Morphological, Structural and Optical Characterization of Bottom-Up Growth of Ag-WO₃ Core-Shell Nano-Cube Heterostructures

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Abstract: A new class of nano-cube core-shell heterostructures containing Ag coating on the top of WO₃ was fabricated. Physical vapor deposition was used to produce WO₃ based nano-heterostructures. All kind of wet toxic chemical process was avoided to make the process simple and contaminant free. Sputtering of WO₃ and a subsequent thermal annealing process was done to create nano-cubes of WO₃. After that, sputtering of Ag was performed to form the Ag-WO₃ core-shell nano-heterostructures (CSNH). The CSNHs were characterized using field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), X-ray diffraction analysis (XRD) and UV-vis spectroscopy. The morphologies, elemental analysis, interfaces, crystallinity, phases, and chemical compositions were analyzed. The bottom-up growth of WO₃ nanocubes was studied using different time periods at 900°C. Ag coating was also studied before and after annealing. Finally, an optical property (band gap) was also analyzed using Tauc plot derive from absorption spectra. The tailoring the band gap of WO₃ from ~2.9eV to ~ 2.45 eV was observed while Ag-WO₃ CSNH formed.

Keywords: nano-cube; heterostructures; bottom-up growth; electron microscopy; bandgap; Ag-WO₃

1. Introduction

In recent years, manipulation and fabrication of oxide-based core-shell heterostructures and the creation of interface among transition metal oxides have presaged the latest era of materials research. It is enabling an exceptionally discrete set of coinciding material properties to be pooled with an escalating degree of experimental control. Transition metal oxides are also known as semiconducting materials having a wide band gap, which can be tuned while being used as heterostructures. To tune the band gap facilitates rapid charge transport [1] and unique photonic[2] properties which are not possible with a single component or similar structures. Transitional metal oxide heterostructures systems have already exhibited such diverse application as a photocatalyst, photodetectors, FET, LED, gas sensor, chemical sensor, super capacitors, solar cells and surface acoustic wave filters [3-7]. To completely utilize these affluence; it is required to comprehend and be able to control the physics on the smallest scales, creating the exploitation of nanoscale heterostructures. Some of these avenues have already been explored for different applications.

Solar energy is a clean and renewable source of energy. It has acknowledged for photo-degradation of environment pollutants [8-13]. Various metal oxide nanostructures are used for photocatalytic applications [14-18]. The photochemistry of oxide nanoparticles has established a significant concern due to their particular photocatalytic behavior [17,19,20]. Apart from this photocatalytic behavior, numerous researches have been conducted on metal oxide semiconductor (such as TiO₂, In₂O₃, WO₃, ZnO, SnO₂) thin film coated gas sensors to detect industrial effluents NH₃, H₂CO, H₂S, ethanol and methanol [21-24]. In recent times, metal oxide nanostructures (such as nanoparticles, nanotubes, nanowires, nanobelts) have proved to be suitable for chemical sensors as
they have a distinctive surface, small-size, and quantum effects. Nanostructures based on transitional metal oxide characteristically have a quicker response due to their very high surface-to-volume ratios. Some literature drew attention towards metal oxide heterostructures, for example, ZnO coated with Ag, WO3, Zinc Tin Oxide (ZTO) and CdS for better photocatalytic and gas sensor application. Similarly, CuO/CaO showed better photocatalytic behavior than simple metal oxide (CuO) nanostructures [3, 5, 17, 25-28]. For better chemical sensing and catalysis, CNT coated Ni/NiO core-shell heterostructures were also studied in the literature [26]. Ag-AgBr coated Al2O3 heterostructure was reported for photo-degradation of industrial contaminants [29]. Ag-coated ZnO, WO3, and MnO2 were also explored for photocatalytic applications, better chemical sensor and supercapacitors respectively [7, 25, 27, 28]. Among the various oxides, WO3 has a graphene-like 2D layered structure [30] with wide band gap (~2.8eV) [31]. This limits its optical responsivity in the visible region of the electromagnetic spectrum for photocatalytic application. Hence, bandgap tuning of WO3 is essential since it governs the energy necessary for the generation of electron-hole pairs. Metal particles such as Ag act as localized surface plasmons (LSP), which attribute electromagnetic waves joined to the combined oscillations of electrons [32]. Ag can tailor the band gap of WO3 in such a way that the spectral response of Ag-coated WO3 heterostructures can be extended to the visible region.

