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WO3 nanoplates derived from NiWO4 were found to have the highest ratio of WO3•2H2O, highest concentration of oxygen vacancy, narrowest band gap, longest electron-hole recombination time, and in turn the highest rate of photodegradation of Azo dye methylene blue.
Tuning the Electronic and Structural Properties of WO₃ Nanocrystals by Varying Transition Metal Tungstate Precursors

Sara Rahimnejadabc, Jing Hui Heab, Wei Chenab, Kai Wceb, Guo Qin Xub

Oxygen vacancy is one type of the most important defects affecting the photocatalytic performance of WO₃. In this paper, WO₃ nanoplates with high density of oxygen vacancies were synthesized from MWO₃ (M= Zn, Cd, Co, Ni) precursors using a sacrificial template method. The structures and morphologies of WO₃ nanoplates were investigated by field emission scanning electron microscopy (FE-SEM), high resolution Transmission Electron Microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) analysis, Photoluminescence (PL), Diffuse Reflectance UV-Vis (DRS UV-Vis) and Time-correlated single-photon counting (TCSPC). The metal tungstates were found to not only act as the precursors but also as structure-directing agents during the growth of WO₃ nanoplates. XRD data revealed that two phases of WO₃·xH₂O (x=1 or 2) were obtained after acid treatment of MWO₃. WO₃ nanoplates derived from NiWO₄ were found to have the highest ratio of WO₃·2H₂O, highest concentration of oxygen vacancy, narrowest band gap, longest electron-hole recombination time, and in turn the highest rate of photodegradation of Azo dye methylene blue. These results show that the structural, electronic and photocatalytic properties of synthesized WO₃ nanoplates can be tuned by varying the transition metal tungstate precursors.

Because of the long-lived photogenerated holes, this strongly suggest that shape and size of WO3 particles may not be the critical factor.

On the other hand, surface oxygen vacancies are intrinsic defects of metal oxides. They are the most reactive sites on the surface and able to modify the electronic and chemical properties of the surface and greatly prolong life time of photoexcited carriers. Therefore the amount of e⁻ and h⁺ on the photocatalytic surface could be a key factor in determining the photocatalytic reaction rate. Liu et al. also reported that the reactivity of a photocatalyst is mainly influenced by its surface geometric and electronic structures. Thus tuning the surfaces structures of WO₃ photocatalysts to generate high-density e⁻ and h⁺ is essential to optimize their photocatalytic performances for targeted reactions. Nowadays surface oxygen vacancy engineering is able to effectively enhance the photocatalytic performances of metal oxides.

Most of WO₃ nanocrystals were synthesized from aqueous solution of transition metal tungstates. Many reports have confirmed the effects of preparation methods, the nature of supports and tungsten precursors on the...
efficiency of WO₃ photocatalysts. However the influence of transition metal tungstate sources on fabricating WO₃ with different optical, electronic and photocatalytic properties has not been systematically studied yet. The present study aims to investigate the effects of precursors on the surface structures and photocatalytic behaviours of WO₃. The monoclinic WO₃ nanoplates with different densities of oxygen vacancies were prepared from transition metal tungstates MWO₄ (M= Zn, Cd, Co, Ni). Their photocatalytic efficiencies were evaluated by photodegradation of methylene blue and are correlated with the changes of defects density in the samples prepared via varying the transition metal tungstate sources.

2. Experimental section

2.1 Chemicals and Materials

Tungsten oxide (WO₃ nanopowder, Sigma Aldrich), methylene blue (MB, Alfa-Aesar), nickel (II) nitrate hexahydrate 99.999%, zinc nitrate hexahydrate 99% (Sigma-Aldrich), sodium tungstate dehydrate 99% (Sigma-Aldrich), cadmium nitrate tetrahydrate (Sigma-Aldrich), cobalt (II) nitrate hexahydrate 99%, nitric acid 70% (Sigma-Aldrich) were used as received without further purification. Ultrapure deionized water was prepared by millipore purification system.

2.2 Preparation of MWO₄ (M= Zn, Cd, Co, Ni)

M (NO₃)₂ and Na₂WO₄ aqueous solutions with a molar ratio 1:1 were mixed at room temperature. The resulting precipitates were transferred into a Teflon-lined stainless steel autoclave at 160°C for 24 h. After hydrothermal treatment, the MWO₄ powders collected after filtration and washing with distilled water were dried in air at 80°C overnight.

2.3 Preparation of WO₃

The synthesized MWO₄ (M = Zn, Cd, Co, Ni) products from previous procedure were immersed in 8 mol·L⁻¹ HNO₃ solution. The duration of acid treatment was varied from 24 h to 72 h depending on tungstate sources. Upon filtration and washing with distilled water, the acid treated products were calcined in a furnace at 500°C for 4 h in air.

