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Organic Pollutant Photodecomposition by Ag/KNbO₃ Nanocomposites: A Combined Experimental and Theoretical Study

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ABSTRACT: Ag nanoislands supported on well-defined orthorhombic KNbO₃ nanowires are synthesized *via in situ* photo-reduction and systematically characterized by XRD, Raman, DRUV-Vis, XPS, PL, TEM, HRTEM and HADDF-STEM. The photoreactivity of the as-prepared Ag/KNbO₃ nanocomposites as a function of Ag contents (0.4–2.8 wt%) is assessed toward aqueous rhodamine B degradation under UV- and visible-light, respectively. It is found that the UV-induced photoreactivity initially increases and then decreases with increasing Ag contents. At an optimal Ag content (ca. 1.7 wt%), the greatest photoreactivity is achieved under UV light, with the photocatalytic reaction rate of 1.7 wt% Ag/KNbO₃ exceeding that of the pristine KNbO₃ by a factor of *ca.* 13. In contrast, visible-induced photoreactivity monotonically increases with increasing Ag contents in the range of 0.4–2.8 wt%. Based on the detected active species and intermediate products in the photocatalytic processes, the conjugated structure cleavage and N-deethylation are proposed to be the predominant pathway in catalyzing RhB degradation under UV and visible-light illumination, respectively. To study the Ag-KNbO₃ interaction and gain an insight into the observed photoreactivity, the electronic properties of Ag/KNbO₃ have

been investigated using spin-polarized DFT calculations. Herein, Ag extended adlayers (1–4 ML) on slab models of the KNbO_3 (101) are employed to mimic large supported Ag nanoislands. A Bader analysis of the electron density shows a small net charge transfer (ca. 0.1 e) from KNbO_3 to Ag nanoislands, which decreases to 0.05 e with increasing Ag coverage up to 4 ML. The electron localization function of Ag/ KNbO_3 (101) illustrates that Ag nanoislands with thickness larger than 2 ML are metallic in nature and weak polarization occurs at the interface. In addition, within the band gap the metallic Ag nanoislands generate a continuum of Ag states, which are suggested to account for different Ag content-dependent behavior between UV and visible-light illumination.

1. INTRODUCTION

The past decade has seen rapid growth of semiconductor-based heterogeneous photocatalysis in areas like organic pollutant degradation,¹ organic synthesis,² hydrogen generation³ and carbon dioxide reduction,⁴ with an ultimate goal of gaining the sustainable energy and environment development. From the viewpoints of direct utilizing the full spectrum of sunlight, combining noble metal cocatalysts (e.g., silver, gold) with semiconductors to form composites is one of the efficient approaches.⁵ First, semiconductor supports can prevent the coalescence of plasmonic nanoislands. Second, the spatial separation of photogenerated electrons and holes at the metal-semiconductor interface could be facilitated.⁶ Third, as a light absorber and a host for active sites plasmonic metals can directly catalyze photocatalytic reactions.⁷ In general, metallic nanoislands show unique localized surface plasmon resonance (LSPR) arising from the collective excitation of conduction electrons. Under resonance conditions, maximum amount of incident energy in the visible regime can be absorbed. To date, LSPR has been extensively studied in photocatalysis,⁸ plasmon-enhanced spectroscopy,⁹ biotechnology,¹⁰ and solar cells¹¹. In the case of plasmonic metal/semiconductor composites, the size and shape of plasmonic metals and semiconductors can each influence the (photo)catalytic performance.¹² Among plasmonic metals, silver (Ag) presents some merits such as relatively low cost and high stability against oxidation in comparison to other noble metals. Despite the importance of Ag/semiconductor composites in heterogeneous photocatalysis, the interplay between plasmonic metals and semiconductors still remains largely unexplored. For instance, relatively few theoretical studies have been devoted to this system, focusing on Ag_n ($n \leq 8$) clusters supported on TiO_2 (101)¹³ and SrTiO_3 (001).¹⁴ Recent studies suggest that Ag extended layers are more realistic than clusters to model the structure and electronic properties of large supported Ag nanoislands.¹⁵ To this end, mechanistic understanding the Ag-semiconductor interaction in a diverse set of Ag/semiconductor composites is essential in order to rationalize the properties of heterogeneous photocatalysts.

In recent years, owing to the unique geometric and electronic structure, perovskite-type metallic oxides (general formula ABO_3 , A and B are two types of cations and O is an oxygen anion) have been extensively investigated in heterogeneous (photo)catalysis.¹⁶ Among perovskite photocatalysts, KNbO_3 is a typical one with the merits like non-toxicity and high photostability. In this work, Ag nanoislands are deposited on orthorhombic KNbO_3 nanowires (NWs) to form Ag/KNbO_3 nanocomposites that are systematically characterized. The photoreactivity, active species and intermediate products in the photocatalytic processes, are evaluated toward rhodamine B (RhB) degradation in water, a model reaction in cleaning up wastewater streams containing organic pollutants. To gain an insight into the observed photoreactivity, the electronic properties of Ag/KNbO_3 are

investigated using first principle density functional theory (DFT) calculations in terms of Bader charges, electron localization function (ELF) and density of states (DOS).

2. EXPERIMENTAL AND THEORETICAL SECTION

2.1 Material Synthesis. All chemicals (ACS grade) were purchased from Alfa Aesar and used without further purification. Milli-Q water (18 M Ω -cm in resistivity, Millipore Corporation) was used throughout the experiments. The detailed synthesis methods for KNbO₃ NWs were described in ref.¹⁷ Ag nanoislands were deposited on KNbO₃ NWs *via* photoreduction. In detail, 0.1 g KNbO₃ NWs was dispersed in 100 mL Milli-Q water and a certain amount of aqueous AgNO₃ solution (5 mg·mL⁻¹) was slowly added into the suspension. The Ag contents were controlled by adjusting the amount of aqueous AgNO₃ solution. The mixture was vigorously stirred for 1 h under UV-light with an intensity of *ca.* 290 mW·cm⁻². The obtained Ag/KNbO₃ precipitates were thoroughly washed several times with Milli-Q water, and then dried at 60 °C for 12 h.

