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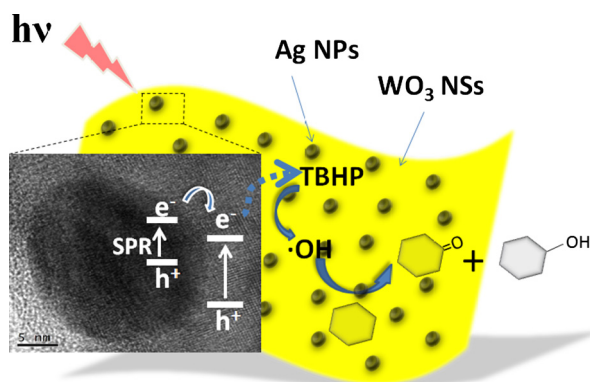
# High-performance silver nanoparticles coupled with monolayer hydrated tungsten oxide nanosheets: The structural effects in photocatalytic oxidation of cyclohexane

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## GRAPHICAL ABSTRACT



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## ABSTRACT

The photocatalytic properties of silver nanoparticles (Ag NPs) coupled with tungsten oxide ( $\text{WO}_3$ ) nanocrystals are investigated to understand structural effects of the  $\text{WO}_3$  nanocrystals in selective oxidation of cyclohexane (CyH). The photocatalytic activity of monolayer hydrated  $\text{WO}_3$  nanosheet - Ag nanoparticle composites ( $\text{WO}_3$  NSs-Ag NPs) is 1.3 times higher than that of  $\text{WO}_3$  nanocube - Ag nanoparticle composites ( $\text{WO}_3$  NCs-Ag NPs). The highest cyclohexane conversion of 40.2% with cyclohexanol and cyclohexanone (KA oil) selectivity of 97.0% is achieved by the photocatalyst of  $\text{WO}_3$  NSs-Ag NPs under solar-light irradiation at room temperature. The  $\text{WO}_3$  NSs-Ag NPs shows good photocatalytic stability without evident decline of catalytic activity after ten cycles. The improved photocatalytic activity in the oxidation of cyclohexane by  $\text{WO}_3$  NSs-Ag NPs is mainly due to the facilitated generation of high-reactive hydroxyl radical ( $\cdot\text{OH}$ ), which is caused by the enhanced light absorption by surface plasmon resonance (SPR) effect of Ag NPs, and the effective charge transfer on the surface of  $\text{WO}_3$  monolayer structure. The design and structural analysis of the  $\text{WO}_3$  NSs-Ag NPs in this research may provide a novel approach for the further development of high-performance photocatalyst.

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## 1. Introduction

Partial oxidation of the relatively inert C–H bond in alkanes with high efficiency and selectivity is one of the most challenging

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reactions in catalytic chemistry [1–3]. Among them, catalytic oxidation of cyclohexane (CyH) to a mixture of cyclohexanone and cyclohexanol (KA oil) becomes increasingly important due to the great need of these products in the further synthesis of  $\epsilon$ -caprolactam, nylon-6 and nylon-6,6 [4,5]. Although great efforts in developing novel catalyst and new process arrangement have been made in the catalytic oxidation of cyclohexane, commercial process is still suffering from the drawbacks of unsatisfactory activities (conversion < 10% and selectivity < 80%), harsh reaction conditions ( $\sim$ 423 K with 1–2 MPa pressure) and excessive amounts of by-products generated by over oxidation [6,7]. Therefore, there is an urgent need to design a durable, easy-to handle, and highly effective catalyst under mild conditions with low environmental costs for cyclohexane oxidation. Recently, heterogeneous photocatalytic oxidation of cyclohexane with wet air or superoxide as oxidant has received increasing attentions. Owing to the easy separation of residual catalysts and fewer by-products formed in the heterogeneous catalytic system, high catalytic efficiency can be achieved [8–10].  $\text{TiO}_2$  based semiconductor nanomaterials were reported as high selective catalyst in the photocatalytic oxidation of cyclohexane [5,11]. Guido Mul et al. performed a series of studies on this reaction and high selectivity beyond 90% to KA oil was observed [12,13]. However,  $\text{TiO}_2$  can only absorb and utilize ultraviolet light, which is a small fraction of the solar light. Carbon-based nonmetal materials, such as graphitic carbon nitride ( $\text{C}_3\text{N}_4$ ) and carbon quantum dot (CQDs) could absorb visible light efficiently, and perform efficient visible-driven photocatalytic property under mild conditions [8,14–16]. And high conversion efficiency with 100% selectivity to KA oil was obtained by the  $\text{C}_3\text{N}_4$ -based photocatalysts reported by Kang's group [14,16]. However, the further applications with those kinds of carbon-based catalysts were significantly limited by the disadvantage of low stability due to the loss of surface groups during the continuous process of photocatalytic oxidation [17].