2.4 Characterization

The morphology and microstructure of the samples were determined by SEM (JEOL-6701F) and TEM (JEM-3010). XRD patterns of the samples were recorded on a Panalytical X′pert XRD system using Cu Ka radiation. The optical absorbance spectra were recorded by a UV-visible spectrophotometer (Shimadzu UV2600). The chemical state and valance band spectra of tungsten trioxides were characterized by X-ray photoelectron spectroscopy. Mg Ka (1253.6 eV) was utilized as the excitation light source and the signal was recorded by Omicron EA 125 at a normal emission angle at room temperature. The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurement at 77 K using Micromeritics ASAP 2020. Photoluminescence (PL) Spectra were measured on a HORIBA Jobin Yvon S.A.S. Fluoromax-4 spectrofluorometer at an excitation wavelength of 320 nm. Fluorescence lifetime was measured on Flurolog HR 320 HORIBA Jobin Yvon S.A.S. time-correlated single photon counting (TCSPC) instrument.

2.5 Photocatalysis measurement

The photocatalytic activities of the prepared samples were evaluated by degradation of methylene blue under simulated solar light irradiation. In a typical run, 50 mg of photocatalysts was dispersed in 50 ml of Methylene blue aqueous solution (5mgL⁻¹). The solution was continuously stirred in the dark for 1 h to establish adsorption-desorption equilibrium before irradiation. The solution was then irradiated under illumination of a 500 W Xe lamp with light intensity of 100 mW/cm² was used as light source for simulated solar light. At each interval of 2 min, sample aliquots were exacted from the reactor, followed by centrifugation (13000 rpm for 5 min) and filtering through a 0.45 µm PTFE syring filter (Millipore) to remove the photocatalysts. The concentration of methylene blue was monitored by UV-Vis Spectrophotometer at the maximum absorbance peak (664 nm).

3. Result and discussion

3.1 Structure and Morphology

We first studied how the structures and compositions of WO₃ products are correlated with metal tungstate sources while keeping the other conditions constant. The XRD patterns of the uncalcined samples synthesized by different precursors are shown in Fig. 1. In the case of ZnWO₄, the acid treatment results in pure orthorhombic tungsten oxide hydrate WO₃·H₂O phase (JCPDS No.43-0679) with lattice constants a = 0.5238 nm, b = 1.7040 nm, c = 0.5120 nm. The other three precursors (MWO₄, M = Cd, Co, Ni) result in WO₃·2H₂O phase (JCPDS No.16-0166) with lattice constants of a = 0.7450 nm, b = 0.6920 nm, c = 0.3720 nm mixed with WO₃·2H₂O. This could be seen from the peak assignment marked by diamond and star symbols. Among these three precursors, NiWO₄ has the highest ratio of monoclinic WO₃·2H₂O, which will correlate with the catalytic performance, as we will demonstrate later.
The above showed that both monoclinic WO$_3$·2H$_2$O and orthorhombic WO$_3$·H$_2$O phases could be obtained by varying precursors. Further calcination at 500°C converts the crystal phase of these samples to pure monoclinic WO$_3$ (JCPDS No. 43-1035) as confirmed from the XRD results in Fig. 2. The normalized XRD peaks of the sample (Ni/WO$_3$) derived from NiWO$_4$ have the lowest intensities. This indicates a lower crystallinity, correlating to high oxygen-deficient surfaces.$^{25}$

In Fig. 3, a typical plate is about 270 nm long and 220 nm wide. When the precursor was changed, the plates are of quasi-quadrangular shape (Fig. 3b-d). It is well proved that solvents, impurities and additives in solution can substantially influence the ultimate shape of the crystals by tuning the growth rate and orientation of the crystals.$^{25}$ This effect can be explained by different time duration for completing the process of replacing precursor cation by proton for each precursor, possibly affecting the rate of nucleation, growing, agglomeration and consequently ultimate shape.

Fig. 1 X-ray diffraction (XRD) patterns of the WO$_3$·xH$_2$O products synthesized by different precursors before calcination.

Fig. 2 X-ray diffraction (XRD) patterns of the products synthesized by different precursors after calcination.

Fig. 3 Scanning electron microscopy (SEM) images of the products synthesized by different precursors: (a) Zn/WO$_3$ (b) Cd/WO$_3$ (c) Co/WO$_3$ (d) Ni/WO$_3$.

Fig. 4 HRTEM images of WO$_3$ samples by different precursors. (a) Zn/WO$_3$ (b) Cd/WO$_3$ (c) Co/WO$_3$ (d) Ni/WO$_3$.

