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Selective Synthesis of α -, β -, and γ -Ag₂WO₄ Polymorphs: Promising Platforms for Photocatalytic and Antibacterial Materials

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emission scanning electron microscopy images, and photoluminescence. To complement and rationalize the experimental results, first-principles calculations, at the density functional theory level, were carried out, leading to an unprecedented glimpse into the atomic-level properties of the morphology and the exposed surfaces of Ag_2WO_4 polymorphs. Following the analysis of the local coordination of Ag and W cations (clusters) at each exposed surface of the three polymorphs, the structure-property relationship between the morphology and the photocatalytic and antibacterial activities against amiloride degradation under ultraviolet light irradiation and methicillin-resistant *Staphylococcus aureus*, respectively, was investigated. A possible mechanism of the photocatalytic and antibacterial activity as well the formation process and growth of the polymorphs is also explored and proposed.

■ INTRODUCTION

Polymorphism is the ability of a chemical system to adopt different crystallized structures with identical chemical composition but different stabilities. As the crystal structure determines the properties of a material, polymorphism can have a direct impact on its functional properties and thus on its technological applications. Different polymorphs can have dramatically different chemical, physical, and biological properties. Often these changes in their crystal structure can lead to novel properties and the opening up of potential applications in several research areas, such as photocatalysts, sensing gases, and ion conductors among others.^{1–10}

copy, X-ray absorption near-edge structure spectroscopy, field-

Polymorphs of binary or complex metal oxides are well known in several oxides, namely, TiO_2 , $CaCO_3$, ZrO_2 , and WO_3 as well as zeolites and SiO_2 .^{11–16} These polymorphs have different stabilities and may transform, under particular conditions, from an unstable form (metastable phase) to a more stable polymorph. Metastable polymorphs are relevant for science and technology, offering more promising new design opportunities (both experimental and theoretical) to obtain superior properties for some applications other than their corresponding stable phase.^{17–23} Because of difficulties in

its control, polymorphism has often been considered to be a drawback in technological applications, limiting the development of various multifunctional materials. Therefore, the understanding of the relationship between the crystal structure and its functional properties is essential to the rational design of the synthesis, property, and function of polymorphism.²⁴ Recently, Gentili et al.¹⁰ published a review highlighting representative progress in the control and applications of polymorphism as an additional functionality of materials for technological applications.

Solid-state synthesis methods typically rely on equilibrium routes in which the most stable polymorph is obtained, whereas the metastable solid polymorphs tend to form via nonequilibrium or metastable states,^{25,24,26} which may be attained upon quenching an intermediate of the reaction or by

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different synthesis methods, such as the gas-phase, hydrothermal, mechanochemical, or template synthesis.²⁷ The polymorph-controlled synthesis of inorganic compounds, though crucially important, still remains a great challenge, offering a remarkable opportunity for discovering multifunctional materials with unusual properties.²⁸ While it is well established that the kinetics required to form different polymorphs from a specific precursor can often be manipulated by changing their synthesis conditions to obtain a metastable phase, the relative stability of kinetically accessible phases often falls within a fairly narrow range of energies. However, a fundamental understanding of which metastable phases can be synthesized and whether synthesizability is related to the excess enthalpy of a metastable phase above its thermodynamic ground state is still lacking.^{19,21} Answering this would enable a more rational approach in order to design and synthesize inorganic metastable phases and desirably assist in their experimental realization.^{29,30}

Silver tungstate (Ag_2WO_4) has received considerable attention in recent years due to its attractive characteristics, applicable over a wide range of practical scenarios. Ag_2WO_4 is a wide-band-gap multifunctional semiconductor material that presents structural polymorphism and can crystallize in three different structures. Among them, the α phase is, thermodynamically, the most stable one.^{31–33} In addition to the α polymorph, with orthorhombic structure and space group (Pn2n), the β - and γ -metastable phases, with hexagonal structure and space group $(P6_3/m)$ and cubic structure and space group (Fd3m), respectively, have also been described. α - Ag_2WO_4 presents unique structural properties³⁴ with a wide range of electrical and optical properties that can offer widespread applications including photocatalysis, gas sensors, antibacterial and antifungal agents, and photoluminescence (PL) emission, among others.^{32,34–49}

 Ag_2WO_4 polymorphs have been synthesized by precipita-on, $^{31,37,50-53}$ a conventional hydrothermal method 37,54 a ⁵³ a conventional hydrothermal method,³ tion,³ microwave-assisted hydrothermal method, 34,37,38,55-57 a sonochemical method,^{37,41,58,59} and simple ion exchange.⁶⁰ Recently, controlled precipitation was reported in the preparation of metastable β -Ag₂WO₄,⁵² where the addition of Eu ions was used as a stabilizing agent of the metastable β phase. Similarly, through a facile precipitation process in the presence of surfactants acting as a phase stabilizer, other authors have also reported the obtainment of this polymorph.^{56,61,62} The preparation of β -Ag₂WO₄ through a conventional precipitation route, without any assisted procedure, has also been reported.^{43,63-65} However, to date, the preparation of metastable γ -Ag₂WO₄ has been scarcely reported. For example, this polymorph was obtained through a simple controlled precipitation method at room temperature⁶⁶ and by surfactant assistance.⁶⁷ However, these synthesis processes are frequently unselective because they involve the production of a mixture of the different polymorphs and also affect their dimensions, morphology, microstructure, and subsequent functionality significantly. Different synthesis conditions yield different polymorphs and highlight the complexity of the energy landscape during the crystalformation process.

From a scientific point of view, our interest is to provide novel and selective routes to synthesize α -, β -, and γ -Ag₂WO₄ polymorphs separately. Thus, this study presents an experimental and theoretical investigation of the Ag₂WO₄ polymorphs, which were selectively synthesized from two common precursors thanks to careful control of the synthesis conditions, which revealed an alternative way to control Ag₂WO₄'s polymorphism. Establishing the atomic-scale structure of the surfaces is a key step to modeling this kind of material. Guided by the density functional theory (DFT) findings, we will disclose the delicate morphology and defect control of its antibacterial and photocatalytic mechanisms to comprehend, predict, and explain how these emerge. Finally, a number of insights into the role of the local coordination of the Ag and W cations in the three polymorphs, together with the crystallization process as a function of solution chemistry, will be provided, allowing us to propose a mechanism for the nucleation and growth processes by using the concept of clusters, namely [AgO_x] and [WO_y], as building blocks of the different α -, β -, and γ -phases.

The structures and electronic properties of the assynthesized samples were studied through X-ray diffraction (XRD) with Rietveld refinements, X-ray photoelectron spectroscopy (XPS), and X-ray absorption near-edge spectroscopy (XANES). Their optical properties were studied by using PL emission. Field-emission scanning electron microscopy (FE-SEM) images were employed to analyze their morphological evolution. The performance of the as-synthesized polymorphs as antibacterial agents against methicillin-resistant Staphylococcus aureus (MRSA) and their photocatalytic degradation of amiloride (AML) under ultraviolet (UV) light irradiation were also studied. First-principles calculations, based on DFT, were performed to calculate the relative energy between different phases, their electronic structures, and their surface energies. We applied a joint experimental and theoretical strategy, which we developed ourselves, to rationalize the experimental morphologies of the α -, β -, and γ -Ag₂WO₄ polymorphs.

The article is organized as follows. In Section 2, the experimental methods are presented. This section comprises four subsections: the synthesis procedure, the characterization techniques, the antibacterial and photocatalytic activities, and the computational methods and model systems. Section 3 presents the results and the discussion. The main conclusions are summarized in the last section, Section 4.