2.2 Characterization. The actual Ag contents of the as-prepared photocatalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Optima 4300 DV spectrometer (PerkinElmer). The crystal structure of the as-prepared samples was determined by a Rigaku Corporation X-ray diffraction (XRD-6000) with Cu K α radiation (λ =0.154178 nm, 50 kV, 300 mA) at a scanning rate of 10° min⁻¹ in the 2 θ range of 10–85°. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using Tecnai G2 F20 U-TWIN microscope operating at an accelerating voltage of 200 kV. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed using a JEOL JEM ARM200F (Tokyo, Japan) TEM equipped with two CEOS (Heidelberg, Germany) probe aberration correctors. The spatial resolution of the microscope is 90 pm at an incident angle of 25 mrad. Diffuse-reflectance UV-Vis (DRUV-Vis) spectra were obtained in the range of 200–800 nm using Varian Cary 5000 with MgO as a reference. The Raman spectra were collected on a Renishaw Micro-Raman Spectroscopy System (Renishaw in via plus) with a 514 nm laser. X-ray photoelectron spectroscopy (XPS) data were collected using an ESCALab 250 Xi electron spectrometer from Thermo Scientific Corporation. Monochromatic 150 W Al K α radiation was utilized and low-energy electrons were used for charge compensation to neutralize the samples. The binding energies were internally referenced to the adventitious C 1s line at 284.8 eV. The XPS spectra were fitted by Voigt peak profiles after subtracting a Shirley-type background. Further, the % Lorentzian–Gaussian for the Ag 3d, Nb 3d and O 1s spectra was fixed at 20%. Photoluminescence (PL) spectra were recorded using a FLS 980 spectrofluorimeter (Edinburgh Instruments Ltd.) under 325 nm light excitation.

2.3 Photocatalytic Degradation of RhB. The photocatalytic activities of the as-prepared samples were evaluated toward the degradation of RhB (Alfa Aesar) in water. Briefly, 50 mg Ag/KNbO₃ powder was mixed

with 50 mL RhB (8×10^{-6} M) in a 150 mL Pyrex flask. The mixture was sonicated in cool water for 10 min. Before light illumination, the suspension was magnetically stirred in dark to establish a complete adsorption-desorption equilibrium. A 300 W xenon lamp was located at *ca.* 9 cm away from the bottom of the flask. The irradiation intensity of UV- (λ : 250–380 nm) and visible-light ($\lambda > 420$ nm) in the center of the flask was measured to be *ca.* $300 \text{ mW} \cdot \text{cm}^{-2}$ using a Newport optical meter (842-PE). During the irradiation, the reaction suspension (initial pH = 6.1) was magnetically stirred at room temperature. About 3.5 mL of aliquots was sampled at certain time intervals, followed by centrifugation at 15000 rpm for 5 min to remove catalyst particulates. The optical absorption intensity at 554 nm of the as-obtained dye solution was measured to determine the RhB concentration using a PerkinElmer Lambda 950 UV-vis spectrophotometer. In the case of stability test, for each cycle a fresh dye solution was used and after test the catalyst was thoroughly washed with water by centrifugation for several times, and dried at 60 °C.

2.4 Determination of Reactive Species. To detect the major active species generated in the photocatalytic processes, ammonium oxalate (AO), *t*-butyl alcohol (TBA) and *p*-benzoquinone (PBQ), were introduced into the RhB solution as respective scavengers for hole (h^+), hydroxyl radical ($\bullet\text{OH}$) and superoxide radical ($\bullet\text{O}_2^-$). The trapping experimental procedure is similar to that of the RhB degradation as forthmentioned, except adding scavengers before light illumination. The concentration of AO, TBA and PBQ is 10, 10 and 0.5 mM, respectively.

2.5 Detection of Interimdate Products. The post-reaction products were evaluated using a series of analytical instruments. Total organic carbon (TOC) was detected on a Teledyne Tekmar TOC fusion analyzer. During the TOC analysis, inorganic carbon ions were removed using acid treatment before organic carbon oxidized by a powerful UV reaction chamber to form CO_2 which is evacuated by a CO_2 gas detector. The concentrations of mineralization species like nitrate ions (NO_3^-) were probed by an ion chromatography (ICS-1500, Dionex) with an UVD-500 UV/VIS Detector, and the current was set as 45 mA. The eluent consists of sodium carbonate ($9 \text{ mmol} \cdot \text{L}^{-1}$) and the flow rate is $1.00 \text{ mL} \cdot \text{min}^{-1}$. The volume of analyzed samples is $200 \mu\text{L}$ and the cell temperature was maintained at 35 °C. The intermediates of degraded RhB were monitored on Waters Acquity UPLC H-Class in line with a Waters Xevo G2-S QT of MS equipped with a C18 column (ACQUITY UPLC BEH C18 $1.7 \mu\text{m}$ $2.1 \times 150 \text{ mm}$). The system was operated in a positive ion mode (electrospray ionization, ESI). $5.00 \mu\text{L}$ of aliquots was injected for analysis. The eluent contains water and acetonitrile, with column temperature of 35 °C and flow rate of $0.3 \text{ mL} \cdot \text{min}^{-1}$. The source parameters were listed as following: capillary

voltage 3.50 kV, sampling cone voltage 30.0 V, source offset 350 V, source temperature 100 °C, desolvation temperature 250 °C, cone gas flow 50 L·h⁻¹ and desolvation gas flow 600 L·h⁻¹.

