

Incorporation of Metal Nanoparticle to Enhance Tungsten Oxide (WO₃) Films Properties: A Mini Review

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ABSTRACT

Researchers previously focused on tungsten trioxide (WO₃) modified with noble metals. Different methods were used for syntheses such as pulsed laser deposition, co-sputtering metallic, colloidal chemical method, one-pot method, sol-gel, and hydrothermal methods. The photo-catalytic performance and sensing properties of WO₃ were extremely enhanced. This review aimed to examine the increasing significance of WO₃ based on previous studies and possible future outlook.

Keywords: Incorporation, Metal nanoparticles (MNPs), nanostructure thin film, sensing property, tungsten oxide

1. INTRODUCTION

Semiconductor nanoparticles (NPs) are materials with excellent properties such as electrical, optical, and unique structural features as compared with bulk material [1-3]. The incorporation of NP materials into composites has led to promising catalytically, physical, chemical, and optical properties [4-7]. Tungsten oxide (WO₃) is a yellow powder with a 1473 °C melting point, 1700 °C boiling point, and density of 7.16 g/cm³. It is insoluble in water and acid (except hydrofluoric acid) and soluble in ammonium hydroxide, forming a tungstate [8-10]. WO₃ is an n-type semiconductor material with a wide bandgap (2.8 eV) and exists in different crystallographic phases including orthorhombic, cubic, hexagonal, and monoclinic. It is stable to UV and visible radiation and has excellent sensitivity and selectivity [11-15].

Many differentials of Nano-tungsten (NW) have been generated, such as Nano rods (NRs), NPs, Nano-sheets (NSs), nanowires (NWs), and Nano-flower (NFs) for the industrial scale, resulting from a variety of methods [16-25] such as spray pyrolysis, electrode position, sol-gel, hydrothermal method and anodization [26-29]. WO₃ is a promising material due to its distinct properties such as electro chromic and photo catalytic features [30-33]. Its potential applications include field-emission devices, photo-catalysts, solar energy devices, gas sensors, and electrode materials for secondary batteries [34-43].

In particular, metal NPs with high conductivity such as palladium (Pd), gold (Au), platinum (Pt), copper (Cu), and silver (Ag) are used to enhance the sensing properties or chemical sensitizers [44-46]. Hybrid metal-semiconductor NPs are materials with multicomponent hetero-structure Nano-systems that enhance tenability due to Nano scale interactions between the disparate metal and semiconductor components [47-49].

Many studies have demonstrated the effect of superconductive metals on the properties of WO₃. Several publications have explained the enhancement of properties of WO₃ via core-shell structure, composite, and metal decoration such as Ag, Au, Cu, Pd, and Pt. This study prepared to conduct a literature review on the enhanced properties of WO₃ NPs and Nano composites (NCs) using 23 studies that were conducted from 2006 to 2021.

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2. LITERATURE SURVEY

2.1 Applications of Tungsten Oxide incorporate with Metal Nanoparticle

2.1.1 Sensors

WO₃ thin film gas sensors were synthesised by exciplex pulsed laser deposition in 2006 by M. M. H. Bhuiyan *et al.* The effect of doping of Au, palladium (Pd) or platinum (Pt) on the WO₃ thin film was investigated by DC sputtering during pulse laser deposition. The oxygen pressure and the substrate temperature during deposition were 400 °C and 100 mTorr, respectively. The WO₃ thin films doped with Au, Pt, or Pd had higher sensitivity than un-doped WO₃ thin films [48]. A. Karupphasamy and A. Subrahmanyam in 2007 synthesised Ti-doped WO₃ in the presence of argon and oxygen. WO₃ thin films were doped with Ti by the co-sputtering method. The electrochromic properties of Ti-doped WO₃ were investigated in three steps [49]. Their results showed that the coloration efficiency (CE) and optical modulation (ΔT) for the Ti-doped WO₃ thin film deposited at an oxygen pressure of 4×10^{-3} mbar were superior to ideal CE (66 cm²/C) and ΔT (70%) at 550 nm [50].

In 2008, H. Xia *et al.* fabricated NO₂ gas detectors via the colloidal chemical method to prepare Au and Au-doped WO₃ powders. Their results showed that doped WO₃ sensors have excellent gas sensing properties. Compared with undoped WO₃ [51]. Au-doped WO₃ sensor at 1.0 wt% showed high response, very high response/recovery, good selectivity, and long-term NO₂ stability compared with others at a low operating temperature of 150 °C [52].

In 2011, Pt NP-functionalized WO₃ hybrid NRs and their gas sensing properties were fabricated by a one-pot method by X. Liu *et al.* The decorated Pt-WO₃ sensor exhibited very fast response and recovery times and very high sensitivity compared with the undecorated sensor [53]. The enhancement in sensing property was attributed to the effect of the spill over for Pt NPs and the interaction to support the electronic metal [54].