Metal oxide heterostructures drew attention due to their low cost and better photocatalytic/sensing behavior than precious materials. It can be synthesized using a wide array of methods including solution synthesis, gas phase growth i.e. physical/chemical vapor deposition (PVD/CVD), flame synthesis, air oxidation. Gas-phase methods, specifically CVD and pulsed laser deposition (PLD), were used to maintain atomic level control of stoichiometric ratio and perfect particular site deposition. Due to their high cost and low throughput, these processes are not accepted widely for general industrial applications. Sputtering deposition, another tradeoff gas phase technique, have been considered because of its potential for assembling heterostructures, comparably lower cost and high throughput than other gas phase methods [33].

Here, we report a new choice of core-shell nano-heterostructures (CSNH) of Ag-coated WO3 (Ag-WO3) CSNH. Physical vapor deposition (PVD) technique (sputtering) is used to obtain a thin layer, and a subsequent thermal annealing process was used to grow the Ag-WO3 CSNH. All traditional hydrothermal processes were avoided to keep the process simple and reduce the use of toxic chemicals. The nanostructures were extensively characterized for their phases, crystal structures, morphologies and elemental analysis. A field effect scanning electron microscope (FESEM) was used to understand the growth mechanism and morphology. Energy dispersive x-ray spectroscopy (EDX) was performed to confirm the elemental analysis. X-ray diffraction analysis was also conducted to comprehend the phase and crystalline properties of the materials. Along with this, UV-vis was evaluated to calculate the band gap energies of Ag-WO3, which is optically more viable than WO3 for photocatalytic application.

2. Materials and Methods

2.1 Materials

Silicon (111) wafers were acquired from IWS (Colfax, CA), Isopropyl alcohol (IPA) from Sigma-Aldrich (St. Louis, MO), and Deionized (DI, 18.1 MΩ·cm) water was obtained using a Barnstead International DI water system (E-pure D4641). Both WO3 and Ag targets (2 in. diameter) were purchased from AJA International (North Situate, MA). PVD was performed using an AJA International (North Situate, MA) Orion 3 sputtering system. Thermal annealing was conducted in a box furnace (GMF-110) purchased from MTI Inc. (Redmond, CA). Hexane was used as a solvent for ultra-sonication which was procured from Sigma-Aldrich (St. Louis, MO).

2.2. Growth of WO3 Nano-cubes

A 4” silicon wafer was cleaned using IPA and washed with deionized water. After drying the Si wafer, it was placed into the AJA International (North Situate, MA) Orion 3 sputtering system. The
operating condition for 300 nm thin film of growth was maintained in a high base vacuum pressure of 2×10⁻⁷ torr. Sputtering of WO₃ was led using RF power source at 50 W, 150 V with 6.54×10⁻³ torr working pressure. On top of that, 25.1 sccm Ar flow rate, and 25 rpm substrate rotation speed was maintained at a deposition rate of 0.2 Å/s recorded by a quartz thickness monitor. After sputtering of WO₃ thin film on Si wafer, it was placed in a crucible and air annealed at ~900°C for 180 min, 240 min and 300 min in a box furnace. After thermal annealing, the furnace was then cooled naturally in the air. Approximately, the 2×2 cm² area of a silicon wafer containing WO₃ nanocubes was ultrasonicated using hexane as a solvent to prepare a solution for UV-vis.