2.6 Theoretical Section. The spin-polarized DFT calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) suite of programs.¹⁸ The Kohn-Sham one-electron equations were solved on a basis set of plane waves with energy cutoff of 380 eV and ultra-soft pseudopotentials were used to describe the ionic cores.¹⁹ The exchange-correlation energy and the potential were described by the Perdew-Burke-Ernzerhof (PBE) functional.²⁰ To model the (101) surface of KNbO₃, a slab consisting three NbO-KO bi-layers with either one Nb or one K atom on each layer was used. Brillouin Zone integration was approximated by a sum over special *k*-points selected using the Monkhorst-Pack scheme.²¹ The first NbO-KO bi-layer was allowed to fully relax with the supported Ag, and the bottom two bi-layers were fixed in the lattice position. Both NbO- and KO-terminations were tested, and the results show that NbO-terminated surface was more stable than the KO-counterpart. Enough *k*-points (3×4×1) were chosen to make sure that there was no significant change in the calculated energies when a larger number of *k* points were used. The calculations are sufficiently converged to allow the atomic structures to be optimized until the residual forces on the atoms are less than 0.01 eV/Å.

In the case of Ag/KNbO₃ (101), the Ag coverage is defined with respect to the number of Nb atoms on the surface. To model large supported Ag nanoislands, we considered 1 ML (6.3×10^{14} atoms/cm²), 2 ML (1.26×10^{15} atoms/cm²) and 4 ML (2.52×10^{15} atoms/cm²) in a close-packed arrangement above the supercell. The number of Ag atom in a unit cell (1×1) is 1, 2, 4 for 1 ML, 2 ML and 4 ML, respectively.

The adsorption energy E_{ads} is calculated using the following equation:

$$E_{\text{ads}} = \left[E_{(\text{nAg/surf})} - E_{(\text{surf})} - nE_{(\text{Ag})} \right] / n \quad (1)$$

where $E_{(\text{nAg/surf})}$, $E_{(\text{surf})}$ and $E_{(\text{Ag})}$ represents the total energy of Ag supported on KNbO₃ (101) surface, bare KNbO₃ (101) surface and a single gas-phase silver atom, respectively. “n” is the number of Ag atoms per unit cell.

The surface dipole moment μ is calculated using the following equation:

$$\mu = q/d \quad (2)$$

where q is the charge of Ag and d is the distance between Ag layer and the surface of KNbO₃.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization. Figure 1 displays the XRD patterns of the as-prepared Ag/KNbO₃ samples with various Ag contents (0.4–2.8 wt%). Upon deposition of Ag nanoislands, KNbO₃ supports are still well indexed to orthorhombic KNbO₃ with *Bmm2* space group (JCPDS card 71-2171). No changes of KNbO₃ diffractions and lattice parameters occur. Additionally, no diffraction patterns from Ag are observed in 0.4 wt% Ag/KNbO₃, possibly because the Ag content is below the detection limit and/or Ag nanoislands are finely dispersed on the surface of KNbO₃. As for 1.7 wt% and 2.8 wt% Ag/KNbO₃, the diffraction peak at 2 θ value of 38.1° can be indexed to the (111) crystal plane of metallic Ag (JCPDS card 04-0783), and the peak intensity increases with increasing Ag contents. TEM images (Figure 2(A)) show that the overall morphology of KNbO₃ supports is retained upon the deposition of three-dimensional (3D) quasi-hemispherical Ag nanoislands. Based on statistical TEM measurements, for Ag contents from 0.4 to 2.8 wt% the respective average size of Ag nanoislands is shown to be (12.2 $\pm$ 8.3) nm, (15.8 $\pm$ 7.7) nm, (17.3 $\pm$ 7.3) nm, respectively. Ag nanoislands with either single-crystal structure (Figure 2(C)) or twinned-crystal structure (Figure S1) are frequently observed. Representative HAADF-STEM image of 1.7 wt% Ag/KNbO₃ is shown in Figure 2(C) and corresponding line profiles marked in Figure 2(C) are displayed in Figure 2(D). The interatomic distance is 2.06 Å, which is in agreement with the interplane spacing of Ag (200) plane. As for KNbO₃, the corresponding line profiles fit well to (101) plane. The imaging evidences that Ag 3D nanoislands contain multi-layers and closely contact with KNbO₃ NWs to construct Ag/KNbO₃ nanocomposites.

Figure 3 displays the DRUV-Vis spectra of Ag/KNbO₃ samples. The pristine KNbO₃ NWs exhibit absorption only at wavelength less than 400 nm. Upon Ag deposition, prominent LSPR-derived absorption centered at *ca.* 550 nm is displayed in the visible region, which is consistent with a dramatic sample color change from white (KNbO₃) to gray (Ag/KNbO₃). Moreover, increasing Ag contents significantly intensifies the LSPR absorption. For example, the absorption intensity is increased about one fold from 0.4 to 2.8 wt% Ag. Figure 4 displays the corresponding Raman spectra of Ag/KNbO₃ nanocomposites. For KNbO₃ NWs, the bands located at 192, 280, 532, 595, and 832 cm⁻¹ are attributed to the translational mode of K⁺, blending mode ν_5 , stretching mode ν_2 , stretching mode ν_1 , and the combination of ν_1 and ν_5 , respectively.²² With Ag content increasing, the band intensity at *ca.* 595 and 832 cm⁻¹ is significantly enhanced, due to the surface enhanced Raman scattering (SERS) from metallic Ag nanoislands. To identify the chemical state of Ag/KNbO₃ nanocomposites, XPS measurements were carried out. Figure 5(A) shows Ag 3d core-level spectra. Apparently, the Ag 3d core-level peak can be fitted by using one component, with a doublet at *ca.* 367.8 and 373.8 eV, respectively. Herein, Ag