WO₃ nano-plates (NPTs) modified by Ag NPs for enhancing the selectivity and low-temperature response of WO₃ sensors was developed in 2013 by D. Chen *et al.* They used a wide concentration range (0.5–50 ppm) of NO gases to evaluate gas sensing properties from room temperature to 250 °C. Their results showed the best performance for the sample with 0.5% AgNPs. The operating temperature was excellent at about 170 °C, but a response was also observed at room temperature. The selective response was better for NO gas based on Ag@plate-WO₃ through different gases (CO and H₂) with organic vapours (e.g. acetone, alcohol, benzene, and methanol). The properties of NO sensing for the Ag@WO₃ sensors changed with morphologies of WO₃ nanocrystals (NCs) [55]. The NO sensing performance was enhanced in the WO₃ samples with plate-like structure compared with that in samples with particle-like samples [56].

In 2014, M. Horprathum *et al.* synthesised a highly sensitive sensor to H₂ based on WO₃; DC magnetron sputtering technique and deposition by glancing angle were carried out to fabricate WO₃ NRs, which were decorated with Pt NPs via DC sputtering at different deposition times (2.5–15 s) at 150 °C–350 °C working temperatures over a low H₂ concentration range (150–3000 ppm) [57]. The Pt deposition time increased to 10 s; the H₂ response increased with the deposition time, causing substantial deterioration. Sensors based on Pt-WO₃ NRs have a very high H₂ response at 200 °C from 1530 and 214,000 ppm to 150 and 3000 ppm, respectively [58].

In 2014, X. Bai *et al.* prepared Cu-doped WO₃ hollow fibres by electro-spinning method, followed by sol-gel technique; reasonable sintering operation showed their potential application for semiconducting gas sensors for diabetes diagnosis [59]. The Cu (3 mol%)-doped WO₃ hollow fibres prepared by quenching demonstrated good selectivity to acetone and the high response due to junction structure and high surface-to-volume ratio [60].

In 2015, T. Tesfamichael et al. used Fe materials to dope WO₃ thin films under many concentrations (0%–2.6%) at room temperature via alumina and glass substrates by DC reactive sputtering and annealing for 1 h in the air at 300 °C. The WO₃ thin films deposited on the glass substrate exhibited the same transmittance at 70%, but the WO₃ film's optical bandgap decreased from 3.30 eV to 3.15 eV during doping with Fe (2.6%) [61]. The properties of the NO₂ gas sensor were enhanced by comparison at a low operating temperature of 150 °C due to an enhancement in the defect number more than the (WO₃) thin film [62].

During the same year, N. M. Vuong et al. prepared an easy technique to synthesise extreme porous WO₃ embedded by Au NWs for active sensing of H₂S and CH₄ gases; their technique resulting in a considerable improvement in sensing responsiveness [63]. Au-NPs have been decorated on WO₃ NWs by dipping with the solution of HAuCl₄, followed by oxidation that remarkably improved the performance of the sensors [64].

In 2016, M. Takács et al. added Pt and Au NPs to hydrothermally grow hexagonal WO₃ NRs. The drop casting method activated with WO₃ reference was deposited on the top of a micro hot plate with Au and an inter-digital electrode on top. The gas sensing properties for H₂S and NH₃ were measured at 140 °C–300 °C [65]. The gas sensitivity for H₂S doubled due to noble-metal NPs, whereas no notable impact could be detected for NH₃ [66].

The gaso-chromic response of WO₃ nanoneedles (NNs) was studied in 2016 by M. U. Qadri et al. They used aerosol-supported chemical vapour deposition (CVD) with co-deposition of Pt and Au NPs in a single-step method upon the exposure to NH₃ (100 ppm) [67]. Their results showed that the metal-WO₃ NNs had a very high response but slow recovery dynamics in a few minutes [68]. Noble metals are introduced into sensing materials to increase gas sensing performance. In 2017, Au NP-decorated WO₃ NRs were prepared by L. Liu et al. to enhance the sensitive and selective trim ethylamine (TMA) gas sensors compared with WO₃ NRs [69]. Their study provided strategies and insights into the preparation of sensing materials [70].

A new structure of core-shell NS Au@WO₃ was prepared for NO₂ detection in 2019 by S. Zhao et al. Their results showed that pure WO₃ NSs had poor performance compared with Au@WO₃ CNNSs, due to the enhanced sensing properties of NO₂ in the detection area, response/recovery times and response at the excellent operating temperature of 100 °C [71].

In 2019, via electron beam evaporation, pure, Au and Ag-doped WO₃ nano-structure films were synthesised on glass substrates by G. Adilakshmi et al. They found that the bandgap, film crystallinity, and transmittance decreased with dopants, and the Au and Ag-doped WO₃ thin films exhibited rough surface compared with WO₃ thin films, these films are best suited for gas sensor applications [72]. Moreover, the band gap values for WO₃, Au, and Ag are 3.4, 3.04, and 3.24 eV, respectively [73].

