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Complex Oxides Based on Silver, Bismuth and Tungsten: Syntheses, Characterization and Photoelectrochemical Behavior

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ABSTRACT. Silver-containing complex oxides present interesting light absorption and electronic properties pointing to their applicability for solar fuels generation and environmental remediation. In this vein, the syntheses, characterization and photoelectrochemical properties of the Aurivillius oxide, AgBiW_2O_8 and a tri-phasic material: $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ are described herein. From UV-Vis diffuse reflectance analysis, both oxides nanoparticles exhibited intense absorption at wavelengths <455 nm, with an additional band centered at ~ 500 nm for the tri-phasic material, and attributed to surface plasmon resonance of the metallic Ag phase. The tri-phasic material was further characterized by a variety of structural and spectroscopic probes, indicating a defect-rich crystalline structure. Voltammetric measurements were performed in the dark and under simulated solar irradiation with polarization at potentials more negative than the rest potential. Thin film electrodes of both materials showed p-type semiconductor behavior, with enhanced cathodic photocurrent in the presence of electron acceptors in aqueous media.

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INTRODUCTION

This study was motivated by the recent interest in silver (Ag)-based inorganic semiconductors for photoelectrochemical (PEC) solar fuel generation and photocatalytic (PC) environmental remediation applications. Silver (I) oxide is a narrow bandgap (1.2 eV) p-type semiconductor;¹ however, its technological applicability is hindered by low PEC stability when exposed to light.² On the other hand, compounds containing polyatomic anions based on Ag, such as Ag_3PO_4 , Ag_3VO_4 and $\text{Ag}_6\text{Si}_2\text{O}_7$, show better stability under illumination while preserving optimal light absorption and electronic features such as good carrier transport and a Ag 4d-hybridized valence band structure.³⁻⁵

Bismuth and tungsten-based oxide semiconductors with the Aurivillius structure, of general formula $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$, are also of interest for the above applications.⁶ Thus Bi_2WO_6 , an n-type semiconductor with an energy band gap, E_g of 2.6 eV, exhibited PC activity for degradation of organic pollutants in water, such as rhodamine B dye and stearic acid.^{7,8} Further, it was reported that inducing oxygen vacancies at Bi_2WO_6 surface enhanced its photoactivity for 2,4-dichlorophenol oxidation.⁹ Interesting properties were reported for Bi_2WO_6 modified with Ag particles as well.¹⁰⁻¹² The metallic domains not only acted as electron sinks suppressing electron-hole recombination, but also instigated surface plasmon resonance effects extending the light absorption to the visible range.¹³ Furthermore, the photoelectrode stability could be improved since charge accumulation in the crystal lattice was minimized.¹⁰⁻¹³ Hydrothermal synthesis (HTS) was reported as a practical one-step methodology for preparation of Ag-loaded Bi_2WO_6 composites from a mixture of $\text{Bi}(\text{NO}_3)_3$, K_2WO_4 and AgNO_3 precursors, followed by thermal treatment.¹¹

In contrast to the rather extensive literature on Bi_2WO_6 , corresponding studies on oxides combining all the three metallic elements above (for example, as in: AgBiW_2O_8) are scarce. Thus nanoparticles of AgBiW_2O_8 were prepared by solid-state reaction from a mixture of Ag_2O , Bi_2O_3 and WO_3 .¹⁴ In aqueous suspension with methanol and AgNO_3 as sacrificial reagents, AgBiW_2O_8 exhibited high activity toward both H_2 and O_2 evolution.¹⁴ Another subsequent study, by one of us, discussed the properties of AgBiW_2O_8 particles obtained by solution combustion synthesis (SCS) using Na_2WO_4 , AgNO_3 and $\text{Bi}(\text{NO}_3)_3$ solutions as precursors and urea as fuel.¹⁵ These AgBiW_2O_8 particles, with $E_g = 2.74$ eV, exhibited high PC activity for color removal of methyl orange dye aqueous solutions. Significantly, Pt-modified SCS- AgBiW_2O_8 particles were used for PEC generation of syngas from aqueous formic acid solution; the CO resulting from the 2e⁻ reduction of CO_2 initially photogenerated on the oxide surface, while H_2 was photogenerated on the Pt sites.¹⁵

This paper builds upon these findings and discusses the electrochemical and PEC properties of thin film electrodes of solution combustion synthesized oxides of Ag-Bi-W (hereafter designated: SCS- AgBiW_2O_8 and SCS- Bi_2WO_6). A novel tri-phasic powder consisting of AgBiW_2O_8 , Bi_2WO_6 and Ag (hereafter designated: HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$), was also prepared via hydrothermal synthesis from Na_2WO_4 , AgNO_3 and $\text{Bi}(\text{NO}_3)_3$ solutions as precursors. Two alternative routes were used to contrast a simple, fast way to obtain a single-phase photoactive material (SCS), with a more widely-deployed yet time-consuming method that, in the present case, afforded a multiphasic material with higher crystallinity (HTS). The Ag-

