A novel study of tungsten oxide nanocrystallites as fuel additive for diesel oil

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ABSTRACT

In this paper, a basic solvothermal synthesis using sodium tungstate as a precursor is reported to prepare tungsten oxide (WO₃) particles. XRD data confirmed the highly crystalline nature. The broad peaks of XRD patterns estimated the nanocrystallites of WO₃. The average crystallite size was 95 nm. Scanning electron microscopy showed the morphologically cube-like particles with aggregation that was converted to larger brick-like particle of WO₃ after calcination. WO₃ was used as fuel additive in diesel oil. Fire and flash points of diesel oil were enhanced to 49°C and 54°C respectively. The calorific value was increased up to 36580 Jg⁻¹. Thus fuel efficiency was enhanced by use of WO₃ as an additive. The use of different concentrations of WO₃ (20, 40, 60, 80 ppm) as fuel additive has been also explored in this paper. The observed additive properties of WO₃ suggested the potential applications of such metal oxides.

1. Introduction

Semiconductor oxides have wide range of applications in almost every aspect of modern digital life. Therefore, they are extensively studied since last many decades. The nanocrystals of semiconductor oxides have gained significant interest due to their versatile applications [1]. The broad range of applications of semiconductor oxides is due to their inherent variable oxidation states. Among semiconductor oxides, due to their rapid optical reaction rate, tungsten oxide with different oxidation states of WO₃₋ₓ has been identified as one of the most promising candidates as opposed to other electrochromic materials [2]. In the literature, WO₃ has been extensively studied. For example, Dastan et al. reported the WO₃ recently. They found that various properties of WO₃ like morphological, functional, optical, molecular and thermal properties are influenced by the preparation methods and reactant materials [3]. Because of many structures, such as monoclinic, triclinic, tetragonal, orthorhombic, cubic and hexagonal for pure and oxygen-deficient WO₃, tungsten oxide is a complex substance regarding crystal structure and thermal stability. WO₃ crystallizes in a triclinic structure at ambient temperature and shows structural transition at extreme temperatures. The preceding series of triclinic (30°C), orthorhombic (330°C), monoclinic (330°C) [4] and tetragonal (740°C) were recorded in bulk WO₃ investigations [5]. WO₃ nano-semiconductors, however, typically exhibit different microstructures and properties compared to other fabrication methods under various operating conditions [6]. The crystal structure and colour of tungsten oxide nano-semiconductors are depended strongly on temperature and experimental parameters. Various crystal forms of WO₃ can be reversed by limiting the synthetic conditions and physical parameters [7]. It has been observed that oxygen deficiency is caused by the formation of additional valance states. As a result, colour variations occur in semiconductor oxides. It is also stated that the colour shifted to the characteristic canary yellow of WO₃ with increasing washing steps [8]. The calcination of white precipitate of WO₃ yields the high purity lime-yellow coloured WO₃ powder. The consequence of the insertion/extraction of electrons and charges balancing small ions is one fundamental theory of the coloration method for WOₓ. The colours are meant to correspond with the concentration of oxygen. The change in favourable oxidation detected concurrently with the colour change is possibly motivated by this modification [9].

Because of the large surface area, flexible gap, high chemical stability, nontoxicity, cheapness, abundance, high photocatalytic activity and corrosion resistance properties of WO₃ nano-semiconductors at nano level, numerous articles have been published. It is evident that nano-semiconductors are now being used in different fields due to its unlimited applications include solar cells [10,11], gas sensors [12–14], drug delivery [15], fuel additives (current work), dye degradation [16], water treatment [17–19], Li-ion batteries [20,21], fuel cells [22,23], supercapacitors [24], corrosion [25], dye sensitized solar cells [26], antimicrobial activity [27], fire...
packing and resistance [28], cancer cell treatment [29],
paint and coating industry [30], bone tissue engineer-
ing [31], nano-printing [32], etc. On the basis of these
facts, this is being expected that various products based
on aforementioned properties will be commercially
available soon.

In this research work, we synthesized WO3 parti-
cles using a simple solvothermal approach from sodium
tungstate as precursor. The WO3 nanocrystallites were
characterized by X-ray diffraction (XRD) and scanning
electron microscopy (SEM) techniques. After structural
and morphological analyses, the fuel additive proper-
ties of WO3 nanocrystallites were carried out and dis-
cussed. To the best of our knowledge, these properties
of WO3 nanocrystallites prepared by solvothermal have
not been explored previously.

