



# Greatly improved heat-shielding performance of $K_xWO_3$ by trace Pt doping for energy-saving window glass applications



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## ARTICLE INFO

### Keywords:

$K_xWO_3$   
Pt doping  
Solvothermal  
Near-infrared shielding  
Transparent heat insulation

## ABSTRACT

Pt-doped  $K_xWO_3$  nanorods with excellent near-infrared shielding and heat insulation performance were prepared by solvochemical reduction method using cheap sodium tungstate as raw materials. The effects of K/W ratio and Pt doping on the microstructure, morphology and transparent heat insulation performance of  $K_xWO_3$  particles were investigated. It was found that Pt doping contributed to increasing the content of W in reduced state ( $W^{5+}$  and  $W^{4+}$ ), promoting the uniform growth of hexagonal  $K_xWO_3$  nanorods and decreasing the particle size. Compared with the undoped  $K_xWO_3$  particles, Pt-doped  $K_xWO_3$  samples exhibited improved near-infrared shielding and heat insulation properties. Particularly, when K/W was 0.4, the incorporation of trace Pt (0.1 mol %) greatly improved the near-infrared shielding and transparent insulation properties of  $K_xWO_3$  particles, which is ascribed to its lower powder resistivity and more content of W in reduced state ( $W^{5+}$  and  $W^{4+}$ ). Whereas too much Pt-doping amount tended to decrease the visible light transmittance of  $K_xWO_3$ . The mechanism of Pt doping promoting the  $W^{5+}/W^{4+}$  formation and improving the heat insulation of  $K_xWO_3$  were discussed. It is suggested that the trace Pt-doped  $K_xWO_3$  particles with excellent transparency and heat insulation properties are more suitable for the preparation of transparent insulation films and have broad applications in the field of energy-saving window glasses.

## 1. Introduction

In the summer, air conditioning is usually used to reduce the higher temperature indoor or inside the car caused by direct sunlight, which will cause a great deal of  $CO_2$  emission and global warming while consuming a lot of energy. As is well known, the near-infrared (NIR) radiation (780–2500 nm) accounts for about 50% of the total solar radiation spectrum, and ordinary transparent glass has high transmittance of the whole solar spectrum, almost no heat insulation and energy saving effect. Whereas coating or sticking transparent insulation films on the surface of glass can shield most of heat in sunlight under normal lighting conditions, thereby greatly reducing the indoor temperature and usage frequency of air conditioning, which is of great significance for energy-saving and emission-reduction. At present, inorganic nanoparticles used for transparent heat-insulating film mainly include indium doped tin oxide (ITO) [1], antimony doped tin oxide (ATO) [2], aluminum doped zinc oxide (AZO) [3],  $VO_2$  [4] and  $W_{18}O_{49}$  [5] et al. Among them,  $VO_2$  has a thermochromic effect and temperature-controlled heat insulation performance due to its semiconductor-metal phase transition between 25–68 °C, however, generally the visible light

transmittance of  $VO_2$  film is only 30–40%, and its color is too dark to be easily accepted [4,6,7]. ATO and ITO have stronger reflection of near-infrared light, but both have poorer NIR shielding performance in the region of 780–1500 nm [2,8], and the higher cost of indium source is not conducive to extensive applications. It is reported that AZO has a higher transmittance in the visible light region, however, its reflectivity in the near-infrared region is lower and the heat insulation is not ideal [3,9].  $W_{18}O_{49}$  has been reported to have a good near-infrared absorption/shielding performance and electrochromic property, but it is not stable and easily oxidized [5].

In the past few years, hexagonal  $M_xWO_3$  ( $M=Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $NH_4^+$ ) particles have been attracting considerable interests due to its excellent near-infrared absorption/shielding ability and higher visible light transmittance.  $M_xWO_3$  with hexagonal tungsten bronze structure is particularly suitable for transparent insulation of architectural glazing and automotive glass. The main structure of  $M_xWO_3$  is hexagonal  $WO_3$  in which there are hexagonal tunnels and triangular tunnels and the number ratio is 2:1, but the cation  $M^+$  can only enter hexagonal tunnels due to the limitation of size, and thus the theoretical maximum doping amount is 0.33 [10]. The cation  $M^+$  enters into