Bi-W-based oxide behaved as a p-type semiconductor while Bi_2WO_6 nominally behaved as an n-type semiconductor (as mentioned earlier). The structural, spectroscopic, and electrochemical/photoelectrochemical attributes of these samples, as established by a complementary suite of characterization techniques, are presented below. Finally, the applicability of these materials for solar fuels generation and environmental remediation scenarios, are also briefly discussed.

EXPERIMENTAL METHODS

All chemicals were of P.A. grade and used without further purification. Deionized water from a Milli-Q purification system was used throughout the work.

Synthesis of SCS- Bi_2WO_6 and SCS- AgBiW_2O_8 . The SCS- AgBiW_2O_8 synthesis was described elsewhere.¹⁵ Briefly, AgNO_3 and $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ solutions were homogenized with HNO_3 solution in a ceramic crucible and then an aqueous solution of Na_2WO_4 and urea was added (the Ag:Bi:W molar ratio corresponded to 1:1:2). The resulting suspension was heated in a furnace and maintained at 190 °C for 3 min. Finally, the produced particles were washed and dried. SCS- Bi_2WO_6 particles were obtained from a similar procedure using bismuth and tungsten precursors with a Bi:W molar ratio of 2:1.

Synthesis and characterization of HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$. Firstly, $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ was dissolved in ethylene glycol and HNO_3 aqueous solution; after water addition, the resulting 0.008 mol L^{-1} of $\text{Bi}(\text{NO}_3)_3$ solution was mixed to a 0.2 mol L^{-1} of AgNO_3 solution (in aqueous HNO_3). Then, under magnetic stirring, a 0.2 mol L^{-1} of Na_2WO_4 aqueous solution was slowly added, in adequate aliquots than the Ag:Bi:W molar ratio was 1:1:2. After that, the pH of the resulting suspension was adjusted to 4.0 by addition of finely divided solid NaOH. The suspension was then transferred to a Teflon-lined stainless steel autoclave, sealed and maintained for 24 h at (190 $\pm$ 5) °C. After cooling down at room temperature, the autoclave was opened and an aliquot of the supernatant was collected for analysis. The supernatant analysis revealed the presence of traces of Ag^+ ions (a white precipitate after HCl addition), whereas Bi^{3+} and WO_4^{2-} ions were not identified (in the presence of these ions, black particles of BiI_3 , or yellow particles of H_2WO_4 would precipitate after addition of KI, or HCl solutions, respectively).¹⁶ The particles were washed with 5 cycles of agitation with water and centrifugation; from the second washing cycle on, Ag^+ ions were not detected in the supernatant.

The resulting dried particles (1.0 g) were crushed with acetylacetone (30 μL) and then an aqueous solution of polyethylene glycol, PEG (MW 20000) was slowly added, resulting in a suspension with 10:30:60 mass % of PEG:oxide: H_2O which was submitted to magnetic stirring for 2 h.¹⁷ This suspension was used for preparation of films or powdered samples. The thermal treatment was performed in air atmosphere by heating from ambient temperature to 350 °C (10 °C min^{-1}), maintained at 350 °C for 30 min, and then heated and maintained for 30 min at 450 °C.

Characterization of the HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ powder included UV-visible diffuse reflectance spectroscopy (UV-Vis DRS), performed with a Teflon disc as the reference standard (Cary 5G Varian instrument, equipped with an integrating sphere). From N_2 adsorption/desorption isotherms, determined at 77 K, the specific surface area was determined using the Brunauer-Emmet-Teller (BET) methodology; the measurements were taken on a Quantachrome equipment, after degassing of the particles at 120 °C for 15 h. X-Ray diffraction