2.3. Sputtering of Ag onto WO₃ Nano-cubes

The sample of WO₃ nanocubes on Si wafer was loaded into the sputtering chamber. The high base pressure of the chamber was pumped to below 2×10⁻⁷ torr. Sputtering of Ag was implemented using a DC power source at 15 W, 750 V with 6.54×10⁻³ torr working pressure. Ar flow rate was maintained 25.1 sccm in the chamber with 25 rpm substrate rotation speed. The sputtering rate was 0.6 Å/s recorded by a quartz thickness monitor. The subsequent heterostructures are stated to as Ag-WO₃ core-shell nano-heterostructures (CSNH). Approximately, the 2×2 cm² area of a silicon wafer containing Ag-WO₃ CSNH was ultra-sonicated using hexane as a solvent to prepare a solution for UV-vis before and after 60 min of annealing at inert atmosphere (Ar). The figure, 1 illustrates the schematic fabrication process of CSNH.

![Figure 1. Schematic representation of step-by-step fabrication of Ag-WO₃ CSNH](image-url)
2.4. Characterization Methods

A field emission scanning electron microscopy (FESEM, JEOL-7000, equipped with an Oxford EDX detector) was used for morphological characterization and energy-dispersive X-ray spectroscopy (EDX). Philips X'Pert-MPD X-ray Diffraction (XRD) system was used for phase and crystal structure analysis. UV–vis spectroscopy was implemented (absorbance spectra) using an Ocean Optics USB 4000 spectrometer (Dunedin, FL) equipped with DH-2000 UV-vis-NIR light source. The absorption coefficient is defined by the Beer-Lambert’s law as $\alpha = \frac{2.303 \times \text{Abs}}{d}$, where abs and d are the absorption and thickness of the sample holder. Tauc plots were plotted by assuming direct band gap transition and plotting $(\alpha h \nu)^{1/n}$ vs. $h \nu$ where $n=1/2$. The direct band gap were acquired from extrapolating the straight portion of the plot of $(\alpha h \nu)^{2}$ versus $h \nu$ on X- axis at $\alpha = 0$.

3. Results and Discussion

The figure, 2 represents the FESEM micrograph of WO$_3$ after each step including as sputtered (Figure,2A) and after annealing at 900°C for different time periods (Figure,2B-2D). The formation of nano-cube WO$_3$ was evident from the FESEM images (Figure,2B-2D). Thermal process directly enhances the formation of nano-cube WO$_3$ from the sputtered WO$_3$. This is a bottom-up growth of nanoparticles – the vapor-solid (VS) growth mechanism drives this growth process [33]. The diameter of WO$_3$ nanocubes was varied from ~90nm to ~340 nm (Figure, 2E). The figure,2F represents the EDS analysis of growth particle to confirm the elemental analysis. From the spectrum, Tungsten (W) and Oxygen (O$_2$) peak confirm the growth of WO$_3$.

The figure, 3 shows that FESEM image of Ag-WO$_3$ before (Figure, 3A) and after annealing (Figure, 3C) and their corresponding EDX spectrum (Figure, 3B, and 3D) respectively. From the EDX spectrum, the presence of Ag was confirmed. After annealing, Ag coating was revealed on the edge of the WO$_3$ (Figure, 3C).
Figure 3. FESEM micrograph of Ag-WO₃ CSNH A. Before annealing B. Corresponding EDX based elemental analysis C. After annealing (300°C for 60 min in Ar atmosphere) D. Corresponding EDX based elemental analysis

The figure demonstrates the XRD results of WO₃ after sputtering and different annealing time. As sputtered WO₃ (Figure 4A) shows amorphous characteristics of WO₃. Only Si peak (PDF # 80-0018) was identified as Si was used as a substrate. But after annealing at 900°C for different time periods, the structure started becoming crystalline and monoclinic WO₃ (PDF # 76-1134) was found. No significant change was observed in phase and crystallinity after annealing in different time periods.
Figure 4. XRD patterns for WO₃. A. As sputtered, annealing at 900°C B. 300 min C. 240 min D. 180 min

After coating with Ag on the WO₃, XRD was performed again to confirm the phase and crystallinity before and after annealing (Figure, 5B, and 5C). A clear peak of Ag (PDF # 76-1134) was observed after coating with Ag. The significant change of Ag peak was identified after annealing because of better crystallinity.
Figure 5. XRD patterns of the A. As sputtered WO₃, B. Ag-WO₃ annealed for 60 min at 300°C, C. Ag-WO₃ before annealing D. Annealed WO₃.