EXPERIMENTAL SECTION

Synthesis Procedure. The three different polymorphs of Ag₂WO₄ were synthesized via a simple precipitation method at 25 °C under constant stirring for 10 min without any surfactant, as previously reported in our previous work.34,66,68 Tungstate sodium dihydrate (Na2WO4·2H2O; 99.5% purity, Sigma-Aldrich) and silver nitrate (AgNO₃; 99.8% purity, Sigma-Aldrich) were used as precursor salts as received. In a typical synthesis procedure of Ag₂WO₄ crystals, appropriate quantities of AgNO3 and Na2WO4.2H2O were dissolved separately into 50 mL of deionized water. After 5 min of stirring, to ensure complete dissolution, the AgNO₃ solution was then added to the Na₂WO₄·2H₂O solution with continuous stirring. The resulting suspensions were collected using centrifugation methods. They were washed several times using acetone to remove the remaining ions and then dried in an oven at room temperature for 6 h. The chosen ratio for the precursor concentrations was 2:1 AgNO₃/Na₂WO₄·2H₂O. The concentration values between 0.0035 to 0.33 M were explored to find the most appropriate combination for the selective synthesis of the three polymorphs.

Characterization Techniques. In order to confirm the crystalline phase and purity of the polymorphs, their XRD patterns were obtained and indexed according to the reported patterns of each polymorph. The crystals were characterized using an X-ray diffractometer, model LabX XRD-6000 (Shimadzus, Japan), with a Cu K α irradiation source ($\lambda = 0.15418$ nm) at a scan rate (2θ) of 0.05° s⁻¹ in the range of 5–120°. Their sizes and shapes were examined using a FE-SEM Inspect F50 (FEI Company, Hillsboro, OR) operated at different magnifications. XANES measurements were performed at the XAFS2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS). XANES spectra were collected at W L1 edges in transmission mode at room temperature (using energy steps of 1.0 eV). For the XANES spectral analysis, the background was removed from all of the spectra, which were then normalized by extended X-ray absorption fine structure (EXAFS) oscillation using MAX software.⁶⁹

PL emissions spectra were recorded at room temperature by using a Monospec 27 monochromator (Thermal, Jarrel Ash, USA) coupled to a Hamamatsu Photonics R446 photomultiplier (Japan). A krypton ion laser (Coherent Innova, 200 K, USA) was used as an excitation source (k = 350 nm). The incident laser beam power on the sample was maintained at 15 mW. For chemical environment investigations, X-ray photoelectron spectroscopy (XPS) measurements were performed on a commercial Scientia Omicron ESCA (Germany) spectrometer using the monochromatic Al K α line (1486.7 eV). Normalization was performed using a nonlinear Shirley method. For the binding energy calibration of the elements, the peak of the C 1s element at 248.6 eV was used as a reference.

Photocatalytic Measurements. The photocatalytic activity was analyzed throughout the degradation process of amiloride (AML) under UV light irradiation (in a photoreaction box with six Philips lamps, 15 W, at 254 nm maximum emission and 39 mW cm⁻² optical irradiance). The photocatalytic degradation tests in the presence of Ag_2WO_4 polymorphs were conducted on 50 mg of each photocatalyst placed in contact with 50 mL of a 10 mg L^{-1} (10 ppm) aqueous amiloride solution. Prior to the photodegradation experiments, the mixture of AML and the photocatalysts was kept in the dark for 2 h, under magnetic stirring, to ensure the adsorption-desorption equilibrium. No prominent adsorption effect of Ag₂WO₄ polymorphs on the drug has been observed after 30 min of observation, which established negligible absorption effects. The color removal of the dye solutions was monitored by recording its UV-vis spectra (Jasco V-660 spectrophotometer, λ_{max} = 362 nm for the AML drug solution) at different light exposure times. The experiments were performed in triplicate.

The Langmuir–Hinshelwood model was applied to assess the kinetics of a photocatalytic process, which is well described by the following equation:

$$r = dC/dt = kKC/(1 + KC)$$
(1)

When the concentration is low $(1 \gg KC)$, the above equation can be simplified to a pseudo-first-order equation

$$r = dC/dt = kKC \text{ and } \ln(C/C_o) = -kKt = k_{app}t$$
(2)

where *r* is the reaction rate, *K* is the adsorption coefficient, C_0 and *C* are the initial and residual concentrations of AML, respectively, and *k* is the specific rate constant of the photoreaction. The photocatalytic degradation efficiency (PDE) was calculated according to the following equation:

$$PDE(\%) = (C/C_0) \times 100$$
 (3)

In order to detect the active species formed in this photocatalytic process, the so-called reactive oxygen species (ROS), a quencher experiment was performed by adding ascorbic acid (AA), isopropyl alcohol (IPA), and ammonium oxalate (AO), which are scavengers of the superoxide radical (O'_2), hydroxyl radical (OH*), and hole (h•), respectively.

Antibacterial Activity Test. In this study, a standard methicillinresistant *Staphylococcus aureus* (MRSA) strain obtained from the American Type Culture Collection (ATCC 33591), Gram-positive bacteria, was used in the antibacterial experiments. The protocol for determining the minimum inhibitory and bactericidal concentrations (MIC and MBC, respectively) was performed by following the procedure previously described elsewhere.⁷⁰ In order to better understand the bactericide activity of the Ag_2WO_4 polymorphs, a detailed analysis was performed in FE-SEM and confocal laser scanning microscopy (CLSM). The microorganisms were exposed to the respective subinhibitory concentration of each material in a 24-well plate and were then incubated in a static oven for 24 h. For FE-SEM analysis, the samples were washed with phosphate-buffered saline (PBS), submerged in 5% paraformaldehyde for 1 h, washed twice with PBS, and dissected with ethanol in increasing concentrations (70, 80, and 90% for 5 min). The finishing was done with 100% alcohol in three washes of 5 min each. Afterward, the samples were mounted on metal stubs and held in vacuum dessicators until the analysis.

For the monitoring of viability of the bacteria by confocal microscopy, the cells submitted to treatment were washed twice with PBS and labeled with the LIVE/DEAD BacLight Kit at 25 $^{\circ}$ C, following the manufacturer's recommendations. The analyses were performed under a Carl Zeiss LSM 800 microscope. The images were analyzed in the ZEN BLUE 2.3 System.

Computational Methods and Model Systems. In order to delve into the relationship between the structure and morphology of the α -, β -, and γ -Ag₂WO₄ polymorphs, theoretical calculations were performed using the DFT associated with the Perdew–Burke–Ernzerhof (PBE) formulation for the electron exchange and correlation contribution to the total energy^{71,72} in the VASP program.^{73,74} The electron–ion interaction was described through projector-augmented-wave pseudopotentials. The plane-wave expansion was truncated at a cutoff energy of 460 eV, and the Brillouin zones were sampled through the Monkhorst–Pack special *k*-point grid to ensure geometrical and energetic convergence for the Ag₂WO₄ crystal surfaces. Details of the slab thickness of the different surface models for the α -, β -, and γ -Ag₂WO₄ polymorphs can be found in previous studies.^{34,66,68}

The band-gap energy values and density of states (DOS) were obtained for both the bulk and surfaces of Ag_2WO_4 . To analyze the different kinds of Ag and W clusters at the exposed surfaces of each polymorph, a representation of the corresponding structure was performed by using the VESTA program.⁷⁵

The clean surfaces of each polymorph were simulated as follows: for the α -Ag₂WO₄, the (010), (001), and (101) surfaces have been selected. For β -Ag₂WO₄ and γ -Ag₂WO₄, the (011) and (110) surfaces and the (100), (101), and (111) surfaces have been investigated, respectively. The corresponding values of the surface energies (E_{surf}^i) were calculated with eq 4

$$E_{\rm surf}^{i} = (E_{\rm slab}^{i} - nE_{\rm bulk})/2A \tag{4}$$

where E_{slab}^i is the total energy of the corresponding slab (*i*), *n* is the number of molecular units present in the slab, E_{bulk} is the energy of the bulk of each polymorph, and 2*A* corresponds to the area of both sides of the slab. Calculating the E_{surf}^i values with the Wulff construction results in a polyhedron that depends only on the ratios between the values of the surface energies and symmetry point group.^{76,77}

By combining simulations based on first-principles calculations at the DFT level with experimental studies, our research group has recently proven that this strategy is a valuable design aid to achieving an optimum morphology since it offers a high-fidelity approach that results in the rapid *in silico* prediction of crystal growth habits. In addition, it allows us to establish a correlation among the morphology, properties, and subsequent applications for both micro- and nanomaterials, such as ZnO,⁷⁸ Ag₂O,⁷⁹ Ag₃PO₄,^{80,81} α -Ag₂WO₄,^{34,53} PbMOO₄,⁸² BaWO₄,⁸³ and ZnWO₄,^{84,85} A proof of concept has been developed that demonstrates the automation feasibility of the models^{86–88} used to obtain the set of morphologies available and match the theoretical morphology with the images displayed by FE-SEM. This proof of concept also motivates their continued development.

