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# Fabrication, characterization, and visible-light photocatalytic performance of ternary plasmonic composites

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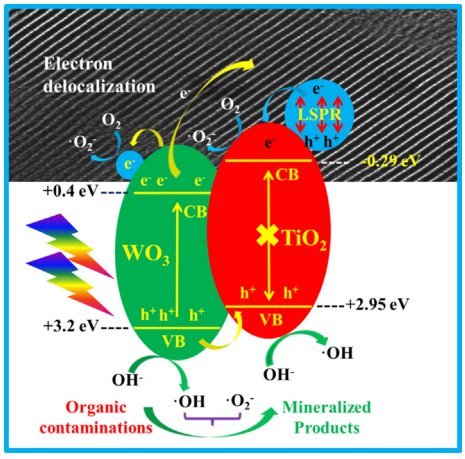
## HIGHLIGHTS

- W-Ti-SBA15 composites with low $TiO_2/SiO_2$ mass ratios and their Ag-contained analogs were fabricated.
- These composites showed enhanced photocatalytic performance in comparison to those with high $TiO_2/SiO_2$ mass ratios.
- Photocatalysis mechanism of these Ag-W-Ti-SBA15 plasmonic composites was proposed.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A group of mesoporous $WO_3$-$TiO_2$-contained SBA15 composites (W-Ti-SBA15) and their Ag-contained plasmonic analogs were fabricated and then systematically characterized by a collection of analytical techniques. Original mesoporous structures with highly ordered channels were well-maintained and $WO_3$-$TiO_2$ could form spherical clusters that were gradually reduced in size accompanying with the decrease of $TiO_2/SiO_2$ mass ratios. Deposited Ag species were confirmed as zero-valence Ag by X-ray photoelectron spectroscopy analysis and exerted almost no effect on the morphology, microstructure, and textural but optical property, by which the visible-light harvesting ability of composites was remarkably strengthened owing to the localized surface plasmonic resonance (LSPR) induced by the metallic Ag. Under visible-light irradiation, W-Ti-SBA15 composites showed satisfactory photocatalytic performance that could be further enhanced by using their Ag-contained ternary plasmonic analogs. The enhancement of photocatalytic efficiency was mainly attributed to the favorable mesoporous morphology, the suitable band alignment, and the LSPR effect. Eventually, a possible photocatalysis mechanism was primarily proposed on the base of reactive radical species trapping experiments.



## 1. Introduction

It is well recognized that anatase ($TiO_2$) is an excellent heterogeneous photocatalyst to mediate environmental contaminants

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removal, evolution of gaseous hydrogen, and selective organic conversion in ultraviolet region, owning to the favorable physicochemical properties [1–3]. For practical applications, the $TiO_2$ should be modified in terms of microstructure and morphology to pursue the extension of light absorption range, the enhancement of photocatalytic performance, and the ease of recovery after utilization [4]. Among several modification strategies that currently intensively researched, the construction of a composite containing $TiO_2$ and another semiconductor component with an appropriate band structure is an effective manner to strengthen the visible-light harvesting and photocatalytic capability as a result of the inhibited recombination of photoinduced charge carriers [5].

Tungsten oxide ($WO_3$) with a relatively narrow band gap (~2.4 eV) has been extensively applied in various fields such as electrochromic devices, dye-sensitized solar cells, gas sensors, and photocatalytic processes [6,7]. It is usually adopted as a suitable candidate to fabricate composites together with $TiO_2$, attributing to the well-matched band gap structure [8–12]. The generated charge carries are able to migrate across heterojunction interfaces towards different components and the recombination of charge carries is thus effectively retarded, hereby improving photocatalytic efficiency [13–15]. In addition, the integration of $WO_3$ into composites induces the enhancement of surface acidity, by which some species with unpaired electrons like $O_2$, $H_2O$, and $OH^-$ are prone to access active sites and convert to oxidative $O_2^-$ and $^{\bullet}OH$ radicals, thus boosting photocatalytic performance [16–18]. If the produced composite incorporates into an appropriate matrix like SBA15, much more active sites can be exposed originating from the decreased particle size and a large amount of pollutant molecules tend to gather around active sites as a result of the strengthened adsorption ability from support, further benefiting photocatalytic processes [19–22].

The deposition of noble metal nanoparticles on surface of semiconductors is another efficient manner to promote photocatalytic efficiency through the formation of schottky junction at the metal-semiconductor interfaces and the LSPR effect by metallic noble elements [23–25]. The former is able to induce the directional migration of electrons and hereby causes the separation of charge carriers [26,27]. The later can enhance the visible-light adsorption and boost the generation of charge carriers. Among mostly used noble metals such as Ag, Pt, Pb, Au, Ag is quite promising due to the low toxicity, antibacterial activity, easy preparation and controllable morphology [28].