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hexagonal tunnels formed by the  $[\text{WO}_6]$  octahedrons, and  $\text{W}^{5+}$  is generated by the reaction of  $\text{WO}_3 + x\text{M}^+ + xe^- \rightarrow \text{M}_x\text{W}_{1-x}^{6+}\text{W}_x^{5+}\text{O}_3$  simultaneously. Research shows that the size of doped cations determines the difficulty of its entering hexagonal tunnels. At present, the cations that can be incorporated into hexagonal tunnels are mainly  $\text{Li}^+$  ( $r=0.076$  nm) [11],  $\text{Na}^+$  ( $r=0.102$  nm) [12],  $\text{K}^+$  ( $r=0.138$  nm) [13],  $\text{Rb}^+$  ( $r=0.152$  nm) [14],  $\text{Cs}^+$  ( $r=0.167$  nm) [15] and  $\text{NH}_4^+$  [16]. Since the radius of  $\text{Cs}^+$  ions ( $r=0.167$  nm) is slightly larger than the size of hexagonal tunnels ( $r=0.163$  nm) [17], more  $\text{Cs}^+$  ions can be fixed in the hexagonal tunnels, so the  $\text{Cs}^+$  doping amount is easier close to the theoretical maximum doping amount. However, the cesium salt is more expensive than potassium salt with lower price. But part of  $\text{K}^+$  in hexagonal tunnels will escape easily, because the radius of  $\text{K}^+$  (0.138 nm) is slightly smaller than  $\text{Cs}^+$ . Therefore, synthesizing  $\text{K}_x\text{WO}_3$  with excellent near-infrared shielding performance from cheap potassium salt is of great significance for practical applications, but it is also difficult and challenging because of the smaller  $\text{K}^+$  radius. In addition, hexagonal  $\text{M}_x\text{WO}_3$  nanoparticles with better transparency and heat insulation were often synthesized by expensive and unstable tungsten hexachloride [17–19]. If a relatively inexpensive and stable sodium tungstate/potassium tungstate is used to replace tungsten hexachloride for synthesis of hexagonal  $\text{M}_x\text{WO}_3$  nanoparticles with excellent transparency and heat insulation properties, it can greatly reduce the production cost and simplify the storage steps of raw materials, which is of great significance to promote its industrialization and practical application.

It is reported that the fundamental cause of NIR absorption of  $\text{M}_x\text{WO}_3$  is local surface plasmon resonance (LSPR) and localized electron polarization [20]. Adachi et al [21] have ever investigated the origin of near-infrared (NIR) absorption of  $\text{Cs}_x\text{WO}_3$  and  $\text{WO}_{2.72}$  by analyzing dielectric constants using Mie scattering theory. It was found that the free electrons in conduction band produce local surface plasmon resonance, and free electron concentration is the main factor affecting LSPR. Schirmer et al [22] found that small polarons transformation occurs between two adjacent W atoms with different states in the capture of near-infrared light, thus the carrier concentration will also affect the NIR absorption due to small polaron transformation. Noble metals (e.g. Ag, Au, Pt) can be used as electron-rich sources to provide electrons, suppress the recombination of electron-hole pairs, and increase the carrier concentration [23]. In CoO/Ag photocathode, Ag can increase the electron mobility, inhibit the recombination of photo-generated electron-hole pairs, and broaden the absorption range of light to the infrared region [24]. It was reported that forming Pt/BiFeO<sub>3</sub> heterojunctions by coating Pt on the surface of BiFeO<sub>3</sub> particles could enhance the separation of photo-generated electron-hole pairs and increased the carrier concentration [25]. At present, noble metal Pt doped photocatalysts with improved carrier concentration and photocatalytic activity have been studied extensively. However, the effect of Pt doping on the near-infrared absorption/shielding and transparent insulation performance of  $\text{K}_x\text{WO}_3$  has not been reported.

In this paper, Pt-doped  $\text{K}_x\text{WO}_3$  nanoparticles were synthesized by solvothermal method using cheap sodium tungstate as tungsten source and potassium sulphate as potassium source. The effects of Pt doping and K/W ratio on the microstructure, near-infrared shielding and transparent heat insulation properties of  $\text{K}_x\text{WO}_3$  particles were investigated. It is exciting that trace Pt doping could contribute to the uniform growth of hexagonal  $\text{K}_x\text{WO}_3$  nanorods, particularly. Especially, when K/W ratio was 0.4, the incorporation of trace Pt (0.1 mol%) could significantly improve the near-infrared shielding and transparent insulation performance of  $\text{K}_x\text{WO}_3$  nanoparticles. The results have great reference value for developing Pt-doped  $\text{K}_x\text{WO}_3$  particles, and the synthesized trace Pt-doped  $\text{K}_x\text{WO}_3$  nanoparticles are more suitable for the preparation of transparent heat insulation films and have promising application prospects in the field of energy-saving window glasses.