The polyhedron energy $(E_{polyhedron})$ values of both morphologies (theoretical and experimental) according to methodology proposed by our research group⁵³ were also calculated. In this study, we went

further and calculated the polyhedron band gap energy value $(E_{eav}^{polyhedron})$ for the α -, β -, and γ -Ag₂WO₄ polymorphs as follows

$$E_{\rm gap}^{\rm polyhedron} = \sum_{i} C_i \times E_{\rm gap}^i \tag{5}$$

where $C_i = A^i/A^{\text{polyhedron}}$ is the ratio of the surface area (A^i) to the total surface area of the polyhedron $(A^{\text{polyhedron}})$ and E^i_{gap} is the band gap energy value of the corresponding surface (i).

RESULTS AND DISCUSSION

Structural Characterization. Figure 1(a-c) shows the XRD patterns of the samples with different ratios between the



Figure 1. XRD patterns of the (a) γ -, (b) β -, and (c) α -Ag₂WO₄ polymorphs synthesized at a stoichiometric precursor ratio of 2:1 and different precursor concentrations.

AgNO₃ and Na₂WO₄·2H₂O precursors. The pattern in Figure 1a is indexed with the cubic γ -Ag₂WO₄ structure, in good agreement with the database (JCPDS 861157). A precursor concentration ratio of AgNO₃/Na₂WO₄·2H₂O equal to 0.33 M/0.165 M was used to obtain this polymorph. The intense, well-defined peaks indicate good crystallinity. By decreasing the concentration of the precursor salts until reaching molar concentrations of 0.04 M AgNO3 and 0.02 M Na2WO4·2H2O, the XRD peaks of the γ -Ag₂WO₄ disappeared and new peaks were identified. The new peaks were matched to the reflections of the hexagonal β -Ag₂WO₄ structure (JCPDS no. 331195), as shown in Figure 1b, in good agreement with our previous study.⁶³ By further decreasing the precursor's molar concentration to 0.007 and 0.0035 M for AgNO3 and Na2WO4·2H2O, respectively, a new XRD pattern was reached. The position and intensity of the well-defined XRD pattern peaks, as displayed in Figure 1c, were indexed to the standard orthorhombic α -Ag₂WO₄ structure (JCPDS no. 34-0061). No peaks related to any secondary phase were identified, indicating the formation of a pristine phase.

Figure 2 presents the 3D structures of the α -, β -, and γ -Ag₂WO₄ polymorphs, at the DFT level, following the optimized values of the geometry. An analysis of the results shows that Ag₂WO₄ polymorphs have a complicated network structure with a remarkable crystallographic inhomogeneity with an intrinsic anisotropy associated with their building blocks (i.e., constituent [AgO_x] and [WO_y] clusters).

W cations have different $[WO_y]$ (y = 4, 5, and 6) clusters, while Ag cations can display different $[AgO_x]$ type-coordination numbers: $[AgO_x]$ (x = 2, 4, 5, 6, and 7) clusters. The



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Figure 2. Unit cell representation of (a) α -Ag₂WO₄, (b) β -Ag₂WO₄, and (c) γ -Ag₂WO₄ structures and Ag–O and W–O bond distances (minimum and maximum).

piling up of these clusters builds the 3D structures of the different polymorphs. In the lattice of α -Ag₂WO₄, each W cation is bonded to six oxygens, forming three different distorted $[WO_6]$ clusters with values of the W–O bond lengths in the range of 1.677-2.238 Å. The Ag cations are found to have [AgO₂] clusters with an Ag–O bond distance of 2.255 Å, two [AgO₄] clusters with Ag–O bond distances in the range of 1.846-2.567 Å, an [AgO₆] cluster with Ag-O bond distances in the range of 2.329-2.743 Å, and two kinds of [AgO₇] clusters with Ag-O bond distances in the range of 2.252 and 3.037 Å. Overall, there are four different distorted $[AgO_x]$ (x = 2, 4, 6, and 7) clusters. The geometry of β - Ag_2WO_4 presents tetrahedral distorted $[WO_4]$ clusters, trigonal-bipyramidal distorted [WO₅] clusters, and two types of distorted [AgO_x] (x = 5 and 6) clusters. Finally, the γ -Ag₂WO₄ polymorph consists of only [WO₄] and [AgO₆] symmetric clusters.

The nature of the structural deviations from ideal orthorhombic and hexagonal symmetries that alter key structural features such as the Ag–O and W–O bond distances strongly influences their oxide electronic structure through 3d orbital occupancy and metal–oxygen orbital overlap. These electronic structure effects follow the elongation and compression of the metal–oxygen bond distances of the different clusters. The modification of the electronic bandwidth by the structural effects of strain alters a number of electronic features, such as the metal d band and O 2p band centers. This has several implications in the electronic properties and a broad range of chemical properties.

XANES is a useful technique that enables the investigation of the local order structure of different materials, providing qualitative information on the absorber atom environment



Figure 3. (a) Normalized W-L1 edge XANES spectra of references γ -WO₃ and Na₂WO₄ and of Ag₂WO₄ samples presenting distinct crystalline phases (α , β , and γ). (b) Detailed region of the XANES pre-edge region displayed in (a).



Figure 4. (Left) Relative concentration (C/C_0) versus time (min) for AML photocatalytic degradation by α -, β -, and γ -Ag₂WO₄ polymorphs under UV irradiation. Photolysis (\bullet), α (\blacktriangle), β (\blacklozenge), and γ (\blacksquare). (Right) Reaction kinetics of AML photodegradation for the different Ag₂WO₄ polymorphs.

such as the symmetry and oxidation state.^{37,89,90} Figure 3 presents the W LI-edge XANES spectra of the Na₂WO₄ and WO₃ reference compounds and the as-prepared Ag₂WO₄ polymorphs (α -, β -, and γ -phases). As can be observed, the environment around the W atoms is quite different for assynthesized Ag₂WO₄ samples, indicating that the environment around W atoms is distinct for the samples. Figure 3a shows that the spectra of β - and γ -Ag₂WO₄ samples and the Na₂WO₄ reference present an intense prepeak (labeled as A) at around 12.1 keV, while the α -Ag₂WO₄ and γ -WO₃ spectra exhibit a shoulder. According to the literature, the physical origin of peak A is related to forbidden electron transitions from 2s \rightarrow 5d orbitals.⁹¹ Yamazoe et al. reported that a less-symmetric structure enhances the intense prepeak because this forbidden electron transition is allowed by mixing the p orbitals of W atoms and the ligand into empty d orbitals.⁹¹ The presence of an intense prepeak in the W-L1 edge XANES spectrum has been reported in the compounds where the W atoms are coordinated by four oxygen atoms, such as Na₂WO₄ and $Sc_2W_3O_{12}$.⁹¹⁻⁹³ On the other hand, this prepeak becomes less pronounced in the compounds where the W atoms are in a distorted octahedral configuration, for example, the γ -WO₃ compound.91-93

A detailed view of the pre-edge region, as depicted in Figure 3b, revealed that the γ -Ag₂WO₄ spectrum pre-edge region is quite similar to the Na₂WO₄ reference, indicating that γ -Ag₂WO₄ exhibits a tetrahedral configuration (i.e., [WO₄] clusters). In the case of the α -Ag₂WO₄ spectrum, it was similar to the γ -WO₃ spectrum, which suggests octahedral coordina-

tion (i.e., $[WO_6]$ clusters). Regarding the β -phase spectrum, a slight reduction in the prepeak intensity and an energy shift toward high values can be seen when compared to the Na₂WO₄ spectrum. These findings can be linked to the presence of $[WO_5]$ clusters in the β -Ag₂WO₄ sample.