3d_{5/2} located at 367.8 eV shows a negative binding energy shift (ca. 0.5 eV) with respect to that of metallic Ag. In general, the mechanisms of core-level shifts are divided into initial state effects where shifts arise because of the chemical bonding, including charge transfer, and into final state effects that take into account shifts due to core-hole screening and relaxation. Previous studies have proved that the observed Ag binding energy shift is predominantly ascribed to final state effects.²³ As shown in our following spin-polarized DFT calculations, the net electron transfer between Ag and KNbO₃ is very small. Since electron transfer is a dominant factor in determining the initial state effects as well as metal-semiconductor interaction, which is shown to be weak between Ag and KNbO₃. Figure 5(B) displays Nb 3d core-level spectra. Compared to pristine KNbO₃, there is a slight positive shift of Nb 3d_{5/2} (ca. 0.3 eV) of Ag/KNbO₃. Likewise, O 1s core-level spectra displayed in Figure 5(C) show a positive shift (ca. 0.2 eV). In general, when Ag nanoislands are deposited on KNbO₃, the positions of the Fermi energy levels are adjusted to the same value, giving to a downward shift of the KNbO₃ Fermi level and an upward shift of the Ag Fermi level. Therefore, both Nb 3d and O 1s are positively shifted. The downward band bending occurred at the energy band edges in KNbO₃ due to the electric field between Ag and KNbO₃. PL is an efficient technique to probe the efficiency of electron-hole recombination. Figure 6 shows the PL spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites. The PL band intensity located at ca. 545 nm slightly decreases upon 0.4 wt% Ag deposition. With further increasing Ag content up to 1.7 wt%, the PL intensity dramatically decreases, indicating a reduced rate of electron-hole recombination. The observed PL intensity decrease is ascribed to the efficient electron transfer from KNbO₃ NWs to Ag nanoislands under light illumination. Nevertheless, the PL intensity increases again upon Ag deposition up to 2.8 wt%. In this case, Ag can adversely either act as a recombination center or cover the surface of KNbO₃ NWs to shield UV absorption, leading to a decrease in charge separation as well as photocatalytic activity. The above PL results demonstrate that there is an optimal Ag content for the most efficient electron-hole separation. As shown in the following section, the variation of PL intensity is consistent with that of the observed photoreactivity.

3.2 Photocatalytic Degradation and Reaction Mechanism of RhB

3.2.1 Photocatalytic Reactivity and Stability. The photocatalytic activities of Ag/KNbO₃ nanocomposites were assessed for RhB degradation under UV-light and visible-light illumination, respectively. For the blank experiment without catalysts, RhB degradation under either UV or visible-light illumination (i.e., photolysis) is negligible (data not shown). To evaluate the photoreactivity quantitatively, the reaction rate constants were calculated based on the Langmuir-Hinshelwood kinetics and the results are presented in Figure 7. First, loading Ag nanoislands onto KNbO₃ NWs to form Ag/KNbO₃ nanocomposites dramatically enhances the

photoreactivity. For example, for 1.7 wt% Ag, the photocatalytic reaction rate of Ag/KNbO₃ exceeds that of KNbO₃ by a factor of *ca.* 13 under UV. Second, the photoreactivity is shown to be Ag content-dependent in the range of 0.4–2.8 wt%. It decreases by either decreasing the Ag contents down to 0.4 wt% or increasing the Ag contents up to 2.8 wt%. In detail, it decreases from $55.38 \times 10^{-3} \text{ min}^{-1}$ to $30.64 \times 10^{-3} \text{ min}^{-1}$ when decreasing the Ag contents from 1.7 wt% down to 0.4 wt% and to $31.44 \times 10^{-3} \text{ min}^{-1}$ when further increasing the Ag contents up to 2.8 wt%. The visible-light photoreactivity of Ag/KNbO₃ was evaluated and displayed in the right panel of Figure 7. The photoreactivity of Ag/KNbO₃ is increased with increasing Ag contents. In detail, the reaction rate constant of Ag/KNbO₃ is about $0.68 \times 10^{-3} \text{ min}^{-1}$ for 0.4 wt% Ag, $4.50 \times 10^{-3} \text{ min}^{-1}$ for 1.7 wt% Ag and $5.00 \times 10^{-3} \text{ min}^{-1}$ for 2.8 wt% Ag. To investigate the photostability of Ag/KNbO₃ nanocomposites, the recycling test was performed and the results are shown in Figure S2. After three cycles of aqueous RhB degradation under either UV- and visible-light illumination, no significant loss of activity of 1.7 wt% Ag/KNbO₃ was observed. Our results demonstrate that Ag/KNbO₃ nanocomposites present high stability in the photocatalytic reactions and can be reused.

3.2.2 Active Species Determination. In order to identify the major active species responsible for RhB degradation, trapping experiments are carried out. Figure 8 shows that all scavengers are able to decrease the degradation efficiency to some degree. In detail, the RhB degradation efficiency is reduced from 95.7% to respective 24.4% and 39.5% in the presence of PBQ and TBA after 90 min UV illumination, indicating that $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are the major active species in the reaction. Under visible-light illumination up to 210 min, the RhB degradation efficiency is reduced from 64.9% to respective 17.2% and 40.4% in the presence of PBQ and AO, suggesting that $\bullet\text{O}_2^-$ and h^+ are the major active species. Nevertheless, $\bullet\text{OH}$ displays a negligible role in the photocatalytic processes. Thus, the reactive species is shown to be wavelength-dependent and $\bullet\text{OH}$ radical displays a more important role under UV compared to visible-light. $\bullet\text{OH}$ can be generated through either H₂O₂ photolysis formed by either two-electron reduction of O₂ ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = -0.33 \text{ V}_{\text{NHE}}$) or oxidation of OH⁻ and H₂O.²⁴ The oxidation power of KNbO₃ VB holes is $+2.2 \text{ V}_{\text{NHE}}$ which is insufficient to oxidize OH⁻ and H₂O to form $\bullet\text{OH}$ ($\bullet\text{OH}$, $E^0_{\text{ox}} = +2.72 \text{ V}_{\text{NHE}}$).²⁵ Thus, $\bullet\text{OH}$ involved in the current photocatalytic system should be produced by the photolysis of H₂O₂ molecules. While, $\bullet\text{OH}$ radical is absent under visible-light due to the insufficient photon energy for the photolysis of H₂O₂ molecules.²⁶ In general, $\bullet\text{O}_2^-$ can be formed by O₂ molecules through accepting electrons ($E^0(\text{O}_2/\bullet\text{O}_2^-) = -0.33 \text{ V}_{\text{NHE}}$). The reduction power of KNbO₃ ($-1.05 \text{ V}_{\text{NHE}}$) is enough to reduce O₂ molecules into $\bullet\text{O}_2^-$. Based on the above radical trapping experimental results, the major

reaction steps functional in the RhB photodegradation processes under both UV and visible-light illumination are shown in the Supporting Information.