Gas sensors based on localized surface plasmon resonance are promising because of their excellent tuneable functional properties, as reported by N. M. Figueiredo et al. in 2020. Au NPs precipitated on the oxide matrix were reduced by treatments such as thermal annealing until 500 °C [74]. Local voids in the Au NP vicinity were present for all temperature ranges and in a broad type of Au-WO₃ NCs [75].

In 2020, W. Li et al. synthesized Au NP-decorated WO₃ NRs, and the electrostatic interaction method was used to deposit Au NPs over 1D WO₃ NRs. The bandgap for WO₃ NRs increased after Au NPs were incorporated due to the dipole moment association of Au NPs and WO₃ NRs under light induction. Au NP/WO₃ NR hetero-structures influenced by NLO were enhanced due to the association of NLS, efficient charge@energy transfer, and free-carrier absorption at the Au NP/WO₃ interface [76]. The Au/WO₃ NR hetero-structures are excellent for optical specific to protect device sensitivity and human eyes from damage due to high-power laser [77].

In 2021, L. Aamir synthesised a novel NC from Ag/WO₃ by co-precipitation. It had an indirect bandgap of 2.9 eV and improved charge separation. The P-type conductivity revealed that silver functions as an acceptor at 1.4 eV up to the valence band [78]. The current-voltage graph for the Ag-WO₃/Ag Schottky junction is summarised with a knee voltage of 0.59 V, thereby suggesting that p-type NC semiconductor can be used for optoelectronic application [79].

Metal oxide semiconductors have attracted attention for use as gas sensors due to their ability to detect toxic gases, and explosive and inflammable gases. WO₃ NPs was developed by D. L. Feng *et al.* in 2021 via decorating with silver and platinum bimetal through combined hydrolysis and hydrothermal strategies. Their results showed that gas sensing for acetone was high, which reduced the recovery times of Ag and Pt/WO₃ NPs relative to the original (WO₃ NPs) [80]. Thus, Ag and Pt WO₃ NPs) have electronic chemical sensitivity, which can improve the absorption of oxygen species. This process accelerated the reaction of the product to enhance the response of sensing for application to other sensing materials, such as gas sensors [81].

2.1.2 Photocatalytic

Au NP-decorated WO₃ NRs were synthesised to enhance a novel photo-catalysis and gas-sensing thin-film material by Q. Xiang *et al.* in 2010. Their results showed that the photo-catalytic performance of (rhodamine B) (RhB) and reducing gas sensing properties (hydrogen, methanol, and ethanol) extremely increased. Au@WO₃ NRs have a very high response for H₂ at 50 ppm with a low recovery time of about 10 s. Their selectivity of H₂ gas detection about $R_a/R_g = (6.6)$ was much higher than WO₃ NRs [82]. The photo-catalytic properties were high for the ultimate dissolution of RhB at 120 min when simulated to solar irradiation [83].

In 2011, M. Qamar *et al.* used highly active visible light-driven NCs with sunlight excitation to remove hazardous water pollutants. The WO₃ surface of visible light-active Nano-structured photo-catalyst was modified by using noble metals, such as Au and Pt. Differences in the photo-catalytic efficiency of NCs were due to the size of the deposited metals [84]. The Pt/WO₃ Nano composite demonstrated good recyclability and stability under the experimental conditions [85].

In 2020, based on the method of cationic adsorption, J. C. D. Álvarez *et al.* prepared a different method for the deposition of Au metallic NP (MNPs) on WO₃. The compound on the WO₃ surface was tested for adsorption efficiency at various times (2, 12, and 16 h) and pH (1, 4, 7, and 10). Complete Au deposition on WO₃ was obtained at 16 h and pH 10 [86]. The optimum performance was obtained by utilizing Au/WO₃ (0.5 wt.%), and Au NPs enhanced the Fermi level towards more negative values. Under optimal Au loading, the water molecules were reduced as the photocatalytic activity increased [87].

2.1.3 Photochemical

In 2019, two various approximations were improved to paper (core/shell) nanostructures (NSTs) based on W/WO₃ in a mixture with H₂ reduction by K. A. Abdullin *et al.* [88]. Their results showed that W/WO₃-NSTs have excellent electro-chemical performance compared with pure WO₃ [89].

In 2019, Y. Liu *et al.* decorated WO₃ with Au NPTs to improve the photoelectron chemical (PEC) performance of photo-anode. Hydrothermal treatment was used to fabricate WO₃ plates on FTO-coated glass, and Au-NPTs were combined by immersing the substrates in Au-NPTs under various time periods [90]. The photo-current density was enhanced under irradiation by simulated sunlight, and the photo-activity improved when WO₃ was decorated with Au-NPTs [91]. This work showed an easy technique to decorate Au-NPTs on WO₃ photo-anodes by improving the performance of solar energy conversion [92].

3. CONCLUSION

The promising properties of WO₃ MNP have been investigated previously, in which researchers focused on enhancing the sensing properties. They found the Incorporated of MNPs into WO₃ improvement the photocatalytic activity, photochemical and sensing properties. These materials used in many applications such as; photo-sensors, gas-sensors and photo-catalytic.

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