Photocatalytic Activity. Figure 4a shows the photocatalytic activity of Ag₂WO₄ toward AML degradation under UV irradiation as a function of time. The different profiles of (C_0/C) versus t are shown for each Ag₂WO₄ polymorph. The results show that photolysis in the absence of catalysts was around 37% after 40 min of exposure. An analysis of the results shows that 92% of AML was photodegraded by α -Ag₂WO₄ at 40 min, while only 70% was degraded in the case of γ -Ag₂WO₄ at the same time under UV irradiation. When β -Ag₂WO₄ was the catalyst used, photodegradation was practically completed within just 30 min under UV irradiation. Overall, the AML photodegradation process with Ag₂WO₄ polymorphs exhibited better photocatalytic activities than without them, implying an efficient use of all Ag₂WO₄ polymorphs for AML environmental remediation. The pseudo-first-order kinetic equation, expressed as $\ln(C_0/C) = k_{app}t$, is shown in Figure 4b. As can be observed, the relation between $\ln(C_0/C)$ and t has a fairly good correlation to the pseudo-first-order model, which indicates that AML degradation can be described well by this kinetic model.

The values of the rate constants for the degradation processes are shown in Table 1. An analysis of the results indicates that β -Ag₂WO₄ exhibits the highest constant rate with a *k* value of 0.114 min⁻¹. This *k* value is 1.9 and 4.1 times that

Table 1. Pseudo-First-Order Rate Constants (k_{app}) , Correlation Coefficients (R^2) , and Photodegradation Efficiencies (PDE) after 30 Minutes for the AML Degradation in Different Ag₂WO₄ Polymorphs

samples	$k_{\rm app}~({\rm min}^{-1})$	R^2	PDE (%)
without catalyst	0.0104	0.98	27
α -Ag ₂ WO ₄	0.059	0.99	83
β -Ag ₂ WO ₄	0.114	0.98	98
γ -Ag ₂ WO ₄	0.028	0.99	56

of α - and γ -Ag₂WO₄, respectively. Better efficiency of the metastable β -Ag₂WO₄ compared to that of α -Ag₂WO₄ has been reported for the dye photodegradation process under visible light.⁶² Under UV irradiation, β -Ag₂WO₄ also exhibited higher photocatalytic activity for methyl orange⁵⁶ and phenol and azo-dye X3B⁴³ degradation than for α -Ag₂WO₄ nanorods. The higher photocatalytic performance of β -Ag₂WO₄ can be ascribed to the differences between the surface structures of each faceted morphology. The particular features of the terminal clusters, the electronic distribution, and the active site population for each surface, among others, can be decisive during the adsorption and degradation process. Recently, some heterostructures have been used for the photodegradation of AML under both visible and UV irradiation.^{94,95} These heterostructures, namely, g-C₃N₄/Nb₂O₅⁹⁴ and Bi₂O₂CO₃/ BiVO₄⁹⁵ with different weight ratios among their components, were successfully used and have exhibited higher photoactivity than their isolated phases. Among all of the compounds, though, the highest kinetic constant value reported is exceeded 7.72 times by the value found in the present work for β -Ag₂WO₄.

Mechanism of Photocatalytic Activity. In order to further understand the behavior of the photocatalytic activity, an analysis of the PL emissions was carried out so as to investigate the recombination probability of the photogenerated charge carriers. Generally, a weaker PL intensity indicates a lower recombination rate of the photoinduced charges, usually resulting in higher photocatalytic activity. The relevant PL spectra are shown in Figure 5 for all Ag₂WO₄ polymorphs. The PL spectra of β - and γ -Ag₂WO₄ reveal highenergy emission peaks in the two samples with similar narrow shapes at around 400–500 nm. Regarding the α -Ag₂WO₄ samples, this peak is not clearly detected due to the presence of a broad, intense low-energy emission band with a maximum



Figure 5. PL spectra for the different Ag₂WO₄ polymorphs.

intensity in the range of 500–800 nm. This result was reported previously by our research group, and this peak can be associated with the presence of the structural disorder and silver or oxygen vacancies in the $[AgO_x]$ (x = 2, 4, 5, 6, and 7) clusters, which induce more deep defects in the forbidden band gap (defect emissions).^{37,48,96} For the α - and β -Ag₂WO₄ samples, the origin of such emission bands has been clarified.⁵² A similar origin can be assumed for γ -Ag₂WO₄. As Figure 5 shows, the emission peaks of the α - and γ -Ag₂WO₄ crystals are the strongest, indicating that the recombination rate of the photogenerated electron (e') and hole (h[•]) pairs is the largest one. Compared to the PL emission peaks of the α - and γ -Ag₂WO₄ crystals, the PL intensity of β -Ag₂WO₄ in the range of 400–466 nm is the weakest one, predicting that the charge combination rate of the photogenerated elect.

An XPS analysis was performed in order to identify the chemical composition of the surface, the chemical environment (binding energy), and the oxidation state of the elements. The photoelectron peaks of the Ag, W, and O elements are clearly presented in the expanded scan of the XPS spectrum in the range from 0 to 1200 eV, as shown in Figure 6a. The C 1s peak is due to the adventitious hydrocarbon from the XPS instrument itself. As shown in Figure 6b, the two characteristic peaks, located between 365.7 and 367.4 eV and 371.75 and 373.45 eV, could be assigned to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. The peaks in α -Ag₂WO₄ are slightly located toward higher bending energies, whereas the peaks in β - Ag_2WO_4 and γ - Ag_2WO_4 shift to a lower binding energy, indicating the variation of the Ag surface state in the different Ag₂WO₄ polymorphs. For all samples, no other peaks were observed in this range, which suggested that metallic Ag⁰ is not formed during preparation. The spectrum of W 4f shown in Figure 6c shows the typical two well-resolved spin-orbit split peaks related to the binding energy of W $4f_{7/2}$ and W $4f_{5/2}$ states, as reported recently in the literature.^{97,9}

According to the literature, the binding energies of W with different valences are arranged as $E(W^{6+}) > E(W^{5+}) > E(W^{4+})$, while the difference between them is ~1.5 eV.⁹⁹ In α -Ag₂WO₄, there were two peaks toward the higher binding energy values among all polymorphs, at 34.5 and 36.5 eV. These bands could be assigned to the W⁶⁺ oxidation state. For β -Ag₂WO₄, the two peaks of W 4f were located at energy binding values ~1.5 eV lower than the α peaks, at 32.95 and 35 eV, as expected for the W⁵⁺ oxidation state. However, the high-resolution W 4f spectrum of γ -Ag₂WO₄ presents two peaks, centered at 31.9 and 34.1 eV. A smaller shift in the energy bending position, very close to W⁵⁺, is observed in this polymorph regarding the expected typical W⁴⁺ oxidation state. This change could be related to a highly distorted tetrahedral cluster on the surface of this metastable polymorph.