3.2.3 Intermediate Product Identification. The TOC measurements were conducted to evaluate the mineralization degree of the most active photocatalyst 1.7 wt% Ag/KNbO₃. The TOC change at 90 min under UV is 2.987 ppm, much greater than that under visible-light (0.425 ppm) at 210 min. In addition, the NO₃⁻ concentration change at 90 min under UV and 210 min under visible-light is 0.3799 and 0.2789 ppm, respectively. The above results are consistent with the different photocatalytic performance between UV and visible-light. Major intermediate products generated in the presence of 1.7 wt% Ag/KNbO₃ nanocomposites were probed by UPLC-MS. Figure S3 shows that 1.7 wt% Ag/KNbO₃ nanocomposites under UV light share the same degradation pathway with pristine KNbO₃ NWs, highlighting N-deethylation and conjugated structure cleavage.¹⁷ Under visible-light illumination, a series of intermediate products are identified (Table S1), including m/z 359 (compound A', retention time 3.99 min), m/z 491 (compound B', retention time 4.46 min), m/z 387 (compound C', retention time 4.59 min), m/z 387 (compound D', retention time 4.66 min), and m/z 415 (compound E', retention time 5.23 min). Figure S4 shows the RhB peak (m/z 44, compound F', retention time 5.75 min) dramatically decreases after 210 min irradiation. Figure S5 shows that the peak area increases with irradiation time, indicating the formation and transformation of the reaction intermediates. Based on the above analysis, we propose the visible-light induced N-deethylation in Figure S6. In detail, N-deethylated intermediate (m/z = 415) is degraded into an intermediate (m/z = 387) and then another intermediate (m/z = 359). Further, one of the hydrogen (-H) and two of the ethyl groups (-C₂H₅) bonded to the nitrogen atom in the RhB molecule are oxidized to carboxyl groups (-COOH) to generate an intermediate with an m/z value of 491. The above analyses confirm that the photodegradation of RhB under visible-light follows a stepwise loss of ethyl groups. It has been reported that most N-deethylation and conjugated structure cleavage is preceded by the formation of a nitrogen-centered and carbon-centered radical, respectively.²⁷ The photogenerated active species •OH is one of the most active oxidants which could directly attack the central carbon of RhB and consequently decolorize RhB. While, the active species h⁺ generated from the LSPR effects of Ag nanoislands under visible-light is a weaker oxidant comparing to •OH generated under UV illumination. Thus, wavelength-dependent degradation pathway is observed in this work. That is, conjugated structure cleavage and N-deethylation is predominant under UV and visible-light illumination, respectively.

The corresponding UV-vis spectral and successive color changes of RhB solutions under UV and visible-light is shown in Figure 9. Obviously, the characteristic absorption band of RhB at 554 nm decreases with

increasing illumination time. Moreover, under visible-light hypsochromic shifts for the maximum absorption band are observed from 554 to 538 nm. The shifts are owing to the formation of five N-deethylated intermediates (i.e., $m/z = 415$, $m/z = 387$, $m/z = 387$, $m/z = 359$ and $m/z = 331$ with maximum absorption at 541, 525, 529, 514 and 502 nm, respectively),²⁸ in agreement with the above UPLC-MS results. Overall, conjugated structure cleavage is predominant over N-deethylation under UV, while N-deethylation is preferred under visible-light.

3.3 Spin-polarized DFT Study of Ag on KNbO₃ (101) Surface. To gain the insight of interplay between Ag nanoislands and KNbO₃, we employed spin-polarized DFT calculations. To model large supported Ag nanoislands, we considered a Ag extended adlayer with coverage ranging from 1 monolayer (ML), 2 ML to 4 ML in a close-packed arrangement above the supercell. Our recent results have proved that the dominant facet exposed on KNbO₃ NWs is (101) with NbO-termination.¹⁷ In the present study, both NbO- and KO-terminations of KNbO₃ (101) were examined, and the results show that NbO-terminated surface is more stable than KO-terminated one. Therefore, we examined the Ag adsorption properties and associated electronic structure of Ag/KNbO₃ (101) with NbO-termination. Figure 10 shows the optimized structure from our DFT calculations. Herein, we employed Ag extended adlayers (1–4 ML) on slab models of the KNbO₃ (101) to describe the observed large Ag nanoislands. Table 1 lists the calculated adsorption energies (E_{ads}), Ag-O bond lengths ($d_{\text{Ag-O}}$), work function change ($\Delta\phi$) and dipole moment (μ) as a function of Ag coverages. Both E_{ads} and μ decrease with increasing coverage, indicating an attractive interaction between the Ag adatoms. Likewise, the $d_{\text{Ag-O}}$ is 2.34, 2.39 and 2.56 Å for 1, 2, 4 ML, respectively. Overall, KNbO₃ is able to stabilize Ag (100)-like structure. The higher the Ag coverage, the more stable the supported Ag adlayers.