Tungsten trioxide ( $\text{WO}_3$ ), as an n-type semiconductor, could absorb visible light less than 450 nm [18]. And it could produce much larger photocurrents with higher photo-current conversion efficiency than other metal oxides with wide band-gap, such as ZnO and  $\text{TiO}_2$  [19,20]. Extensive applications of  $\text{WO}_3$  have been reported in gas sensors, photocatalysts, field-emission devices, photochromic devices and energy devices etc [21–24]. It's worth mention that  $\text{WO}_3$  with layered structures could be exfoliated into thin two-dimensional (2D) nanosheets (even monolayer) via a simple wet chemical process, which could further extend its application. For example,  $\text{WO}_3$  nanosheets or nanoplates with decreased size could reduce the diffusion paths and expose maximum active sites, which make it promising for the design of high-performance heterogeneous catalyst. Moreover, the electronic band structure of  $\text{WO}_3$  nanocrystals is mainly depended on its size and thickness [20]. Thinner nanosheet may result in wider band gap, which enhances the redox ability of the hole-electron pairs. On the other hand, Ag nanocrystals are known to possess catalytic activities for some photocatalytic oxidation reactions [25–27]. The surface plasmon resonance (SPR) effect offers Ag nanocrystals with enhanced adsorption of visible light, which leads to the photogenerated metallic electron-hole pairs and induces remarkable photocatalytic abilities in Ag nanocomposites [28,29]. Moreover, Ag nanocrystals could be attached onto  $\text{WO}_3$  nanosheets or nanoplates to form  $\text{WO}_3$ -Ag nanocrystal composites with good dispersion, which may act as an excellent catalyst for the oxidation of cyclohexane.

Herein, the free-standing monolayer  $\text{WO}_3$  nanosheets ( $\text{WO}_3$  NSs) with the width of around 200 nm and the thickness of 0.6 nm were synthesized via polar molecules-assisted wet chemical exfoliation. Remarkably, comparing to traditional  $\text{WO}_3$  nanocubes ( $\text{WO}_3$  NCs,  $\sim$ 150 nm), the electronic band structure of monolayer  $\text{WO}_3$  NSs is quite different. The work function of monolayer  $\text{WO}_3$

NSs is about 5.38 eV, which is less than that of  $\text{WO}_3$  NCs (5.74 eV). On this basis, photocatalysts of  $\text{WO}_3$  nanosheet - Ag nanoparticle composites ( $\text{WO}_3$  NSs-Ag NPs) and traditional  $\text{WO}_3$  NCs-Ag NPs are prepared for the comparison study in the cyclohexane oxidation. Due to the monolayer structure of  $\text{WO}_3$  NSs, the highest cyclohexane conversion of 40.2% with 97.0% KA oil selectivity was achieved by  $\text{WO}_3$  NSs-Ag NPs, which is 1.3-fold improvement of cyclohexane conversion than that of  $\text{WO}_3$  NCs-Ag NPs. The possible mechanism involved in the photocatalytic oxidation of cyclohexane is also discussed in the study.

## 2. Material and methods

### 2.1. Material

Yellow tungstic acid ( $\text{H}_2\text{WO}_4$ , 99%), sodium tungstate ( $\text{Na}_2\text{WO}_4$ , 99%), oleylamine (OA, 99%), nitric acid, silver nitrate ( $\text{AgNO}_3$ , 99%), acetone, ethanol (absolute), methanol (absolute), acetic acid (absolute), tert-butyl hydroperoxide (TBHP, 70%), diethylene glycol (EG, 98%) and triphenylphosphine ( $\text{PPh}_3$ , 99%) were purchased from Aladdin Company.

### 2.2. Synthesis of monolayer $\text{WO}_3$ NSs

Typically, 400 mg of  $\text{H}_2\text{WO}_4$  powder and 5 mL of acetic acid were added into a 50 mL beaker under ultrasonication for 30 min. Then 30 mL of OA was added into the mixture and ultrasonicated in iced water for another 30 min. After that, the mixture was transferred into a 45 mL Teflon-lined autoclave, followed by pumping argon for 5 min. the reaction system was sealed and kept at 140 °C for 12 h, and a colorless reaction mixture could be obtained. When excessive acetone was added into the colorless mixture, white precipitate of tungstate-based inorganic-organic hybrids (OA- $\text{WO}_3$ ) were formed. This white precipitate was centrifuged and washed with ethanol twice. Then OA- $\text{WO}_3$  was dispersed in a certain amount of 5 mol L<sup>-1</sup> nitric acid solution and stirred for about 72 h at room temperature till light-yellow suspension was obtained. Finally, the mixture was centrifuged at 2000 rpm for 15 min to remove the non-exfoliated component. After the obtained supernatant has been vacuum-filtrated over a cellulose membrane with 0.22  $\mu\text{m}$  pore size and fully washed with deionized water, the monolayer  $\text{WO}_3$  NSs were obtained.

### 2.3. Synthesis of $\text{WO}_3$ NCs

For comparison, 150 nm  $\text{WO}_3$  NCs were also prepared as follow: 500 mg of  $\text{Na}_2\text{WO}_4$  was dispersed in 10 mL of 1.2 mol L<sup>-1</sup> nitric acid solution with 30 min of ultrasonication. Then the mixture was hydrothermally treated at 160 °C for 16 h. After the obtained yellow suspension has been vacuum-filtrated over a cellulose membrane with 0.22  $\mu\text{m}$  pore size and fully washed with deionized water, the  $\text{WO}_3$  NCs were obtained.

### 2.4. Synthesis of photocatalyst

Photocatalyst of  $\text{WO}_3$  NSs-Ag NPs and  $\text{WO}_3$  NCs-Ag NPs were prepared by a vacuum photo-reduction method. Typically, 50 mg of monolayer  $\text{WO}_3$  NSs or  $\text{WO}_3$  NCs was dispersed in 25 mL of EG (or methanol) and ultrasonicated in iced water for 30 min. After adding the  $\text{AgNO}_3$  solution (30 mg of  $\text{AgNO}_3$  in 5 mL of EG or methanol), the reaction system has been processed by vacuum photo-reduction and maintained continuous stir for 4 h till the color of reaction system was changed from yellow to black. The sample of  $\text{WO}_3$  NSs-Ag NPs or  $\text{WO}_3$  NSs-Ag NPs was centrifuged and washed with deionized water.

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