The peaks in the O 1s spectrum (Figure 6d) in α - and γ -Ag₂WO₄ are asymmetrical, with a main O 1s core-level peak and an additional smaller tail or shoulder extending toward higher energies. Tentatively, the O 1s line with this characteristic has been considered in several systems as being formed by two components. This multicomponent approach can be divided into two bands. The low-energy component, generally with a major contribution, at ~529–530 eV, is ascribed to the crystal lattice oxygen (O^{2–}). The high-energy component could, alternatively, be assigned to surface defects, as an oxygen vacancy (V_O), and/or to chemisorbed oxygen species, as the surface hydroxyl group (OH). The components pubs.acs.org/IC

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Figure 6. (a) Expanded XPS spectra of α -, β -, and γ -Ag₂WO₄ nanocrystals and high-resolution XPS spectra of (b) Ag 3d, (c) W 4f, and (d) O 1s for each Ag₂WO₄ polymorph.

associated with OH may be influenced by the presence of oxygen vacancies. $^{100-102}$

For β -Ag₂WO₄, the intensity of the peak at high energy, at 531.6, clearly increases. This can imply that more V_O and/or OH groups on the surface of this polymorph can appear and contribute to its photocatalytic reactions. Different authors have pointed out that the presence of V_O and/or OH plays an active role during surface reaction phenomena.^{103–107} According to the results above, we suggest that V_O and/or OH on the surface of the β -Ag₂WO₄ photocatalyst could improve the photoactivity of the AML degradation process.

With the purpose of further exploring the mechanism of AML photodegradation, trapping experiments were carried out to identify which reactive species take part in the degradation process. AA, IPA, and AO scavengers for O'_2 , radical OH*, and h[•], respectively, were added to the photocatalytic system, and the results are shown in Figure 7. In addition, in order to know how much each of the scavengers inhibits the photodegradation, a "blank" containing AML only and the polymorphs without any scavenger was also used.

An analysis of the results included in Figure 7 shows a decrease in the photodegradation efficiency with the addition of all of the scavengers. The decrease was more pronounced when adding AA and AO, implying that O'_2 and h^{\bullet} play important roles in the photodegradation process in the α - and β -polymorphs, while the γ -phase shows a less-efficient photodegradation process with the participation of h^{\bullet} . It should be noted that OH* radicals were not the dominant active species. After gathering the XPS analysis and scavenger tests, we can suggest that the photogenerated h^{\bullet} 's in the valence band are trapped by the surface OH⁻ group to produce the hydroxyl radical, OH*, while the e''s in the conduction band are taken up by molecular oxygen, O_2 , to generate



Figure 7. Effects of different radical scavengers on AML degradation in α -, β -, and γ -Ag₂WO₄ polymorphs under UV irradiation.

superoxide radical O'_{2} , which can be considered to be the most important species in the photocatalytic activity.

In catalytic applications, the structural stability of a photocatalyst is a crucial parameter. After the photocatalytic process, the photocatalysts were separated from the solution by centrifugation between experiments. Later on, they were collected and the Ag₂WO₄ polymorphs were identified through XRD analyses. The patterns, displayed in Figure 8a, showed that the characteristic diffraction peaks of all of the samples still exist, which indicates certain photochemical stability of the three photocatalysts. Remarkably, for the β - and γ -phases, a relatively weak diffraction peak located at $2\theta = 38.1^{\circ}$ (Figure 8b), which corresponds to the (111) lattice plane of Ag



Figure 8. (a) XRD of α -, β -, and γ -Ag₂WO₄ microcrystals after the photocatalysis process. An amplification of corresponding Ag⁰(111) lattice plane is shown in (b).

(JCPDS no. 65-2871), was detected. However, this diffraction peak does not appear for α -Ag₂WO₄.

Other characteristic diffraction peaks of Ag located at $2\theta^{\circ}$ = 44.3, which correspond to the (200) plane, were not observed, confirming that the Ag phase is present in a very small concentration. This behavior can be understood in terms of a possible capture of some photoexcited electrons by Ag⁺ ions to form metallic Ag⁰ on the Ag₂WO₄ surface, as reported by our group for Ag-based materials under electron beam irradiation.^{40,64,96,108–113}

Antibacterial Activity. Through the counting of colonyforming units per milliliter (CFU/mL), similar antibacterial activity was observed between the β - and γ -phases, which in turn were superior to that in its α -phase. As Figure 9 shows,



Figure 9. Summary of \log_{10} CFU/mL MRSA values for inhibitory and subinhibitory concentrations of α -, β -, and γ -Ag₂WO₄. Control MRSA = 8.21 (±0.94) log10 CFU/mL.

the MBC values found for the materials were 62.5 μ g/mL for α -Ag₂WO₄ and 31.25 μ g/mL for β - and γ -Ag₂WO₄. It can also be observed that, even at the subinhibitory concentrations, all materials showed a reduction in the quantity of microorganisms when compared with the control.

The effects of the treatment with Ag_2WO_4 were analyzed through SEM microscopy images. Figure 10 shows a significant



Figure 10. FE-SEM micrographs of MRSA: (a) untreated and treated with (b) α -, (c) β -, and (d) γ -Ag₂WO₄.

reduction in the number of MRSA cells in the groups treated with α -Ag₂WO₄ (Figure 10b), β -Ag₂WO₄ (Figure 10c), and γ -Ag₂WO₄ (Figure 10d) in relation to the control (Figure 10a). Morphological changes in the cells in contact with the materials can be observed, which appear to have a shriveled surface.

The confocal laser microscopy images corroborate the findings in FE-SEM and CFU/mL, as shown in Figure 11. In comparison to the control (Figure 11a), all materials were effective at eradicating MRSA. When treated with the materials in β - and γ -phases, MRSA culture presents greater damage compared to the group treated with the α -phase of the material. Bacterial viability was monitored by the damage to the cell membrane caused by the treatments. When the cells



Figure 11. MRSA confocal laser scanning microscopy images: (A) untreated and treated with (B) α -, (C) β -, and (D) γ -Ag₂WO₄.

had their membranes compromised, they were marked in red and considered dead or were in the process of dying. When they had their membrane intact, they were marked in green and considered to be alive. Although β - and γ -phases showed similar antibacterial activity, it is possible to observe a greater number of nonviable cells in the bacterial culture treated with the β -Ag₂WO₄ (Figure 11c).

As a result of the metabolism and respiration of aerobic beings, low levels of ROS such as superoxide (O'_2) and hydrogen peroxide (H_2O_2) are produced. Although the cells have defense mechanisms against them, through superoxide dismutase and catalase, high concentrations of O'_2 and H_2O_2 overload the defense mechanisms of microbial cells, making them highly susceptible to other ROSs, such as OH* and singlet oxygen $(^1O_2)$.¹¹⁴ Semiconductor materials, such as Ag₂WO₄, are known to have the ability to release ROS. These, in turn, when in contact with microorganisms, are responsible for membrane damage, which lead them to death.^{40,115} Specifically in bacteria, proteins are affected by the rapid rates of reaction with ROS.¹¹⁴

Morphology and Surfaces Analysis. Most chemical reactions involved in the photocatalytic and antibacterial activity do not occur in the bulk phase but at a surface or interface. Their efficiency is strongly dependent on the exposed surfaces, which possess different atomic configurations and electronic properties. Modification of the charge-transfer processes ultimately result in distinct abilities. Then, the interplay between molecules/bacteria and active sites on the topmost surface of solid semiconductors determines their photocatalytic and antibacterial potential. These surface effects can be explained by three viewpoints: they may (i) generate ROS, (ii) release metal ions to destroy bacterial DNA and protein, or (iii) gather nanoparticles on the surface of the bacterial cell membrane and thus destroy the cell membrane and interrupt transmembrane electron transfer.^{116,117}

Figure 12a–c shows a number of FE-SEM images of the pure Ag_2WO_4 polymorphs under the experimental conditions.