The detailed structural and morphological characteristics of tungsten oxides were further investigated by HR-TEM. Fig. 4d shows that the synthesized Ni/WO$_3$ is not well crystallized. The HRTEM image shows the lattice fringes of 0.366 nm which can be readily assigned to (200) crystal planes. Fig. 4a-c show HR-TEM images of WO$_3$ derived from MWO$_4$ (M= Zn, Cd, Co). The result shows clear
crystal lattice, which can be assigned to the preferential orientation at (200) and (020) directions. Since (200) and (020) of WO$_3$ have equal surface energy and show the same adsorption ability$^{54}$, no correlation was observed between crystal facets of WO$_3$ and dye degradation. BET surface area measurements of the samples were carried out at liquid nitrogen temperature, and the corresponding values are summarized in table 1. The specific surface area of the sample varies insignificantly, indicated that the WO$_3$ particle size was not crucial for photodegradation of azo dyes methylene blue.

Table 1 Comparison of Physical properties of different photocatalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m$^2$ g$^{-1}$)</th>
<th>BJH adsorption average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/WO$_3$</td>
<td>20.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Cd/WO$_3$</td>
<td>17.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Co/WO$_3$</td>
<td>15.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Ni/WO$_3$</td>
<td>18.5</td>
<td>10.2</td>
</tr>
</tbody>
</table>

3.2. Electronic and Optical properties

To gain insight into the effect of different metal tungstates on the electronic and optical properties of WO$_3$ nanoplates, the chemical states and surface chemical compositions of the resultant crystals were determined by XPS. The O1s spectra of the WO$_3$ samples in Fig. 5 can be described as the superposition of three peaks located at 530.0, 531.2, and 533.0 eV. The O 1s peak at 533.0 eV indicates loosely bound oxygen, which is from H$_2$O molecules on the surface of WO$_3$. The peak at 530.0 eV is attributed to the O$^-$ ions mainly from bulk WO$_3$. The intensity at 531.2 eV is associated with O$^2-$ in the oxygen deficient regions with the matrix of WO$_3$.$^{55}$ In the oxygen deficient surface region; OH$^-$ groups are bonded to the metal cations to maintain the charge balance. Thus, the O 1s intensity of OH$^-$ is related to the oxygen vacancy density. Since the concentration of lattice O$^2-$ should not be sensitive to surface electronic structures; we normalize other peaks to this peak at 530.0 eV.$^{56}$ As Table 2 shows, the relative peak intensity at 531.2 eV of Ni/WO$_3$ is the highest among the four samples, correlating with the concentration of oxygen vacancies in WO$_3$ samples.

Table 2 O 1s signals for WO$_3$ based different precursors with the Relative Oxygen Species Amounts (The amounts of surface O$^-$OH, H$_2$O species were determined by XPS from the O1S peak (530.0, 531.3, 533.0 eV for O$^-$, OH$^-$, H$_2$O respectively).

<table>
<thead>
<tr>
<th>Peak Position (eV)</th>
<th>Zn/WO$_3$</th>
<th>Cd/WO$_3$</th>
<th>Co/WO$_3$</th>
<th>Ni/WO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>530.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>531.3</td>
<td>0.19</td>
<td>0.40</td>
<td>0.48</td>
<td>0.62</td>
</tr>
<tr>
<td>533.0</td>
<td>0.11</td>
<td>0.19</td>
<td>0.18</td>
<td>0.19</td>
</tr>
</tbody>
</table>

To evaluate the effect of oxygen vacancy on the energy gap of the WO$_3$ samples prepared under different conditions, the optical properties of WO$_3$ samples were probed using UV-visible diffuse reflectance spectroscopy.

The DR UV–vis spectra of WO$_3$ derived from MWO$_4$ (M= Zn, Cd, Co, Ni) are shown in Fig. 6. It could be found that...
The optical absorption edge was estimated to be ~460 nm for WO₃ derived from ZnWO₄ and ~510 nm for WO₃ derived from NiWO₄, respectively. Combined with XPS results, with the increase of surface oxygen vacancy, the absorption edge of WO₃ gradually moved to longer wavelength.⁵⁵,⁵⁷ We concluded that WO₃ derived from NiWO₄ has the highest O vacancy concentrations and thus the narrowest band gap as well as the best visible light response.

The relevant PL emission spectra and fluorescence lifetime times of WO₃ samples were investigated and presented in Fig. 7 and 8. All samples have similar emission profiles. The blue emission peaks at 409 and 421 nm can be assigned to oxygen vacancies in WO₃.⁵⁸ The WO₃ sample derived from NiWO₄ has a significantly lower luminescence intensity compared to other WO₃ samples. Thus in this case we can observe the much lower PL intensity, which indicates the lower recombination rate of photo-induced electron-hole pair.