2. Experimental section
2.1. Chemicals used
Hydrated sodium tungstate (Na2WO4·2H2O, 99%),
ammonium chloride (NH4Cl, 98%), urea (CO(NH2)2,
99%), diethylene glycol ((HOCH2CH2)O, 99%), distilled
water and ethanol (C2H5OH, 99%) were used without
any further refining for the synthesis of WO3 nanocrys-
tallites. All these chemicals were of analytical grade.
These chemicals were supplied by international stan-
dard suppliers.

2.2. Synthesis of WO3 nanoparticles
WO3 nanocrystallites were synthesized by solvothermal
method. First of all, 3.2 g of sodium tungstate was
dissolved in 20 ml distilled water. Ammonium chloride
solution was prepared by mixing 6.4 g of ammonium
chloride in 20 ml distilled water. Both solutions were
mixed under constant stirring for 15 min. Then, this
reaction mixture was sonicated for 30 min followed by
the addition of 1 g of urea. The reaction mixture was
sonicated for 1 h followed by addition of 40 ml diethy-
lene glycol. After that, this mixture was added to stain-
less steel autoclave (Teflon-lined). The autoclave having
reaction mixture was heated at 200 °C for 4 h. At the
end, a yellow-coloured suspension with white precipi-
tates was obtained. These as prepared nanocrystallites
were centrifuged and washed with ethanol and distilled
water until the pH reached 7. After washing, the dry-
ing of the precipitates was carried out at 60 °C for 4 h.
This synthesized material was divided into two portions:
as prepared WO3 (a) and WO3 (b). WO3 (b) was calci-
nated at 600 °C for 3 h in an electric furnace. Finally, lime
yellow-coloured precipitates were obtained. The entire
process of synthesis is shown in Figure 1.

![Figure 1. Preparation of tungsten oxide nanocrystallites.](image)

![Figure 2. SEM images of WO3 nanoparticles without annealing: (a) at 2000X and (b) at 6000X.](image)
2.3. Fuel additive properties studies

WO₃ suspensions with different concentrations (20, 40, 60 and 80 ppm) were made by adding stoichiometric quantities of WO₃ nanocrystallites in 0.1 dm³ of diesel oil. The parameters such as fire and flash point, cloud and pour point, specific gravity, kinematic viscosity and calorific values were studied after sonicating the samples for 5 min.

3. Results and discussion

3.1. Morphological analysis

The morphology of as-prepared WO₃ and annealed WO₃ was carried out at room temperature. The electron microscopic technique was used for this purpose. The obtained images for both types of WO₃ at different magnifications are shown in Figures 2 and 3. SEM observations showed more irregular shapes (flake like morphology) along with coagulations. Whereas some cube-like particles showed in SEM results of WO₃(a) that is headed by an arrow in Figure 2. Moreover, it showed a lot of aggregation therefore morphology is not clear in WO₃(a) (Figure 2). This is because a hydrothermal process is a wet chemical synthesis process that utilized the moisture contents in the material to generate steam which helps to form the structure and shape of the material. Therefore the resulting material is still slightly wet, even after drying which led to a material with low crystallinity. Whereas the material annealed at 600 °C is in finer powder form and more crystalline. However, the particles size increased as temperature increased.

![Figure 3. SEM images of WO₃ nanoparticles with annealing: (a) at 2000X and (b) at 6000X.](image)

![Figure 4. Powder X-ray diffraction graph of WO₃.](image)
Therefore, the SEM images showed an increase in particles size after calcination at 600 °C and the smaller size particles showed in Figure 3 are actually the broken parts of that larger brick-like particles. It is clearly seen from SEM images that the particles look comparatively more disperse in WO₃(b) because of the removal of water molecules at high temperature, but morphology of WO₃(b) was destroyed after calcination (Figure 3). It is also reported in the literature that when the water content is removed after calcination, the aggregation is reduced [33]. Further, it is also noted that the crystallite sizes increased with increasing calcination temperature.

3.2. Structural analysis by XRD

Room temperature conventional powder diffraction technique was used for structural elucidation of both as-prepared WO₃ and annealed WO₃. The XRD patterns were recorded in 2-theta range (20–65°). The diffraction pattern shown in Figure 4 was indexed to the monoclinic structure with 2-theta range 20–65°. The XRD patterns are shown in Figure 4.