Figure 6. UV-vis absorption spectra of WO₃ (A), Ag-WO₃ before (B) and after annealing (C)

The figure, 6 shows the UV-Vis absorption spectra of the WO₃ (Figure, 6A), Ag-WO₃ before (Figure, 6A) and after (Figure, 6A) annealing. It was observed that there is a lot of changes in major excitation absorption peaks compared to the WO₃ (~250 nm) and Ag-WO₃ (before ~275 nm and after annealing ~ 280 nm).
The direct band gap of the CSNH (Figure, 7) was estimated from Tauc plots of $h\nu$ versus $(\alpha h\nu)^2$ for the absorption coefficient $\alpha$. The band gap of WO$_3$ was calculated ~ 2.9 eV which matched with the literature[31]. The band gap of Ag-WO$_3$ was calculated (Table 1) 2.68 eV and 2.45 eV before and after annealing respectively. The band gap tailoring was identified due to the morphology of CSNH and quantum confinement effect [34]. Interfaces of Ag-WO$_3$ nanocubes heterostructures strongly affects the charge transfer and separation mechanisms[33]. This is due to the Ag nano-layer which is act as a localized surface plasmons (LSP). This separation mechanism attributes the electromagnetic waves to combine the electron oscillations[32]. And this process allows reducing the band gap (Figure, 8.) of the core cell structure. Subsequently, this tailoring band gap permits more visible light interaction with the CSNH than controlled WO$_3$. Tuning the band gap features, the CSNH reflects the promise of this heterostructures as a photocatalysis.

### Table 1. Summary of the band gap analysis using UV-vis absorption

<table>
<thead>
<tr>
<th></th>
<th>Band Gap (eV)</th>
<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td>WO$_3$</td>
<td>2.9</td>
<td>428</td>
</tr>
<tr>
<td>Ag@WO$_3$</td>
<td>2.68</td>
<td>464</td>
</tr>
<tr>
<td>Annealed Ag@WO$_3$</td>
<td>2.45</td>
<td>506</td>
</tr>
</tbody>
</table>

**Figure 7.** Band gap energy of WO$_3$, Ag-WO$_3$ before and after annealing using UV-vis absorption
4. Conclusions

In summary, the study reports the fabrication of core-shell nano-heterostructures. The fabrication comprised of WO₃ nano-cubes coated with a thin shell of polycrystalline Ag avoiding all wet chemical routes. Sputtering of WO₃ was done on Si substrate, and then the thermal growth of WO₃ nanocubes was performed in a box furnace, and again Ag was coated on the surface of the WO₃ nanocubes by sputtering. The morphologies, interfaces, elemental analysis, crystal structures, phases and band gaps of the heterostructures were characterized using FESEM, EDX, XRD and UV-vis spectroscopic methods. FESEM images confirmed the particle size, morphologies of the WO₃ and the interfaces created between Ag and WO₃. EDX supported the elemental analysis of CSNH. On top of that, XRD approved the crystallinity and monoclinic phase of WO₃ and presence of polycrystalline Ag coating. In conclusion, band gap analysis of Ag-WO₃ nano-cubes heterostructures exposed alterations of absorption peaks compare to pristine WO₃ nanocubes and band gap tailoring which could be accredited to the quantum confinement effects of heterostructures.

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Author Contributions: N. C. and M.I. designed the experiments; M.I. performed the experiments; N. C. and M.I. analyzed the data, M.I. wrote the paper

Conflicts of Interest: The authors declare no conflict of interest.
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