The Ag extended adlayers are partly positively charged ($\sim 0.1e$), which decreases from 0.1 to 0.05 e with the increasing of Ag coverage from 1 ML to 2 ML. In the case of 4 ML, Ag is metallic. We also calculated the electron localization function (ELF) of Ag/KNbO₃ (101). The 2D slice of ELF projected perpendicular to the surface is plotted in Figure 11. One can see that the effect of Ag deposition on the surface is not significant. Figure 11(A) shows that the deposition of 1 ML Ag only introduces slight polarization of electron density on the surface, which decreases with increasing Ag coverage up to 2 ML (Figure 11(B)) and almost disappears after the growth of the second layer (Figure 11(C)). Accordingly, the possible surface polarization can only be achieved by limiting the growth of Ag to one layer. The multilayer structures of Ag on KNbO₃ (101) inhibit the electron polarization on the surface. To get the detailed interplay between Ag and KNbO₃, the partial density of states (PDOS) were calculated (Figure 12). As shown in Figure 12 (A), the calculated band gap of KNbO₃ (101) is 2.0 eV, which is lower than the experimental value of 3.2 eV. It is generally accepted that the calculated band gap by

DFT is often underestimated.²⁹ The electronic states of Ag adlayers appear mixed with the top of O 2p valence band. The ionic nature of Ag is clearly shown at the coverage of 1ML (Figure 12(B)), which is also demonstrated by the highest positive charge for Ag among the systems studied. With the Ag coverage increasing to 2 and 4 MLs, the metallic nature becomes more and more dominant. The supported Ag layers behave like Ag bulk surface in term of electronic properties, where a continuum of Ag states is formed within the band gap (Figure 12 (C) and (D)). The metallic Ag nanoislands act as electron-hole recombination centers at high Ag contents like 2.8 wt%, which can help the visible-light-induced LSPR.

3.4 Discussion. The deposition of Ag nanoislands onto KNbO₃ NWs has been shown to enhance the photocatalytic performance. Figure S7(A) shows the band structure of Ag/KNbO₃ nanocomposites. As reported in our previous work,¹⁷ the valence band (VB) maximum of KNbO₃ NWs lies at 2.2 eV and the band gap of KNbO₃ is 3.25 eV. Because KNbO₃ is a p-type semiconductor,³⁰ the Fermi level is rather close to the VB maximum. As for Ag nanoislands, the Fermi level is -4.26 eV.³¹ On the basis of aforementioned XPS results, interfacial electron transfer occurs between Ag and KNbO₃ to reach an equilibrium and form a Schottky barrier, albeit the amount of electron transfer is small. Accordingly, the Fermi levels of KNbO₃ and Ag nanoislands are aligned to form a new Fermi level. And the energy band of KNbO₃ bends downward toward the interface.³² Under UV-light illumination, electrons in the VB of KNbO₃ are excited to the CB with simultaneous holes generation in the VB. As presented in Figure S7(A), the energy level of CB bottom is higher than the new Fermi energy level of Ag/KNbO₃. Consequently, the photoexcited electrons could transfer from KNbO₃ NWs to Ag nanoislands driven by the potential energy shown in Figure S7(B). Thus, the photogenerated electrons and holes in KNbO₃ would be separated efficiently to reach the surface and trigger the photocatalytic reaction. In addition, Ag nanoislands can absorb UV-light due to the interband transition from 4d electrons to 5sp to cause dye degradation.³³ Therefore, the higher Fermi level of Ag than that of KNbO₃ and photocatalytic activity of Ag nanoislands should synergistically enhance the photoreactivity. However, the excessive surface Ag concentration can also adversely act as a recombination center and partly shield the UV absorption on KNbO₃, resulting in a decrease in the photocatalytic activity. Therefore, the photoreactivity of Ag/KNbO₃ is decreased after the Ag contents exceed the optimal amount.

It is well known that LSPR arises from light-excitation induced collective oscillations of the electrons on the Ag surface.³⁴ Under visible-light irradiation, electrons in the Ag nanoislands are photoexcited through intraband excitations within the sp band. Unlike the mechanism under UV, the visible-light driven photocatalytic process includes plasmonic sensitization, i.e., an electron-transfer process from Ag nanoislands to KNbO₃ NWs via

LSPR (Figure S7(C)).³⁴ By rapid injecting hot electrons into the CB of KNbO₃, Ag nanoislands are positively charged (i.e., Ag⁺ ions). In addition, RhB can be excited to form agitated RhB (RhB*) by absorbing visible-light *via* photosensitization. When RhB* absorbs on the surface of KNbO₃, electron transfer occurs from RhB* to KNbO₃ generate oxidized RhB (RhB⁺). Subsequently, the injected electrons can migrate to the KNbO₃ surface to reduce surface absorbed O₂ molecule to form reactive species •O₂⁻. Further, Ag⁺ ions are also reactive species.³⁵ The above active species will be responsible for the degradation and mineralization of RhB. The highest photoreaction rate constant of Ag/KNbO₃ under visible-light is 5.00×10⁻³ min⁻¹, possibly due to the reversed charge transfer within Ag/KNbO₃ nanocomposites under visible-light compared to UV-light. The energy barrier formed in the junction of Ag/KNbO₃ nanocomposites is unfavorable for the charge transfer from Ag to KNbO₃, and the advantage of Ag/KNbO₃ is thus reduced under visible-light.

The electronic properties of Ag/KNbO₃ revealed by first principle DFT approach show some implications on the observed photoreactivity. Herein, Ag atoms are arranged in close-packed ML above the appropriate supercell to model large Ag nanoislands supported on KNbO₃ (101) surface. First, the relative low adsorption energy compared to gas phase confirms the wetting of Ag adlayerd on the surface. According to the PDOS calculated using DFT, the VB and CB are mainly composed of O 2*p* and Nb 3*d*, respectively. Upon 1 ML Ag deposition, Ag-derived states dominantly appear around the E_f. Increasing Ag coverage up to 2-4 ML further forms continuous Ag *s*-like states within the bandgap. The above results evidence visible-light-induced photocatalytic performance of Ag/KNbO₃. Prior experimental studies suggested that metallic Ag in zero-valent state is responsible for the photoreactivity.³⁶ Based on the DFT simulations, Muhich et al. reported that under UV-light for a Pt₃₇ cluster supported on anatase TiO₂ (101), Pt derived-states completely bridge the band gap and act as electron-hole recombination for relatively high Pt loadings.³⁷ Likewise, our results observe similar phenomenon in the case of Ag/KNbO₃ at higher coverage of Ag. Accordingly, the observed photoreactivity first increases and then decreases with increasing Ag contents under UV-light. In addition, the metallic Ag nanoislands at higher coverage also benefit LSPR under visible-light to generate electron-hole pairs and catalyze organic pollutant mineralization.