The XRD patterns showed main diffractions planes at two theta values 23.05°, 23.51°, 24.29°, 26.55°, 28.65°, 33.21°, 34.11°, 35.51°, 41.55°, 47.21°, 48.19°, 49.87° and 63.17°. These diffraction planes were indexed as (002), (020), (200), (120), (121), (022), (202), (021), (222), (004), (040), (400), (143) respectively. This obtained XRD was matched with JCPDS#96-210-6,383 [34]. As clear from XRD graph, relatively broad peaks have been observed. This broad peaks appearance is the evidence of nanocrystalline WO₃. The small intensity peaks around 45° depicted the presence of water molecules in as prepared WO₃(a). Tungsten oxide has polymorphism behaviour. The oxides with polymorphism behaviour usually exhibit in more than one crystal structure. Thus WO₃ also exhibits more than one crystal system. These are hexagonal, tetragonal, triclinic, cubic, monoclinic and orthorhombic [4]. These different crystal forms of WO₃ can be tailored by limiting the synthetic conditions. At 600 °C, it shows the monoclinic structure as shown in the XRD pattern which is the stable state at room temperature (Figure 5a and c).

Based on the space group P2₁/C(14), the resulting material is primitive monoclinic and has prismatic centrosymmetric structure (Table 1).

It can be seen from XRD structure that one unit cell contains eight molecules of tungsten oxide in which oxygen atoms are interconnected with each other, i.e. each tungsten atom is bonded with six oxygen atoms, three of them shared with other adjacent molecules (Figure 5b and d). The obtained results regarding structural elucidation from XRD data have already been reported in the literature [35]. The summary of details of space group, crystal system, density, lattice parameters, atomic coordinates, bond angles and bond lengths are given in Table 1.

3.2.1. Formation mechanism

Solutions of sodium tungstate and ammonium chloride were mixed under constant stirring followed by the addition of urea. The urea acted as a stabilizer and maintained the morphology and structure.
Table 1. The crystal data of WO₃ from XRD analysis.

| Parameters                  | Results                                                                 |
|-----------------------------|-------------------------------------------------------------------------|
| Name                        | Tungsten oxide nanocrystallite (WO₃)                                    |
|                            | O₃W                                                                    |
|                            | Monoclinic                                                             |
|                            | P 21/c                                                                 |
|                            | 14                                                                     |
|                            | 8 (Figure 4(b))                                                       |
|                            | 2                                                                     |
|                            | a, b, c                                                                 |
|                            | 7.3060 Å, 7.54000 Å, 7.6920 Å                                         |
|                            | β                                                                      |
|                            | 90.8810°                                                              |
| Calculated density         | 28,300 g cm⁻³                                                          |
| Atomic coordinates         | X Y Z                                                                 |
| W₁                          | 0.02 80.03 70.746                                                      |
| W₂                          | 0.53 40.02 30.750                                                      |
| O₁                          | 0.71 40.48 40.007                                                      |
| O₂                          | 0.22 50.47 40.007                                                      |
| O₃                          | 0.71 60.04 30.708                                                      |
| O₄                          | 0.99 80.26 20.712                                                      |
| O₅                          | 0.20 60.04 20.995                                                      |
| O₆                          | 0.51 90.25 90.789                                                      |
| Bond distance [Figure 4(d)] | W₁–O₂ 1.73290 Å                                                        |
|                            | W₁–O₃ 1.95229 Å                                                        |
|                            | W₁–O₄ 2.11511 Å                                                        |
|                            | W₁–O₅ 2.16535 Å                                                        |
|                            | W₁–O₆ 1.85182 Å                                                        |
|                            | W₂–O₁ 1.78610 Å                                                        |
|                            | W₂–O₂ 2.18399 Å                                                        |
|                            | W₂–O₃ 1.85926 Å                                                        |
|                            | W₂–O₅ 1.74230 Å                                                        |
|                            | W₂–O₆ 1.93709 Å                                                        |
| Bond angles                 | O₂–W₁–O₄ 92.6682°                                                      |
|                            | O₂–W₁–O₃ 94.3092°                                                      |
|                            | O₂–W₁–O₅ 170.4803°                                                     |
|                            | O₂–W₁–O₆ 99.165°                                                       |
|                            | O₁–W₂–O₂ 77.9856°                                                      |
|                            | O₁–W₂–O₃ 81.6166°                                                      |
|                            | O₁–W₂–O₅ 93.4481°                                                      |
|                            | O₁–W₂–O₆ 81.9709°                                                      |