Fig. 7 PL spectra (using excitation at 340 nm) of WO₃ samples.

The much lower PL intensity indicates the lower recombination rate of photo-induced electron-hole pair and the presence of oxygen vacancies would facilitate the charge separation process. As reported, the oxygen vacancies are demonstrated to be electron donors in semiconductor⁵⁹ and can be considered to enhance the donor density in heterogeneous WO₃-xH₂O/WO₃ sample derived from NiWO₄.

The significant difference between the WO₃ samples is in the PL decay lifetime, as shown in Table 3. The PL decay of metal oxides comes from the recombination of nonradiative (T1) and radiative (T2) processes. The radiative process originates from the recombination of photogenerated electrons and holes.⁶⁰ Therefore we calculated the T2 values of different samples through double exponential decay fitting. The T2 values of as-prepared are all greater than that of the commercial products (5.78 ns). In addition, Ni/WO₃ has the longest radiative decay time (8.84 ns). This longest lifetime corresponding to the slowest PL decay clearly shows a prolonged e⁻·h⁺ recombination process.

Correlating with the formation mechanism of WO₃ samples, WO₃-xH₂O was formed by the acid treatment and survived somehow after calcination. This facilitates the transfer of electrons to the surface of photocatalysts due to its highly conducting properties. Therefore the probability of photogenerated e⁻·h⁺ recombination decreases greatly by increasing the lifetime of photoexcited holes. On the other hand, the higher amount of O vacancies on the WO₃ sample from WO₃-xH₂O which was formed after NiWO₄ acid treatment can increase the amount of charge carrier trapping sites on the surface which preventing the rate of e⁻·h⁺ recombination and increase the life time of e⁻ and h⁺ hole recombination.

The photocatalytic activities of resultant WO₃ crystals were evaluated by monitoring photodegradation of azo dye methylene blue. Among the WO₃ samples prepared from different precursors, the Ni/WO₃ exhibits the highest reaction rate; the rate constant is 5.01×10⁻² min⁻¹ as shown in Fig. 9. The rates constant were 3.49×10⁻², 2.46×10⁻², and 2.41×10⁻² min⁻¹ for other two samples. Correlating with Table 1, we found specific surface area is not the sole
The relation between the different metal sources and reaction rate constant may mainly come from the crystallographies of uncalkined samples. In the process of acid treatment on MWO₃ precursors, the hydrogen atoms exchange with lattice metal ions of MWO₄ crystals, forming WO₃·xH₂O (x=1 or 2). Up on annealing these samples, the contained water molecules desorb and WO₃ nanoparticles are formed. The crystalliferous water as in WO₃·H₂O has weak interaction and is facile to release with no distortion on the WO₆ octahedrons duringconversion to WO₃. Therefore the formed WO₃ nanoparticles have less concentration of oxygen defects. In contrast, in WO₃·2H₂O (in fact [WO₃(H₂O)]·H₂O)⁶¹, there is one coordination water per W octahedron. This water molecule serves as a ligand, which is in fact part of the WO₆ octahedrons. Desorption of this coordinated water should leave a ligand defect, which will finally become an oxygen defect given no external oxygen atoms healing this vacancies during the formation of WO₃ nanoparticles. The comparison between WO₃·2H₂O and WO₃·H₂O will explain Zn/WO₃, which is from the pure WO₃·H₂O, has the lowest concentration of surface oxygen defects and thus the lowest photocatalytic efficiency and Ni/WO₃ is of the highest. Nevertheless, the uncalkined samples derived from Co, although of higher ratio of WO₃·H₂O than that of Cd (Fig. 1) is unexpectedly of the higher oxygen vacancies. Therefore, other properties from the metal ions, rather than the sole crystallography, also play roles to control the oxygen vacancies, which are interesting in our future study.

![Image of photoluminescence decay curves](image_url)

**Conclusions**

We have investigated the relationship between photocatalytic activities of WO₃ samples derived from different transition metal tungstate sources (M= Zn, Cd, Co, Ni) for dye degradation. We found that the concentration of oxygen vacancies of WO₃ sample generated from precursors is the decisive factor to the photocatalytic efficiency. The sample derived from NiWO₄ is of the highest ratio of OH⁻ to O²⁻, longest PL lifetime decay and thus the highest photocatalytic efficiency. Our study may inspire the study of preparing precursors to optimize the photocatalytic efficiency of WO₃.

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**Notes and references**