Figure 12. Experimental FE-SEM images of (a) α -Ag₂WO₄, (b) β -Ag₂WO₄, and (c) γ -Ag₂WO₄ polymorphs synthesized at different precursors concentration ratio. The theoretical morphologies are included for comparison purposes.

The analysis of images shows that all samples are composed mainly of microsized particles. A wide particle size distribution can be observed. The final morphologies respond to the intrinsic anisotropic growth habits of the three polymorphs. The morphology of the α -Ag₂WO₄ orthorhombic structure is composed of the (010), (001), and (101) surfaces, while for the β -Ag₂WO₄ hexagonal structure, it is formed by the (110) and (011) surfaces. The morphology of the γ -Ag₂WO₄ cubic structure is composed of (001), (011), and (111) surfaces. Table 2 shows, for each crystal morphology, the values of E_{surf} , the percentage contribution (% cont) of each surface, $E_{gap}^{surface}$, $E_{polyhedron}$, and $E_{gap}^{polyhedron}$.

Table 2. Surface Energy $(E_{surf'} J/m^2)$, Percentage Contribution (% cont) of Each Surface for the Experimental Morphology, Band Gap Energy for Each Surface $(E_{gap}^{surface}, eV)$, Polyhedron Energy of Each Experimental Morphology $(E_{polyhedron}, J/m^2)$, and Band Gap Energy of Each Experimental Polyhedron $(E_{gap}^{polyhedron}, eV)$

Morphology	E _{surf}	% cont.	$E_{gap}^{surface}$	$E_{polyhedron}$	$E_{gap}^{polyhedron}$
α-Ag ₂ WO ₄	(010) – 0.80	14%	1.39	_	
	(001) – 0.20	36%	0.65	0.35	1.01
$E_{gap}^{bulk} = 1.69 eV$	(101) – 0.32	50%	1.15	-	
β-Ag ₂ WO ₄	(011) – 0.22	19%	1.61	- 0.11	1.62
$E_{gap}^{bulk} = 1.62 eV$	(110) – 0.08	81%	1.62		
γ-Ag ₂ WO ₄	(100) – 1.23	20%	1.84		
	(110) – 1.17	28%	1.37	1.13	1.57
$E_{gap}^{bulk} = 1.84 eV$	(111) – 1.07	52%	1.58		

The theoretical morphologies in Figure 12 were obtained by changing the stability of the surfaces that formed the theoretical morphology (ideal) (i.e., by increasing/decreasing the calculated values of E_{surf}). The information about the ideal morphologies can be found in Table SI-1 (Supporting Information). By adjusting the ratio of the E_{surf} values of each surface in each polymorph, the complete map of available morphologies can be obtained.^{66,68,77}

The energy profile connecting the ideal (obtained directly from the relation of the surface energy values and the Wulff construction) and theoretical (coinciding with the experimental FE-SEM images) is obtained by calculating $E_{\text{polyhedron}}$, as shown in Figure 13. This procedure can be considered to be an effective tool for investigating the mechanisms of morphology transformation and crystal growth from thermodynamic and kinetic points of view.⁵³

The ideal morphology of α -Ag₂WO₄ is formed by the (001), (010), and (100) surfaces with a parallelepiped-like shape. To achieve the experimental FE-SEM morphology, α -Ag₂WO₄ passes along the A–D intermediate morphologies. Therefore, it is first necessary to increase the E_{surf} of the (010) surface (morphology A), followed by an E_{surf} increase in the (100) surface to obtain morphology B. These two steps increase the value of $E_{polyhedron}$, which results in a maximum point. The next two steps involve the decrease in the E_{surf} in the (001) surface (morphology C) and the increase in the E_{surf} in the (110) surface (morphology D). From here, the last decrease in the (101) surface takes place in order to obtain the experimental morphology.

In the case of β -Ag₂WO₄, the reaction path to go from ideal to experimental FE-SEM images takes place along one maximum (morphology A) involving an E_{surf} increase in the (011) surface followed by an E_{surf} decrease in the (110) surface. In the γ -Ag₂WO₄ polymorph, it is only necessary to



Figure 13. Polyhedron energy profile connecting the theoretical (ideal) and experimental morphologies: (a) α -Ag₂WO₄, (b) β -Ag₂WO₄, and (c) γ -Ag₂WO₄. Values of E_{surf} in J/m². The intermediate morphologies along the pathways are indicated with letters.

decrease the E_{surf} value in the (111) surface to connect the ideal to the experimental morphology observed in the FE-SEM analyses.

Connecting Morphology and Activity. It is known that the properties of the materials are morphology-dependent. Exposed surfaces are the interface between a material and its environment. The interplay between molecule/bacteria and active sites on the topmost surface of the solid determines its activity in heterogeneous catalysis and as an antibacterial agent. Thus, it is essential to characterize, in as much detail as possible, the surface structure and electronic properties of materials to rationalize both adsorption and degradation processes at the exposed surface of the three polymorphs. Unfortunately, the experimental techniques often adopted for such a characterization are not sensitive enough to the solid topmost surface. With the support of calculations, the type of atoms, the structure, and the electronic characteristics of the clusters at the top of each surface were found to be facetdependent, which affects the activation of the adsorbed AML and MRSA significantly. This type of analysis allows us to find an adequate relationship between structure and function. Figure 14 shows the geometries of the exposed surfaces for the

different polymorphs. The use of the Kröger–Vink notation¹¹⁸ makes possible an analysis of the number of Ag–O and W–O breaking bonds in the superficial clusters. Each surface presents different kinds of atoms and local coordination on the top of the surface, together with the presence of complete coordinated and undercoordinated clusters and neutral oxygen vacancies (represented by V_o^*).

As Figure 14a shows, all α -Ag₂WO₄ surfaces display the $[WO_6]_d$ and $[AgO_5 \cdot 2V_o^x]$ clusters on the top of the surface, where subindex "d" means distorted. The (010) surfaces also present $[AgO_4]_d$ clusters. The (001) and the (101) surfaces present $[AgO_4 \cdot 3V_o^x]$ and $[WO_5 \cdot V_o^x]$ clusters, while on the (001) surfaces the $[AgO_4 \cdot 2V_o^x]$ clusters also appear. The (011) and (110) surfaces of β -Ag₂WO₄ (Figure 14b) are formed by the $[WO_4]_d$ and $[AgO_3 \cdot 2V_0^x]$ clusters. Beyond these two kinds of clusters, on the (011) surface there are also $[AgO_4 \cdot 2V_o^x]$ and $[WO_4 \cdot V_o^x]$ clusters. On the (110) surface, the $[AgO_2 \cdot 3V_o^x]$ and $[WO_3 \cdot V_o^x]$ clusters are also presented. On the γ -Ag₂WO₄ surfaces (Figure 14c), the (100) surface is constituted of distorted $[WO_4]_d$ and undercoordinated $[AgO_5 \cdot V_o^x]$ clusters. The top of the (101) surface is formed by three different kinds of clusters: $[WO_4]_d$, $[AgO_3 \cdot 3V_o^x]$ and $[AgO_4 \cdot 2V_o^x]$. The (111) surface is the most organized structure. The top of this surface is formed exclusively by undercoordinated $[AgO_3 \cdot 3V_o^x]$ clusters.