4. CONCLUSIONS

The photoreactivity toward aqueous RhB degradation by Ag/KNbO₃ nanocomposites was shown to be excitation light wavelength- and Ag content-dependent. Modifications of KNbO₃ with Ag nanoislands (0.4–2.8 % in weight) not only enhanced the photoreactivity of KNbO₃ NWs under UV, but also rendered KNbO₃ NWs photoreactive under visible-light owing to LSPR. Overall, Ag/KNbO₃ nanocomposites display more enhanced reactivity under UV than that under visible-light. In the case of optimal Ag content (ca. 1.7 wt%), the maximum enhancement in terms of photocatalytic reaction rate is achieved under UV, and Ag/KNbO₃ ($55.38 \times 10^{-3} \text{ min}^{-1}$) exceeds KNbO₃ ($4.20 \times 10^{-3} \text{ min}^{-1}$) by a factor of *ca.* 13. Upon visible-light irradiation, there is increment in the reaction rate constant, i.e., 0.68×10^{-3} , 4.50×10^{-3} and $5.00 \times 10^{-3} \text{ min}^{-1}$ for 0.4, 1.7 and 2.8 wt% Ag, respectively. Further, the reactive species is shown to be wavelength-dependent and •OH plays a more important role under UV than under visible-light. Accordingly, the conjugated structure cleavage and N-deethylation play a predominant role in catalyzing RhB degradation under UV and visible-light illumination, respectively. The Ag-KNbO₃ interaction has been revealed using spin-polarized DFT calculations. A Bader analysis of the electron density shows a small net charge transfer ($\sim 0.1 \text{ e}$) from KNbO₃ surface to Ag nanoislands, which decreases to 0.05 e with the increasing Ag coverage. The ELF plots of Ag/KNbO₃ (101) illustrate that Ag extended adlayers larger than 2 ML are metallic in nature and weak polarization occurs at the Ag-KNbO₃ interface. Nevertheless, the deposition of Ag nanoislands onto KNbO₃ results in continuous states within the band gap and increases electron density at Fermi level. Consequently, in the Ag content range of 0.4–2.8 wt%, UV-induced photoreactivity first increases then decreases with Ag contents, while visible-derived one monotonically increases with increasing Ag contents. Our results demonstrate that dispersing plasmonic metal particles across the perovskite surfaces is an efficient approach for enhancing organic pollutant degradation, and potentially has broad implications in other areas like water splitting.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

Any additional relevant notes should be placed here.

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Figure and Table captions

Figure 1. XRD patterns of Ag/KNbO₃ nanocomposites with various Ag contents.

Figure 2. Representative TEM and STEM images of KNbO₃ NWs and 1.7 wt% Ag/KNbO₃ nanocomposites. (A) A typical KNbO₃ NW. (B) 1.7 wt% Ag/KNbO₃. (C) HAADF-STEM image of a typical Ag nanoisland and (D) corresponding line profiles showing the image intensity as a function of position along X–X' and Y–Y' in (C).

Figure 3. DRUV-Vis spectra of Ag/KNbO₃ nanocomposites as a function of Ag contents.

Figure 4. Raman spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites.

Figure 5. XPS spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites. (A) Ag 3d core-level. (B) Nb 3d core-level. (C) O 1s core-level. The spectra were fitted by using one peak of mixed Gaussian-Lorentzian line shape. The Nb 3d core-level of KNbO₃ NWs is adapted from ref.¹⁷ Published by The Royal Society of Chemistry.

Figure 6. PL spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites.

Figure 7. Photodegradation of RhB on Ag/KNbO₃ nanocomposites. Ag/KNbO₃ under UV (left panel) and visible-light (right panel). The photocatalytic performance of KNbO₃ NWs is adapted from ref.¹⁷ Published by The Royal Society of Chemistry.

Figure 8. Degradation efficiency for the photodegradation of RhB with selected scavengers in the presence of 1.7 wt% Ag/KNbO₃ after (A) 90 min of UV illumination and (B) 210 min of visible-light illumination.

Figure 9. UV-vis spectral changes of RhB solutions in the presence of 1.7 wt% Ag/KNbO₃ (A) under UV and (B) under visible-light. Corresponding successive color change of RhB solutions under (C) UV and (D) visible-light illumination.

Figure 10. Structure of Ad adlayers on KNbO₃ (101). Side view of (A) KNbO₃ (101), (B) Ag/KNbO₃ (101) with 1 ML Ag, (C) Ag/KNbO₃ (101) with 2 ML Ag, (D) Ag/KNbO₃ (101) with 4 ML Ag. Corresponding top view of (E) KNbO₃ (101), (F) Ag/KNbO₃ (101) with 1 ML Ag, (G) Ag/KNbO₃ (101) with 2 ML Ag, (H) Ag/KNbO₃ (101) with 4 ML Ag.

Figure 11. Side view of ELF plots of Ag/KNbO₃ (101) with Ag coverage of (A) 1 ML, (B) 2ML and (C) 4 ML, where the projected 2D slices perpendicular to the surface are displayed. The isosurface level was chosen as 0.02 e/a_0^3 (a_0 = Bohr radius). The color bar represents the probability of finding the electrons.

Figure 12. Partial density of states (PDOS) of (A) KNbO_3 (101), (B) Ag/KNbO_3 (101) with 1 ML Ag, (C) Ag/KNbO_3 (101) with 2 ML Ag and (D) Ag/KNbO_3 (101) with 4 ML Ag.

