was studied by the degradation of Methylene blue (MB) dye under day light and analysis was performed using UV-Vis spectroscopy. In oxidized state, MB is blue in colour but when exposed to a reducing agent it reduces to leuco methylene blue (LMB) which is colourless [24]. For studying the reduction of the dye, samples containing 50 ml of 0.05mM MB were taken, 0.05g of the synthesized MoO$_3$ was added to the vials, then carefully mixed and subjected to direct sunlight. After activating the reaction under direct sunlight illumination, the UV-visible spectra of this reaction mixture were reported at intervals of 5 minutes. Within a few minutes of reaction time, the distinctive color of the dyes vanished, indication successful reduction of dye.
3. Results & Discussion

3.1 Characterization

Figure.1 (A) shows SEM surface morphology of synthesized MoO$_3$ nano material. The surface morphologies of nanomaterial show presence of a rod like structure. The energy dispersive spectrum (EDX) is shown in Figure.1 (B) which specifies the level of purity in the synthesized nanomaterial. The EDX pattern shows peaks characteristic to molybdenum (Mo) and oxygen (O) with weight percentage of 42.63 and 57.37 respectively.

UV–Vis spectra and dynamic light scattering (DLS) analysis were used to investigate the optical properties and particle size analysis of the synthesized nanomaterial. Uv-Visible spectroscopy analysis resulted in $\lambda_{\text{max}}$ value of 235 nm which is a characteristic peak of MoO$_3$ nanomaterials (Refer Fig 2A) (25). Particle size analysis by DLS confirmed its hydrodynamic diameter as ~ 58 nm.

FTIR is considered to be an effective method to investigate a specific interaction in the composite PCMs. Figure.2 (B) shows the FTIR absorption spectrum of the nano MoO$_3$-Paraffin. FTIR spectra was obtained
in the range of wave numbers from 450 to 4000 cm\(^{-1}\). The FTIR spectra of MoO\(_3\) show characteristic peaks that are attributed to the fundamental vibrational modes of Mo=O [26]. Spectra of paraffin reveal the presence of carbon-hydrogen stretching and bending bands in the range of 1,000 to 3,000 cm\(^{-1}\) [27]. The graph of MoO\(_3\)-Paraffin composite showed the presence of all the individual characteristic peak of both the compounds thus proving efficient embedment and uniform distribution of the nanoparticles in the phase change material. Similar peaks were observed on analysis after repetitive thermal cycles showcasing chemical stability of the phase change material and the nano-additive. The appearance of both individual peaks from MoO\(_3\) and Paraffin in the FTIR spectrum of our novel nanoenhanced PCM composite indicates no interaction took place between the nanoparticle and the phase change material and thus they did not alter the properties of one another.

3.2 Thermal storage studies

Charging and discharging analysis have been undertaken to investigate the thermal properties of MoO\(_3\)-paraffin mixtures. As-synthesized MoO\(_3\) was integrated into the phase change material (PCM) and the heat transfer rates and thermal conductivity were compared to the pristine counterpart. The melting curves of paraffin dispersed with MoO\(_3\) are represented in Figure 3(a). The melting curves were plotted for pure paraffin and composites with MoO\(_3\) wt. % in the range of 0.5% to 2 wt. %. These PCM composites started at an initial average ambient temperature of 23°C. The temperatures were increased beyond their phase change temperatures and were heated up to an average temperature of 75°C. The heating curves for pure paraffin and combinations of paraffin with the various amounts of MoO\(_3\), i.e., 0.5 wt.%, 1 wt.% , 1.5 wt.% and 2 wt.% were plotted. It was evaluated that the heating rate for 1.5wt. % of MoO\(_3\) added to paraffin is 18.28% which is the highest value. As seen from Table.1 it is evident that the heat transfer rate increases steadily for 0.5 wt.% - 1.5 wt.% and thereafter decrease for 2 wt.%. This indicates that the heat transfer rate hits saturation when 1.5 wt.% of MoO\(_3\) was added to paraffin.

![Figure 3](image.png)

**Figure 3.** (A) Heating curves and (B) Cooling curves of pure paraffin and paraffin doped with different MoO\(_3\) wt. %
The cooling curves were plotted for pure paraffin and combinations of paraffin with the different MoO$_3$ wt. %. For cooling cycles the PCM mixtures started at an initial temperature of 75°C and were analyzed until temperatures were cooled down to room temperature of 25°C. The cooling rates of the different concentrations are 26.66%, 30%, 43.33% and 23.34% for 0.5 wt.% , 1 wt.% , 1.5 wt.%, and 2 wt.%.