In a previous study, the synthesis and photocatalytic assessment of mesoporous W-Ti-SBA15 composites were investigated, and these heterojunction-structured composites showed enhanced photocatalytic efficiency in comparison to single-component samples [29]. However, the photocatalytic performance was not as that good as we had expected, mainly attributing to the serious aggregation of $TiO_2$ particles since the excess amount of titanium precursor was added during synthesis. In order to achieve the further advancement of photocatalytic performance, in this study we tried to reduce the mass ratio of $TiO_2/SiO_2$ for the sake of the maximal exposure of active sites to contaminant molecules. In addition, silver nanoparticles were introduced on the surface of above composites to construct a ternary Ag-W-Ti-SBA15 plasmonic system. As far as we know, there is no relevant investigation regarding the construction and photocatalytic evaluation of ternary Ag-W-Ti-SBA15 plasmonic composites.

In the current study, a series of W-Ti-SBA15 composites and their Ag-decorated counterparts were fabricated and were fully characterized. The original mesoporous structure was well conserved even after decorating metallic Ag species. W-Ti-SBA15 composites showed satisfactory photocatalytic performance toward the degradation of dye rhodamine B (RhB) under visible-light irradiation. As expected, Ag-contained Ag-W-Ti-SBA15 plasmonic composites exhibited relatively high photocatalytic efficiency comparing with their W-Ti-SBA15 analogs. The enhancement of catalytic outcome was discussed and a possible photocatalysis mechanism was proposed basing upon active species trapping experiments.

## 2. Materials and methods

### 2.1. Materials

Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$) and sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) were purchased from Aldrich Chemical Co. and ACROS Organics, respectively. Hydrochloric acid (HCl, 36–38%, AR), silver nitrate ($AgNO_3$, AR), titanium sulfate ($Ti(SO_4)_2{\cdot}9H_2O$, CP), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, AR), nitroblue tetrazolium (NBT, AR), and other chemicals involved were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used directly as received without further purification. Rhodamine B (RhB, AR) was purchased from Shanghai SSS Reagent Co., Ltd. (Shanghai, China). Deionized water was used throughout the experiment.

### 2.2. Synthesis of W-Ti-SBA15 composites

The synthetic procedure was similar to the previous study except that the amount of titanium and tungsten precursors was greatly reduced [29]. A series of W-Ti-SBA15 mesoporous composites were prepared and nominated as 5%WTSx, where 5% and x were defined as theoretical mass ratios of formed $WO_3/TiO_2$ and $TiO_2/SiO_2$, respectively. Sample $WO_3/TiO_2$ with a mass ratio of 5% was fabricated according to a same procedure as above except the absence of silicon source and denoted as 5%WT. In addition, N-doped $TiO_2$ (N-$TiO_2$) was synthesized in the light of a previous report for comparison [30].

### 2.3. Synthesis of Ag-W-Ti-SBA15 plasmonic composites

Since the as-synthesized sample 5%WTS0.1 showed the best photocatalytic behavior and was specifically selected to prepare Ag-W-Ti-SBA15 plasmonic composites. In a typical procedure, the sample 5%WTS0.1 (1 g) in deionized water (40 mL) was ultrasonicated for 30 min to make a suspension that was subsequently added with a desired amount of $AgNO_3$. After a vigorous stir of 900 r/min (JB-2A constant temperature agitator, Shanghai INESA Scientific Instrument Co., Ltd, China) at room temperature for 5 h in dark, methanol (20 mL) was added into the reaction system that was then exposed to a 400 W halogen lamp (Institute for Electric Light Source, Beijing) equipped with a $NaNO_2$ solution (2 M) to remove ultraviolet-light (<400 nm) for 20 min. The resultant precipitate was collected by centrifugation, washed with ethanol and deionized water for at least five times to completely remove silver cations, and dried at 60 °C for 12 h to provide final products. For simplicity, these composites were denoted as xAgWTS and x herein was referred to a theoretical mass ratio of Ag versus WTS.

### 2.4. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) using a Cu Kα radiation source (λ = 1.5406 Å). The X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific ESCALAB 250XI system. Binding energies were calibrated with the containment carbon (C1s = 284.6 eV). The morphology and microstructure of obtained samples were recorded on transmission electron microscopy (TEM, JEOL JEM-2011) and the chemical composition of samples was determined by X-ray energy dispersion spectroscopy (EDS). The specific surface areas were mea-