Summary

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Multielement–Doped Tungstic Acids via Submerged Photosynthesis for Enhanced All-Solar Photoelectrochemical Responses

The purpose of this dissertation is to achieve multielement doping of tungstic acid via the submerged photosynthesis of crystallites (SPsC) method, in order to enhance the performance of bifunctional materials capable of simultaneously solar conversion and storing energy, enabling more flexible solar energy storage.

First, in Chapter 1, I discussed the motivation for developing solar energy storage materials and how to achieve low-cost and efficient solar energy storage. In Section 1.1.1, I reviewed the history of energy development over the past century. Through comparison, I concluded that clean and unlimited solar energy not only serves as an excellent alternative to fossil fuels but also offers the flexibility to generate electricity without the need for large power plants or extensive grid infrastructure. This decentralized nature has the potential to significantly improve human living conditions. However, due to fluctuations in sunlight availability, it is essential to establish an effective method to store solar energy during peak sunlight hours for use during periods of insufficient sunlight.

In Section 1.1.2, I briefly reviewed the historical development and fundamental principles of solar energy. In Section 1.1.3, I compared the existing methods for solar energy storage,

which can generally be categorized into photothermal, photochemical, and photoelectrochemical approaches. Among them, photothermal systems offer high energy conversion efficiency. However, in a society that primarily relies on electricity, the applications of thermal energy storage are limited. Photochemical methods suffer from several drawbacks, such as limited availability of reactants, excessive production of byproducts, low fuel stability, difficulties in storage, and poor energy conversion efficiency. In contrast, photoelectrochemical systems can directly convert solar energy into electrical or chemical energy. The main limitation of this method lies in its low energy conversion efficiency. Therefore, starting from Section 1.2, I began to elaborate on the research background related to improving photoelectrochemical bifunctional electrodes.

In Section 1.2, I introduced several commonly used photoelectrochemical bifunctional electrodes and highlighted the potential of tungstic acid. Tungstic acid is a compound derived from tungsten oxide with incorporated structural water. Tungsten oxide materials have already demonstrated their ability to form tungsten bronze compounds under light irradiation. This reaction is also called a photochromism property widely. Moreover, this bronze compound formation process coincides with the charging reaction of tungsten oxide. Therefore, it is reasonable to infer that tungsten oxide can drive charging reactions through light irradiation, which aligns precisely with the concept of photoelectrochemical bifunctional electrodes.

Recent studies have shown that the incorporation of structural water into tungsten oxide increases its energy storage capacity during charging. However, to date, there have been no studies focusing specifically on the photoelectrochemical bifunctional performance of tungstic acid. Thus, in this research, I aim to analyze the photoelectrochemical bifunctional electrode performance of tungstic acid and explore strategies to enhance its properties.

In Section 1.3, I explained how the doping strategy improves the solar energy conversion performance of tungstic acid by modulating the local electronic states of the solid, reducing thermal losses and extending the absorption range of solar light. Moreover, co-doping with multiple elements can further enhance the photoelectrochemical bifunctional electrode performance of tungstic acid. However, current doping techniques typically require high-

temperature and high-pressure synthesis environments, which result in high production costs and hinder the widespread adoption of photoelectrochemical bifunctional electrodes.

To address this issue, Section 1.4 introduces the SPsC method, a novel fabrication strategy that has emerged in the past decade. The SPsC method enables chemical reactions to form solids under ambient temperature and pressure, driven solely by light irradiation in pure water. This significantly reduces both the raw material and energy costs. While the SPsC method has demonstrated excellent performance in the single element doping of transition metal oxide semiconductors, there have been no reports of its successful application in the multielement doping. Therefore, the realization of multielement doping in tungstic acids via the SPsC method would represent the world's first ambient-temperature, ambient-pressure, low-cost chemical approach for such synthesis. This breakthrough would carry significant implications not only for chemistry but also for industrial applications.

Therefore, in Section 1.5, I summarize the objective of this dissertation: to verify whether the SPsC method can be employed to synthesize multielement–doped tungstic acids, and to investigate how such multielement doping enhances the photoelectrochemical bifunctional electrode performance of tungstic acids.

In Chapter 2, I synthesized pure tungstic acid using the SPsC method to serve as a reference for comparison with the doped samples discussed in later sections. The experimental procedure was straightforward: a fixed amount of tungsten metal was dissolved in 20 mL of 10 wt% hydrogen peroxide solution to form a peroxo-polytungstic acid (PPTA) solution. The resulting solution was then irradiated with 365 nm UV light (30–50 mW/cm^2) for three days to obtain the final product. The synthesized sample was characterized using X-ray diffraction and electron microscopy, and its light absorption properties were analyzed using a UV–Vis–NIR spectrophotometer.

The experimental results presented in Chapter 2 demonstrate that UV irradiation effectively promotes nucleation and crystal growth in the PPTA solution. In the absence of UV

irradiation, the resulting precipitation consists of aggregated nanoclusters with low crystallinity. In contrast, UV-irradiated PPTA generated highly crystalline orthorhombic $WO_3 \cdot H_2O$ nanoflakes. However, these $WO_3 \cdot H_2O$ nanoflakes did not exhibit a significant advantage in light absorption, as revealed by the UV–Vis–NIR experimental results. This indicates the necessity of further modification of tungstic acids to enhance their optical properties.

In Chapter 3, Mo–W binary nanocompounds were synthesized using the SPsC method, based on the approach described in Chapter 2. Quantitative amounts of W and Mo metals were individually dissolved in 20 mL of 10 wt% hydrogen peroxide to form PPTA and peroxo-polymolybdic acid (PPMA) solutions, respectively. These precursor solutions were then mixed in various ratios and irradiated under 365 nm UV light (30–50 mW/cm^2) for three days to obtain the final products.