Highest heat transfer rate is observed at 1.5 wt. % and hence, the optimized percentage of MoO$_3$ in the pure paraffin was 1.5 wt.%. The enhanced heat transfer rates of the nano doped PCM are credited to the addition of the suitable amount of nano MoO$_3$ in the paraffin wax. Nano MoO$_3$ possesses high thermal conductivity which enhances interfacial thermal conductance of pure paraffin [28]. The influence of nanoparticles on the overall heat transfer rate during this melting process has been shown to be heavily dependent on the degree of natural convection throughout the phase transition process. Therefore, the heating and cooling speeds of PCMs are able to be enhanced. Since MoO$_3$ is in the nanoregime can act as a nucleating agent resulting in the acceleration of heat transfer [29]. The small size and the large surface area of the nano MoO$_3$ molecules allows for higher mobility moreover it increases the phonon interaction between nano MoO$_3$ and paraffin molecules. Consequently, increased interaction leads to higher transmission of heat energy from MoO$_3$ to the base paraffin material. Hence, nanoenhanced PCM has shown much faster heat transfer aiding to these factors. The higher concentration, of the nanomaterials homogeneously in cooperated in the paraffin wax, the higher the dispersion of the heat through the nanocomposite for better thermal heat storage [30]. However addition of nanomaterial beyond the saturation point can result in reduction of thermal properties due to agglomeration of nanomaterials in the paraffin wax.

### 3.3 Photocatalytic Studies

Fig. 4 shows the absorption spectra for the dye degradation at regular intervals. It is inferred from the graph that at absorption peak reduces sharply (~57%) in the initial 5 min followed by a gradual reduction in the efficiency with the increase in time (refer Fig. 4). Almost complete degradation was observed after 15 min. The mechanism of photocatalytic degradation of methylene dyes by the nano MoO$_3$ photocatalyst is explained below. When photons having energies equal or greater than band gap energy of nano MoO$_3$ are irradiated onto its surface, the electrons (e$^-$) present in the valence band of nano MoO$_3$ are excited to its conduction band, while holes (h$^+$) remain in the valence band. The holes being highly oxidizing will either oxidize the pollutant dye directly or by forming strong hydroxyl radicals OH$^\cdot$. The excited electrons present in the conduction band can reduce oxygen into superoxide anions which consequently form superoxide radicals (O$_2^\cdot$). Finally, pollutant dyes are decomposed by the ‘•OH and O$_2^\cdot$’ as shown below: [31]

\[
\text{Photo-oxidation:} \quad h^+ + \text{dye} \rightarrow \text{dye}^+ \rightarrow \text{degraded products}
\]
\[
\begin{align*}
    h^+ + H_2O & \rightarrow H^+ + OH^- \\
    h^+ + OH^- & \rightarrow OH^-
\end{align*}
\]

Photo-reduction:
\[
\begin{align*}
    e^- + O_2 & \rightarrow O_2^- \\
    2 e^- + O_2 + 2H^+ & \rightarrow H_2O_2 \\
    e^- + H_2O_2 & \rightarrow OH^- + OH^- \\
    H^+ + \text{dye} & \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

**Figure 4.** Absorption spectra for the MB degradation at regular intervals by nano MoO$_3$

**Table 2.** Photocatalytic degradation efficiency of nano MoO$_3$

| Degradation time (min) | Degradation % |
|------------------------|---------------|
| 0                      | 0             |
| 5                      | 57.98         |
| 10                     | 89.25         |
| 15                     | 93.83         |

**4. Conclusions**

In this study, nano MoO$_3$ was successfully fabricated having a diameter of 58nm and characterized using UV Visible spectroscopy showing characteristic peak. The enhancements in the heat transfer rate of PCM with various weight percentages of nano MoO$_3$ were analyzed and it was concluded that maximum heat transfer was 20.28% and 35.71% in heating and cooling cycles respectively with 1.5 wt.% doping MoO$_3$. Photocatalytic catalytic degradation abilities of nano MoO$_3$ was also successfully confirmed by the degradation of methylene blue. The study showed the photocatalytic activity of the synthesized nano MoO$_3$ was 93.83% as observed by the reduction of methylene blue dye. Nano MoO$_3$ exhibits an excellent ability to enhance the heat transfer rate of paraffin wax PCM thereby showing prospective applications in thermochemical energy storage devices. The development of such photocatalysts also has the potential for large-scale application of heterogeneous photocatalysis under visible light to reduce water contamination and environmental pollution.
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