## 2. Experimental section

### 2.1. Preparation of Pt-doped $\text{K}_x\text{WO}_3$ powder

Potassium sulphate ( $\text{K}_2\text{SO}_4$ ), sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) (CA) and chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) are all analytical reagents and used as raw materials.

Pt-doped  $\text{K}_x\text{WO}_3$  powders were prepared by solvothermal and thermal reduction method using sodium tungstate as W source and potassium sulphate as K source, respectively. In a typical procedure, excess dilute hydrochloric acid was poured into 0.159 mol/L sodium tungstate solution quickly under stirring to get yellow tungstic acid gel suspension, and then the gel suspension was washed with de-ionized water and alcohol three times respectively to get stable tungstic acid ethanol dispersion. Then, an appropriate amount of potassium sulphate, citric acid, chloroplatinic acid and tungstic acid ethanol dispersion were added into a Teflon-lined autoclave with 200 ml internal volume, and the mixture was magnetically stirred constantly until to obtain a uniform precursor solution with citric acid concentration 1.0 mol/L. Then the solvothermal reaction was conducted at 190 °C for 72 h and the obtained blue precipitates were collected by centrifuging and washing with de-ionized water and alcohol three times, and then dried at 60 °C for one night. Finally, the dried product was heat-treated in  $\text{H}_2$  atmosphere at 450 °C for 30 min and dark blue powders were obtained.

The as-prepared  $\text{K}_x\text{WO}_3$  nanoparticles with K/W (mol)=0.2, 0.3 and 0.4 were named as 0.2KW, 0.3KW and 0.4KW, respectively. In the meantime, Pt-doped  $\text{K}_x\text{WO}_3$  samples with introduction of 0.1 mol% Pt into 0.2KW, 0.3KW and 0.4KW samples from chloroplatinic acid aqueous solution were expressed as 0.2KW-0.1%Pt ( $\text{H}_2\text{O}$ ), 0.3KW-0.1%Pt ( $\text{H}_2\text{O}$ ) and 0.4KW-0.1%Pt ( $\text{H}_2\text{O}$ ) respectively. Pt-doped  $\text{K}_x\text{WO}_3$  samples with introduction of 0.1 mol%, 0.3 mol%, 0.6 mol% and 0.9 mol% Pt into 0.4KW from chloroplatinic acid ethanol solution were expressed as 0.4KW-0.1%Pt (ET), 0.4KW-0.3%Pt (ET), 0.4KW-0.6%Pt (ET) and 0.4KW-0.9%Pt (ET), respectively.

### 2.2. Preparation of Pt- $\text{K}_x\text{WO}_3$ films

Pt-doped  $\text{K}_x\text{WO}_3$  thin films were prepared from polyvinyl alcohol (PVA) dispersion of Pt- $\text{K}_x\text{WO}_3$  particles with PVA as film former. Firstly, Pt-doped  $\text{K}_x\text{WO}_3$  powders were dispersed in 10 wt% aqueous solution of PVA in 70 °C water bath to obtain the coating liquid with good dispersibility. Subsequently, Pt-doped  $\text{K}_x\text{WO}_3$  thin films were uniformly coated on the surface of slides by roll coating method.

### 2.3. Characterization

The morphology and microstructure of the powder samples were observed by scanning electron microscopy (SEM, JSM-7800F, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100(UHR)). The phase compositions of the samples were determined by X-ray diffraction analysis (XRD, Shimadzu XRD-7000S) using graphite-monochromized  $\text{CuK}\alpha$  radiation. The surface composition of the sample and the binding energies of W in the sample were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The UV-Vis-NIR transmittance spectra of the Pt-doped  $\text{K}_x\text{WO}_3$  films at wavelength 300–1100 nm and 260–2500 nm were measured using a modular solar cell spectral performance testing system (7-SCSpec III, SOFN Instruments Co., Ltd.) and a spectrophotometer (HITACHI U-4100) respectively. The electric resistivity of the  $\text{K}_x\text{WO}_3$  and Pt-doped  $\text{K}_x\text{WO}_3$  powder samples were measured by powder resistance tester (ST2722, Suzhou Jingge Electronic Co., Ltd.) with the pressure being 4 MPa.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared  $\text{K}_x\text{WO}_3$  and Pt-doped  $\text{K}_x\text{WO}_3$  powders with different K/W molar ratio. It is obvious

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