Figure 6. Effect of fire and flash WO₃ nanocrystallites (a) without annealing and (b) with annealing.

of resultant product. Then this mixture undergoes sonication followed by the addition of diethylene glycol to remove the unwanted bonding between molecules and weak Vander wall’s forces of attraction between them. The main purpose of sonication was to get rid of impurities. Diethylene glycol acted as a surfactant that restricted the particles aggregation. Further, the diethylene glycol also played role in homogeneous dispersion of particles. Therefore after the hydrothermal treatment at 200 °C for 4 h, the cubic unit cells arranged in the form of monoclinic structure were obtained. The white-coloured precipitates were obtained with yellow-coloured suspensions.

\[ \text{Na}_2\text{WO}_4 + 2\text{NH}_4\text{Cl} \rightarrow \text{WO}_3 \cdot \text{H}_2\text{O} + 2\text{NaCl} + 2\text{NH}_3 \]  

These precipitates were washed with ethanol to remove the impurities and suspended ions (Na⁺, Cl⁻) in final product. Finally, after drying white-coloured precipitates of WO₃, H₂O powder was obtained. The hydroxides were not obtained due to the lower concentration of hydroxyl ions (1). Water molecules were removed during calcination and the precipitates turned yellow because of the change of internal structure, morphology and removal of water molecules at high temperature.

3.3. Tungsten oxide nanocrystallites as fuel additive

After detailed structural and morphological investigations of as-prepared WO₃ and annealed WO₃, their potential application studies were carried out. The potential application studies include the fuel additive properties. Following fuel additive properties of diesel oil were carried out using prepared WO₃.

3.3.1. Fire and flash point

Fire and flash points of pure diesel oil are 70°C and 79°C respectively which is higher than the diesel oil modified with both WO₃ (A) and WO₃ (B) nanocrystallites. However, these were decreased with increased WO₃ concentration of fuel additive in both cases. The graph showed a linear decrease in fire and flash points that means synthesized material is a good catalyst to increase the efficiency of fuel. But this decrease in fire and flash points is more prominent in case of WO₃(b) (up to 49 and 54°C respectively, at 80 ppm) as compared to WO₃(a) (up to 58 and 62°C respectively, at 80 ppm).

As per graph, the decrease of fire point in case of WO₃(a) was almost linear and continuous but the decrease in flash point was abrupt (Figure 6a). Whereas, with WO₃(b) the decrease in values was not continuous.
as values decreased dramatically when concentration increased to 20 ppm (Figure 6b). However with increasing concentration up to 80 ppm, the decrease in values was not significant. This temperature difference indicated that diesel fuel modified with WO3(b) can perfectly be used as analytical as well as commercial scale. The decreasing fire and flash point of diesel fuel indicated the burning of fuel at lower temperature after adding fuel additive [36].

3.3.2. Cloud and pour point
Pure diesel has cloud point 11 °C. The pure diesel has pour point 4 °C. These both points of pure diesel are higher than those of diesel oil modified with WO3(a) (2 and −6 °C respectively) and WO3(b) (−2 and −7 °C respectively). The maximum efficiency in terms of pour point and cloud point was achieved for additive concentration increased up to 80 ppm. The detailed values are given in Table 2 and 3. The results of these two modified fuels depicted that the catalytic power of WO3(b) nanocrystallites is significantly higher than WO3(a) nanocrystallites. As clear from the graphs, the decrease of cloud and pour points in both cases was linear and continuous (Figure 7a and b).

Cloud and pour point values are known as freezing properties of fuel. Since fuel additive at nano-level can be dispersed easily in the diesel oil, therefore, it got dispersed everywhere among the molecule of fuel. Besides, these particles restricted the wax crystals to in touch with each other and diesel fuel did not solidify at lower temperatures. Thus decrease in cloud and pour point values did not allow the fuel freeze in low-temperature areas that means additive perfectly catalyses the diesel fuel. Thus the engine performs efficiently in such severe weather conditions [37].