When compared to ideal morphologies, the appearance in the experimental morphology of a new surface, namely (101) in $\alpha\text{-}Ag_2WO_4$ and (110) in $\beta\text{-}Ag_2WO_4$ crystals (as seen in Figure 13), is a related fact that follows the existence of undercoordinated W atoms on the top the surface: $[WO_5 \cdot V_0^x]$ in (101) and $[WO_3 \cdot V_o^x]$ in (110). However, for γ -Ag₂WO₄, the (111) surface of its experimental morphology presents a majorly exposed surface with only $[AgO_3 \cdot 3V_o^x]$ clusters. The undercoordination of $[WO_v]$ clusters on a surface usually generates more instability than $[AgO_x]$ clusters, whose surfaces are stabilized under experimental conditions to be exposed in the final morphology. Thus, the (101) surface with one oxygen vacancy of the octahedral $[WO_5 V_0^x]$ cluster in α -Ag₂WO₄ and the (110) surface with one oxygen vacancy of the tetrahedral $[WO_3 V_0^x]$ cluster in the β -Ag₂WO₄ morphology seem to be the most active surfaces for the corresponding polymorph.

Table 2 gathers the E_{gap} values of the bulk, surfaces, and each morphology $(E_{gap}^{polyhedron})$ for α -, β -, and γ -Ag₂WO₄ crystals correlated to their E_{surf} . In passing from a six-faceted crystal (prism) to an eight-faceted crystal (rod-like) of α -Ag₂WO₄, $E_{gap}^{polyhedron}$ shows a slight variation from 0.99 to 1.01 eV. At the same time, surface (100) disappears and surface (101) gains importance. In the case of the $\bar{\beta}$ -Ag₂WO₄ phase, the $E_{gap}^{\mathrm{polyhedron}}$ variation from ideal to experimental morphology is minimized from 1.61 to 1.62 eV but higher in value than in the α -Ag₂WO₄ phase. Computational calculations indicate that the morphology of the β -Ag₂WO₄ crystal has the (011) surface as the predominantly exposed surface. By adjusting the relation of the $E_{\rm surf}$ values in order to obtain the experimental morphology, the (110) surface plays an important role in the overall morphology, more so than for the (011) surface with similar band gap energy values. For γ -Ag₂WO₄, in passing from ideal to experimental morphology, the $E_{gap}^{polyhedron}$ value increases from 1.46 to 1.57 eV due to the appearance of the (111) surface. However, the β -Ag_2WO₄ crystal presents a low $E_{\rm gap}$ bulk value (1.62 eV) compared to the α - and γ -phases (1.69 and 1.84 eV, respectively), conferring on β -Ag₂WO₄ crystals a better ability to act as active sites for AML degradation since a



Figure 14. Representation of the exposed surfaces of each Ag_2WO_4 polymorphism: (a) α - Ag_2WO_4 , (b) β - Ag_2WO_4 , and (c) γ - Ag_2WO_4 . The undercoordinated clusters of Ag and W cations are highlighted.

low recombination rate between photogenerated e' and h^{\bullet} on the crystal surface can be produced.

The main factor responsible for both the photocatalytic and the antibacterial activity is a low recombination rate between photogenerated e'-h[•] pairs on the surface of the Ag_2WO_4 polymorphs. The photogenerated charges undergo a series of redox reactions with oxygen molecules, O_2 , and water, H_2O , on the surface to generate ROS with extreme chemical activity. The h[•] on the surface reacts with H_2O to yield OH* and H[•] radicals, while e' can be trapped by O_2 adsorbed on the surface to generate O'_2 radicals:

$$h^{\bullet} + H_2 O \to OH^* + H^{\bullet}$$
(6)

$$e' + O_2 \to O_2' \tag{7}$$

These OH* and O^\prime_2 radicals induce the degradation of AML and antibacterial activity.

An analysis of the results gathered in Table 2 shows that the (101) and (001) surfaces are the main components, 50 and 36%, respectively, of α -Ag₂WO₄ morphology. On the (101) surface, there is an accumulation of e' in the complete distorted $[WO_6]_d$ clusters together with e' depletion and positive charge accumulation in the undercoordinated $[AgO_5 \cdot 2V_o^x]$, $[AgO_4 \cdot 3V_o^x]$, and $[WO_5 \cdot V_o^x]$ clusters, creating a potential difference which is able to form a local electric field. These differences in the charge of the different clusters on the surface have an influence on the transfer of the photogenerated e'-h[•] to the outside. On the (001) surface, this charge-separation process is from distorted $[WO_6]_d$ clusters to undercoordinated $[AgO_4 \cdot 3V_o^x]$, $[AgO_4 \cdot 2V_o^x]$, $[AgO_5 \cdot 2V_o^x]$, and $[WO_5 \cdot V_o^x]$ clusters. For β -Ag₂WO₄, the exposed (110) surface represents 81% of

its morphology and $e'-h^{\bullet}$ separation taking place from the distorted $[WO_4]_d$ cluster to the undercoordinated $[AgO_3 \cdot 2V_o^*]$, $[AgO_2 \cdot 3V_o^*]$, and $[WO_3 \cdot V_o^*]$ clusters. This makes β -Ag₂WO₄ the most active polymorph out of the three. The results indicate that the exposed surfaces can enhance the migration of photoinduced e', suppressing the recombination of charge carriers and improving the antibacterial and photocatalytic activity. Thus, it can be concluded that the source of h^{\bullet} is the undercoordinated $[AgO_x \cdot zV_o^x]$ and $[WO_y \cdot zV_o^x]$ clusters, while the source of e' is the distorted $[WO_y]_d$ clusters. The following mechanisms for the photocatalytic and antibacterial activity can be concluded:

$$[AgO_x \cdot zV_o^x] + H_2O \to OH^* + H^{\bullet}$$
(8)

$$[WO_{v} \cdot zV_{o}^{x}] + H_{2}O \rightarrow OH^{*} + H^{\bullet}$$
(9)

$$[WO_{y}]_{d} + O_{2} \rightarrow O_{2}^{\prime} \tag{10}$$

Formation Mechanisms of Ag₂WO₄ Polymorphs. Both the intimate mechanisms behind the structural evolution process from the reagents/precursors to intermediate samples and the formation of the final product's 3D structure in solution are far from being well understood. For inorganic solids, structural and bonding analyses during crystal synthesis are particular complex and are usually ambiguous on the atomic scale. This is partially due to the lack of efficient realtime methods of identifying all of the chemical species, the *in situ*-formed intermediates, and the reactions involved. Here, an attempt has been made to put forward a formation mechanism of Ag₂WO₄ polymorphs from precursors as a function of solution chemistry. pubs.acs.org/IC

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Figure 15. Dissolution/dehydration/nucleation processes for the formation of the different Ag₂WO₄ polymorphs.

The formation of a solid includes the nucleation and growth steps. Nucleation is a kinetically controlled process during which atoms, ions, and/or molecules aggregate into small clusters at the beginning in a reversible way until they form stable nuclei. The latter are then able to grow into crystallites and crystals. Nucleation via intermediate states is typical of a two-step nucleation mechanism, along a nonclassical nucleation mechanism.

The crystallization process generally involves a very complex sequence of steps, including the formation of primary units via dissolution, hydration/dehydration, nucleation, and crystal growth. There are multiple complex equilibria between transient species that occur rapidly in solution, which favor the prevalence of some building blocks over others. However, neither the nucleation reaction pathways nor the nature of the building blocks can be controlled.