Based on material characterization by X-ray diffraction and electron microscopy, it was found that varying the ratio of W and Mo ions in the precursor solution led to the formation of three distinct crystal structures. When Mo ions were in large excess relative to W, the resulting products were gray α-$MoO_3 \cdot H_2O$ nanowires. When the Mo/W ratio was approximately equal, aqua-blue $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices were obtained. Conversely, when W ions were in large excess, green $WO_3 \cdot H_2O$ nanoflakes were formed. Energy-dispersive X-ray spectroscopy confirmed that the dopant elements were uniformly distributed within the nanoparticles. X-ray photoelectron spectroscopy revealed a high concentration of oxygen vacancies.

By comparing UV–Vis–NIR experimental results with absorption coefficient computational results based on *ab initio* calculations, it was determined that the synergic effect of Mo doping and oxygen vacancy formation significantly enhanced the infrared absorption of $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices. Furthermore, due to their smallest particle size and favorable crystalline-defect structure, the $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices exhibited the best electrochemical energy storage performance. Therefore, among the three types of crystal structures, $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices represent the most promising candidates for photoelectrochemical energy storage materials.

In Chapter 4, I demonstrated that multielement doping significantly enhances the light absorption properties of $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices, improving their solar energy storage capacitance. The experimental procedure was identical to that described in Chapter 3, with the only modification being the introduction of additional metal dopants. After the formation of $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ nanorices, metal powders of Cu, Fe, and Mn were added directly into the reaction solution. The mixture was then subjected to an additional day of UV irradiation. This process yielded the multielement–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ samples.

From the Rietveld refinement analysis of the X-ray diffraction patterns, it is evident that the crystal structure of $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ remains unchanged after doping with Cu, Fe, and Mn. The variations in lattice parameters suggest the incorporation of dopants, which induces lattice distortion. Electron microscopy further confirms that the multielement–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ retains their nanorice morphology. Additionally, energy-dispersive X-ray spectroscopy (EDS) results verify that the SPsC method enables uniform incorporation of dopants within the nanoparticles.

Starting from the X-ray photoelectron spectroscopy analysis, the characterization results began to differ for the Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ and Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$. The Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ exhibited a higher concentration of oxygen vacancies. However, after co-doping with Fe and Mn, the oxygen vacancy concentration decreased. This trend was reflected in the UV–Vis–NIR experimental results: the Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ showed the strongest infrared absorption, while the Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ exhibited the highest visible light absorption due to the dopant energy levels introduced by Fe. As a result of these optical properties, the theoretical solar energy absorption efficiency of both Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ and Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ reached 81%, representing a 27% improvement compared to the undoped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$.

To compare the photoelectrochemical energy storage performance of Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ and Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$, I conducted further surface and band structure analyses. High-angle annular dark-field scanning transmission electron microscopy revealed a high concentration of oxygen vacancies on the surface of Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$, while Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ exhibited almost no oxygen vacancies. These findings are consistent with the X-ray photoelectron spectroscopy results. However, a notable distinction was that Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ displayed a significant number of planar defects on the surface, suggesting a higher density of energy storage active sites and implying superior photoelectrochemical energy storage performance.

Mott-Schottky analysis further revealed a higher photocarrier concentration in Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$. This can be attributed to its significantly higher doping concentration compared to the Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$, leading to higher carrier densities. This conclusion is supported by density of states calculations based on *ab initio* simulations. Additionally, UV–Vis–NIR experimental data showed strong agreement with the computational results of absorption coefficient from ab initio calculations. These results collectively suggest that although Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ achieves comparable theoretical solar energy conversion efficiency of Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ due to the synergistic effect of Cu doping and oxygen vacancies, the Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ with higher photocarrier concentration and greater density of energy storage sites, expected to exhibit superior photoelectrochemical energy storage performance.

Finally, the results of the photoelectrochemical energy storage performance analysis were consistent with the findings from surface and band structure analyses. The Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ exhibited a higher photocurrent response compared to the Cu–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$. Under both dark and illuminated conditions, the Cu/Fe/Mn–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ demonstrated larger electrochemical capacitance than both the Cu–doped and undoped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$. Notably, the photo-generated capacitance of the Cu/Fe/Mn–doped sample was 18.7 times greater than that of the undoped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$, confirming that multielement doping can effectively enhance the photoelectrochemical energy storage performance of tungstic acid.

According to above results, I made a summary in Chapter 5. In this dissertation, I demonstrated that multielement–doped tungstic acid synthesized via the SPsC method exhibits excellent performance in solar energy storage. UV irradiation successfully synthesized unary, binary, and multielement–doped tungstic acids with great crystallinity at room temperature in an environmentally friendly H_2O_2 solution, offering a low-cost and non-pollution process., which cannot be achieved by traditional process.

From the comparison of absorption experiments and the *ab initio* absorption coefficient calculations, it was confirmed that the incorporation of different dopant elements into tungstic acids results in a cocktail effect. This effect enables the tungstic acids to absorb a wider range of wavelengths, achieving full-spectrum solar absorption. The increase in full-spectrum solar absorption due to multielement doping leads to a 27% enhancement in solar absorption for multielement–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ compared to $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$.

The increase in solar light absorption significantly boosted the generation of photogenerated charge carriers, facilitating photoelectrochemical energy storage reactions. Moreover, defects in the crystalline structure of multielement–doped $Mo_xW_{1-x}O_3 \cdot 0.33H_2O$ provide more active sites for energy storage. These features led to an 18.7 times enhancement in photo-induced capacitance.

This dissertation marks the first time that multielement doping has been used to enhance the performance of a photoelectrochemical energy storage device, and it is also the first time that such a device has been fabricated under room temperature and atmospheric pressure. These findings are a milestone toward the realization of all-solar energy storage.