3.3.3. Specific gravity and kinematic viscosity
The specific gravity and kinematic viscosity values of pure diesel oil are 0.8309 g cm$^{-3}$ and 1.79 $\times$ 10$^{-6}$ m$^{-2}$ s$^{-1}$ respectively. Fuel additives were used to observe the change in specific gravity and kinematic viscosity values of diesel oil. When these nanocrystallites such as WO3(a) and WO3(b) of 20 ppm concentration were added to fuel, the strange phenomenon was noticed. A significant escalation in the values of both specific gravity (0.8562 g cm$^{-3}$ and 0.8638 g cm$^{-3}$ respectively) and kinematic viscosity (1.94 $\times$ 10$^{-6}$ m$^{-2}$ s$^{-1}$ and 1.99 $\times$ 10$^{-6}$ m$^{-2}$ s$^{-1}$ respectively) was observed. This increase continued by increasing both catalysts dosage. As shown in graph, it is clear that WO3(b) comparatively behaved as an efficient catalyst as increase in values of specific gravity and kinematic viscosity with WO3(b) was more prominent and made diesel fuel more viscous as compared to pure diesel oil and with WO3(a) nanocrystallites (Figure 8a and b).

Diesel fuel allowed these nanocrystallites to enter the spacing between layers. Therefore, the compactness of fuel got increased which can be seen by increasing values of kinematic viscosity in graph. Graphs showed that the rate of flow of liquid decreased with increasing catalyst dosage which means this fuel additive increased the friction among layers of fuel. Turbulence flow of diesel decreased in engine by adding fuel additive. Consequently, it provides enough lubrication to engine but it might increase the amount of exhaust and smoke emission production upon burning. Thus the amount of dosage can be laid between these two contradictory facts. Same in case of specific gravity also increased upon additive concentration as it filled the spaces between layers and fuel layers became compact.
by the introduction of attractive forces such as Van-de-wall’s forces between them. Higher specific gravity referred to fill inter-atomic distance that means increased energy content of diesel fuel with fuel additive. As a result, the performance of diesel fuel could be efficiently increased [38].

3.3.4. Calorific values
With the addition of different concentrations of WO$_3$(a) and WO$_3$(b) nanocrystallites (20, 40, 60, 80 ppm), the calorific values of diesel fuel were measured (Tables 2 and 3). It can be seen from graph that the calorific values of pure diesel oil are lower as compared to modified diesel oil with WO$_3$(a) (34,130 J g$^{-1}$) and WO$_3$(b) (36,580 J g$^{-1}$) (Figure 9a and b).

The unit amount of heat energy released after burning of unit volume of fuel is referred to as calorific value. Increasing calorific values depicted the exothermic reaction means more heat energy produced by less amount of fuel. Thus the less amount of fuel is consumed. As per experimental observations, the tungsten oxide nanocrystallites in both forms provided oxygen for the oxidation of fuel. Therefore, sites for oxygen transport are available in the structure of nano semiconducting fuel additive as it acts as catalyst in fuel. The fuel molecules get adsorbed on the surface of
nano-semiconducting material where enough oxygen transport sites available as at nano-level it has increased active sites.

Thus the fuel has a significant amount of oxygen supply for burning of fuel. Consequently, WO$_3$(b) makes a significant increase in calorific values of fuel comparatively because the crystallinity and dispersion increased of tungsten oxide after annealing. Although, particle size was smaller before annealing but active sites were not exposed to fuel due to a lot of aggregation. Therefore, water molecules evaporated at high temperatures which caused the aggregation of particles in WO$_3$(a) nanocrystallites without annealing [39].

Summing up, the above discussion revealed that WO$_3$(a) and WO$_3$(b) nanocrystallites have increased the performance and physical characteristics of diesel fuel. As kinematic viscosity, calorific values and specific gravity get increased upon additive addition whereas the fire and flash points and cloud and pour points get plunged. As a result the engine efficiency gets increased.

4. Conclusion

In this research work, WO$_3$ nanocrystallites were successfully synthesized via simple solvothermal synthesis approach. WO$_3$ is a low cost material and shows its absorption in visible region. Moreover, I presented experimental results on the formation of tungsten oxide nanocrystallites which demonstrated the effect of annealing on its morphology, structure, elemental composition and catalytic properties. The crystal structure and colour of tungsten oxide nanocrystallites are dependent strongly on temperature, experimental parameters which were revealed by the characterization of final product. SEM observations showed more irregular shapes along with coagulations. The size of particles is smaller than the material annealed at 600°C which is comparatively larger. Tungsten oxide crystallized in a monoclinic structure at high temperature explained by the X-Ray diffraction technique. Further, the fuel additive application of WO$_3$ was also studied. Kinematic viscosity and specific gravity get increased upon additive addition, whereas the fire and flash points and cloud and pour points get plunged. As a whole, total energy content and engine efficiency got increased.

Acknowledgement

Author is thankful to the University of Hafr Al Batin, Saudi Arabia.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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