In a typical precipitation method, the precursor salts are dissolved in an aqueous environment. In this aqueous solution, the dissolution process is very fast and the corresponding ions are quickly solvated by the H₂O molecules along a barrierless process. Na₂WO₄·2H₂O and AgNO₃ were the starting materials. First, Na₂WO₄·2H₂O(aq) was dissolved to form $(WO_4)^{2-}(aq)$ (eq 11), while AgNO₃ was dissolved to form Ag⁺, which forms the $(Ag(H_2O)_6)^+(aq)$ complex in aqueous solutions (eq 12). These two equations represent the dissolution processes, step 1, in which $(WO_4)^{2-}(aq)$ is the precursor of the $[WO_{v}]$ clusters (eq 13), while (Ag- $(H_2O)_6)^+(aq)$ is the precursor of $[AgO_x]$ clusters (eq 14). At this stage, dissolution/dehydration/nucleation processes take place with the concomitant formation of the $[AgO_r]$ (x = 2, 4, 5, 6, and 7) and $[WO_y]$ (y = 4, 5 and 6) clusters as structural precursors to form the 3D lattice of Ag₂WO₄ in the solid state (eqs 15-17). These clusters, which can be considered to be the structural entities preceding nucleation, are often called prenucleation clusters.^{119,120}

Increasing evidence has shown that nucleation pathways involving disordered prenucleation species exist in the crystallization process of inorganic materials. The collision and aggregation of these clusters, which contain more solute (and solvent) molecules than their surrounding environment, are not only able to form a large amorphous phase but also have an influence on the nucleation kinetics to rearrange and render a 3D crystalline phase first and then a polymorphic selection.^{24,26,30,119,121} In this context, we can suggest that the clusters in the reaction environment preceding the nucleation process, step 2, will strongly influence the formation mechanism and subsequently the formation of the assynthesized polymorphs.

In the present case, the concentration of precursors in the stoichiometric ratio of 2:1 controls the reaction pathway of the nucleation, step 1, to obtain the different Ag_2WO_4 polymorphs, while the crystallization process of these polymorphs, stage 3, involves the formation of $[AgO_x]$ (x = 5, 6), $[WO_y]$ (y = 4, 5), $[AgO_x]$ (x = 2, 4, 6, and 7), and $[WO_6]$ clusters, respectively.

At the concentration of $AgNO_3/Na_2WO_4 \cdot 2H_2O$ equal to 0.33:0.165, $[AgO_6]$ and $[WO_4]$ clusters are formed, and the γ -Ag_2WO_4 polymorph is reached (eq 15). At concentrations of AgNO_3/Na_2WO_4 \cdot 2H_2O equal to 0.04:0.02 and 0.007:0.0035, β - and α -Ag_2WO_4 polymorphs, respectively, are selectively obtained (eqs 16 and 17). In Figure 15, a schematic representation is displayed.

$$Na_2WO_4 \cdot 2H_2O \rightarrow (WO_4)^{2-}(aq) + 2H_2O(l) + 2Na^+(aq)$$
(11)

$$AgNO_{3}(aq) \rightarrow (Ag(H_{2}O)_{6})^{+}(aq) + (NO_{3})^{-}(aq)$$
 (12)

$$(WO_4)^{2-}(aq) \to [WO_y], y = 4, 5, 6$$
 (13)

$$(Ag(H_2O)_6)^+(aq) \rightarrow [AgO_x], x = 2, 4, 5, 6, 7$$
 (14)

$$[AgO_6] + [WO_4] \rightarrow \downarrow \gamma - Ag_2WO_4(s)$$
(15)

$$[AgO_x], x = 5, 6 + [WO_y], y = 4, 5 \to \downarrow \beta - Ag_2WO_4(s)$$
(16)

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Figure 16. Schematic representation of the energy profiles for the crystallization progress of the different Ag₂WO₄ polymorphs.

$$[AgO_x], \ x = 2, 4, 6, 7 + [WO_6] \to \downarrow \alpha - Ag_2WO_4(s)$$
(17)

It is clear that, in crystals of Ag_2WO_4 polymorphs precipitated and grown under selected reaction conditions, when the concentration of both $AgNO_3$ and Na_2WO_4 · $2H_2O$ precursors is reduced and their ratio is modified, both the obtained polymorphs and the corresponding morphologies change. It is also known that the energy barrier for nucleation is lower upon increasing the solution concentration, so crystals tend to nucleate more rapidly. Nucleation in such solutions leads to the formation of the γ - Ag_2WO_4 polymorph. However, the nucleation in dilute solutions has slower growth, so disordered crystals may be obtained (i.e., α - and β - Ag_2WO_4 polymorphs).

This is an example where at low concentrations of precursors, the probability of the formation of disordered clusters with low symmetry in medium and short ranges (i.e., the constituent clusters) in the formation of $[AgO_x]$ (x = 2, 4, 6, 7) and $[WO_6]$, and $[AgO_x]$ (*x* = 5, 6) and $[WO_y]$ (*y* = 4, 5) of the α -and β -Ag₂WO₄ polymorphs, respectively, is favored. At higher concentrations of precursors, the crystallization kinetics process is slower, the effective shocks decrease, greater organization prevails, and symmetry in the crystalline structure (i.e., the appearance of $[AgO_6]$ and $[WO_4]$ of the γ -Ag₂WO₄ polymorph) is enhanced. This shows that the dominant species in the initial solutions differ and the coordination of ions is also different, affecting the ionic supply to the nucleation centers and consequently promoting the formation of different polymorphs. This implies that the nucleation pathway and crystal precipitation from solutions is a rather complicated process, and aspects such as the solution components, bond lengths, and bond angles of the local coordination of Ag and W cations, $[AgO_x]$, x = 2, 4, 5, 6, 7 and $[WO_y]$, y = 4, 5 and 6, together with oxygen anion coordination and the proximity of ions might affect the crystal morphology and the final formation of each polymorph. Thus, it was possible to assume that several formation mechanisms were involved. A schematic representation of the energy profile along the crystallization process leading to the obtainment of the 3D structure of the

different Ag_2WO_4 polymorphs is proposed in Figure 16. Although the tuning of the microcrystal morphology can be ascribed to these active species and their concentrations, further investigation, such as implementing atomistic simulation techniques to describe the growth kinetics and the proper formation pathway of current crystals, is still needed.

CONCLUSIONS AND OUTLOOK

Polymorphism is the ability of solid materials to exist in structurally distinctive arrangements. While displaying the same chemical stoichiometry, with identical repeating formula units, Ag_2WO_4 polymorphs are simply "packed" (or connected) differently, forming various crystal symmetries and lattices with different properties. Therefore, the ability to experimentally control and predict polymorph formation is vital to gaining consistent access to its desired applications.

The main conclusions of this work can be summarized as follows: (i) The study suggests a procedure that may enable the selective synthesis of α -, β -, and γ -Ag₂WO₄ polymorphs without the need for surfactants, which are undesirable in industrial-scale production. (ii) The catalytic mechanism involves the efficient separation of photogenerated e'/h• pairs. The active substance capture tests indicate that two kinds of generated active species $(O_2 \text{ and } h^{\bullet})$ play an important role in the photodegradation process of α - and β polymorphs, while in the γ -phase it shows a less-efficient photodegradation process with the participation of h[•]. (iii) For the first time, the antimicrobial capacity of Ag₂WO₄ metastable phases is reported. Specifically, β -Ag₂WO₄ was more effective, requiring half of the concentration for the elimination of the methicillin-resistant Staphylococcus aureus. (iv) We demonstrate, building on DFT results, that there is a relation between morphology and photocatalytic/antibacterial activity based on the different numbers of unsaturated superficial Ag and W cations (local coordination, i.e., clusters) of each surface of the three polymorphs. (v) A mechanism for the crystallization processes of the three Ag₂WO₄ polymorphs, involving dissolution, dehydratation/hydratation, and nucleation steps, is proposed.

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The present results provide critical information to expand our fundamental understanding of the precursors' effect along the synthesis of the three polymorphs, a field that has so far remained unexplored. We hope that this study will ultimately aid the understanding of the structural and functional differences among the different kinds of polymorphs and contribute to the development of structure–property relationships in these intriguing Ag_2WO_4 -based materials. Further work in extending this protocol and verifying its applicability in other kinds of compounds and chemical transformations is in progress.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03186.

The following parameters for theoretical morphology are provided in a table: surface energy (J/m^2) , percentage contribution (% cont) of each surface, band gap energy for each surface (eV), polyhedron energy (J/m^2) , and the band gap energy (eV) (PDF)

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Notes

The authors declare no competing financial interest.

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