Table 1. Ag coverage θ (ML) on the surface and the calculated adsorption energies E_{ads} (eV), Ag-O bond lengths $d_{\text{Ag-O}}$ ($\text{\AA}$), change in work function $\Delta\phi$ (eV) and dipole moment μ (D) for Ag adsorption on the KNbO_3 (101) surface.

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θ (ML)	E_{ads} (eV/Ag atom)	$d_{\text{Ag-O}}$ (Å)	$\Delta\phi$ (eV)	μ (D)
1	-2.40	2.34	0.27	1.12
2	-2.70	2.39	1.15	0.69
4	-2.94	2.56	1.95	0.0

Figure 1. XRD patterns of Ag/KNbO₃ nanocomposites with various Ag contents.

Figure 2. Representative TEM and STEM images of KNbO₃ NWs and 1.7 wt% Ag/KNbO₃ nanocomposites. (A) A typical KNbO₃ NW. (B) 1.7 wt% Ag/KNbO₃. (C) HAADF-STEM image of a typical Ag nanoisland and (D) corresponding line profiles showing the image intensity as a function of position along X–X' and Y–Y' in (C).

Figure 3. DRUV-Vis spectra of Ag/KNbO₃ nanocomposites as a function of Ag contents.

Figure 4. Raman spectra of KNbO_3 NWs and Ag/KNbO_3 nanocomposites.

Figure 5. XPS spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites. (A) Ag 3d core-level. (B) Nb 3d core-level. (C) O 1s core-level. The spectra were fitted by using one peak of mixed Gaussian-Lorentzian line shape. The Nb 3d core-level of KNbO₃ NWs is adapted from ref.¹⁷ Published by The Royal Society of Chemistry.

Figure 6. PL spectra of KNbO₃ NWs and Ag/KNbO₃ nanocomposites.

Figure 7. Photodegradation of RhB on Ag/KNbO₃ nanocomposites. Ag/KNbO₃ under UV (left panel) and visible-light (right panel). The photocatalytic performance of KNbO₃ NWs is adapted from ref.¹⁷ Published by The Royal Society of Chemistry.

Figure 8. Degradation efficiency for the photodegradation of RhB with selected scavengers in the presence of 1.7 wt% Ag/KNbO₃ after (A) 90 min of UV illumination and (B) 210 min of visible-light illumination.

Figure 9. UV-vis spectral changes of RhB solutions in the presence of 1.7 wt% Ag/KNbO₃ (A) under UV and (B) under visible-light. Corresponding successive color change of RhB solutions under (C) UV and (D) visible-light illumination.

Figure 10. Structure of Ag adlayers on KNbO_3 (101). Side view of (A) KNbO_3 (101), (B) Ag/ KNbO_3 (101) with 1 ML Ag, (C) Ag/ KNbO_3 (101) with 2 ML Ag, (D) Ag/ KNbO_3 (101) with 4 ML Ag. Corresponding top view of (E) KNbO_3 (101), (F) Ag/ KNbO_3 (101) with 1 ML Ag, (G) Ag/ KNbO_3 (101) with 2 ML Ag, (H) Ag/ KNbO_3 (101) with 4 ML Ag.

Figure 11. Side view of ELF plots of Ag/ KNbO_3 (101) with Ag coverage of (A) 1 ML, (B) 2ML and (C) 4 ML, where the projected 2D slices perpendicular to the surface are displayed. The isosurface level was chosen as $0.02 \text{ e}/a_0^3$ (a_0 = Bohr radius). The color bar represents the probability of finding the electrons.

Figure 12. Partial density of states (PDOS) of (A) KNbO_3 (101), (B) Ag/KNbO_3 (101) with 1 ML Ag, (C) Ag/KNbO_3 (101) with 2 ML Ag and (D) Ag/KNbO_3 (101) with 4 ML Ag.

Supporting Information

Organic Pollutant Photodecomposition by Ag/KNbO₃ Nanocomposites: A Combined Experimental and Theoretical Study

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Table S1. Identification of major intermediate products derived from RhB degradation by UPLC-MS (positive ion mode ESI mass spectra) in the presence of 1.7 wt% Ag/KNbO₃ nanocomposites under visible-light.

Peak	Retention time [min]	m/z	Formula
A'	3.99	359
B'	4.46	491
C'	4.59	387
D'	4.66	387
E'	5.23	415
F'	5.75	443

Figure S1. High-resolution TEM image of a typical Ag nanoisland in 1.7 wt% Ag/KNbO₃ with twinned-crystal structure.

Figure S2. Recycling test of 1.7 wt% Ag/KNbO₃ in the photocatalytic degradation of aqueous RhB under (A) UV and (B) visible-light.

Figure S3. Total ion chromatography of RhB and temporal photodegraded intermediate products in the presence of 1.7 wt% Ag/KNbO₃ nanocomposites under UV.

Figure S4. Total ion chromatography of RhB and temporal photodegraded intermediate products in the presence of 1.7 wt% Ag/KNbO₃ nanocomposites under visible-light.

Figure S5. The change of MS peak intensity corresponding to major RhB intermediate products catalyzed by 1.7 wt% Ag/KNbO₃ nanocomposites under visible-light.

Figure S6. Proposed photodegradation pathways of RhB in the presence of 1.7 wt% Ag/KNbO₃ nanocomposites under visible-light.

Figure S7. (A) Schematic illustration of energy band position in Ag/KNbO₃ nanocomposites. Schematic representation of the charge transfer within Ag/KNbO₃ nanocomposites under illumination of (B) UV-light and (C) visible-light. CB: conduction band, VB: valence band, e⁻: electron, h⁺: hole, E_f: New Fermi level, E_{fm}: Fermi level of metallic Ag, E_{fs}: Fermi level of semiconductor KNbO₃.

The stepwise reaction steps and associated carrier transfer in the RhB degradation processes are summarized as following:

1. Under UV illumination:

2. Under visible-light illumination:

TOC