(XRD) measurements were taken at ambient temperature using a RINT2000 Rigaku equipment with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation, with 0.02° step size and 10 s per point. The diffractograms of crystalline phases were compared with those of standards as reported in the International Centre for Diffraction Data (ICDD) database and in the Inorganic Crystal Structure Database (ICSD). Rietveld refinement was accomplished considering the contribution of monoclinic AgBiW₂O₈, orthorhombic Bi₂WO₆, cubic Ag and Ag₂WO₄. The fittings were evaluated in terms of the weighted and expected factors (R_{wp} , R_{ex}), and their ratio, which corresponds to the goodness-of-fit (χ^2). High-resolution transmission electron microscopy (HR-TEM) images, with fast Fourier Transform (FFT) patterns, were obtained on a Hitachi H-9500 instrument, with samples supported on carbon (300-mesh) film. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD instrument, equipped with Al-K α monochromatic source, charge neutralizer and hemispherical electron energy analyzer. Peak fitting was performed with XPSPeak 4.1 software, using binding energy values normalized to adventitious carbon (284.8 eV). Photoluminescence (PL) spectroscopy measurements were carried out at ambient temperature on a time correlated single-photon counting (TCSPC) equipment from Edinburgh Analytical Instruments, model FL 900 with a multichannel plate photomultiplier detector (Hamamatsu R3809-U-50). Excitation beam was generated by a pulsed diode laser operating at $\lambda_{exc}=375 \text{ nm}$ (model PLED 370).

Preparation and characterization of electrodes of Ag-Bi-W oxides. Aqueous suspensions of SCS-Bi₂WO₆ and SCS-AgBiW₂O₈ with 10:30:60 mass % of PEG:oxide:H₂O were prepared using the already described procedure.¹⁷ Transparent conductive glass-FTO pieces were used as substrate (TCO22-15, 15 Ω/sq , Solaronix S.A, Switzerland) after a previous ultrasonic cleaning step in isopropyl alcohol. Electrodes were prepared by deposition of a thin film of the suspension on the substrate: adhesive tape was used to delimit a 1.0 cm² area, where the oxide suspension was spread using a glass rod. After drying at room temperature, the tape was removed, and the electrode was subjected to thermal anneal (air atmosphere, 30 min at 350 $^\circ\text{C}$ and 30 min at 450 $^\circ\text{C}$). This procedure assures elimination of PEG and organic residues resulting in porous films with adhesion to different substrates.¹⁷ A dry oxide loading of $\sim 1.5 \text{ mg cm}^{-2}$ was estimated on the substrate surface via this procedure.

The morphology of the Ag-Bi-W based oxide films deposited on glass-FTO was examined by scanning electron microscopy on a JEOL JSM 63601V instrument.

The electrochemical properties were investigated in a three-electrode cell assembled with quartz or with an optical glass window (ca. 90% transmittance for $\lambda > 300 \text{ nm}$). The working electrode, with geometrical area of $(1.0 \pm 0.1) \text{ cm}^2$, faced a Pt wire ring as a counterelectrode and the reference electrode, Ag/AgCl (in aqueous 3 mol L⁻¹ of KCl) was placed inside in a Luggin capillary. The experiments were performed using ca. 10 mL of neutral aqueous solutions containing KNO₃, Na₂SO₄ or NaClO₄ in concentrations ranging from 0.05 to 0.5 mol L⁻¹ as supporting electrolyte. PEC studies were carried out with supporting electrolyte solutions containing methyl viologen dichloride (40 mmol L⁻¹) or AgNO₃ (5 mmol L⁻¹) as electron acceptors. Prior to the measurements, the electrolyte was saturated with gaseous N₂, argon, O₂ or CO₂ by flushing the gas through the solution for 30 min; then, during the measurements, the same gas was maintained over the solution.

The electrochemical measurements were performed using either Solarton Instruments SI 1280 B or Ecochemie Autolab PGSTAT 302-N potentiostat/galvanostat units, in ambient illumination ("dark") and under front-side polychromatic irradiation. Irradiation was provided by a 1000 W

Arc Xe lamp combined with an infrared filter, collimators and a monochromator (Oriel) for spectral resolution from 300 to 750 nm. The irradiance was measured with Kettering or Newport power meters and was nominally 100 mW cm^{-2} .

Action spectra (or incident photon to current conversion efficiency (IPCE) vs. wavelength profiles) were acquired in aqueous solution with 0.1 mol L^{-1} of KNO_3 and 5 mmol L^{-1} of AgNO_3 . The electrode was polarized at 0.4 V (open-circuit potential in the dark) for this purpose, and the photocurrent was measured while the incident irradiation was scanned from 290 to 750 nm (intervals of 10 nm, maintained for 50 s). At every wavelength (λ , nm), the IPCE value was estimated from the steady state photocurrent (j_{ph} , mA cm^{-2}) and the intensity of incident monochromatic irradiation (I_{in} , mW cm^{-2}), using the expression: $\text{IPCE} = (1240 \times j_{\text{ph}}) / (\lambda \times I_{\text{in}})$.

RESULTS AND DISCUSSION

Characterization of Ag-Bi-W oxides. The structural characterization of the greyish SCS- AgBiW_2O_8 nanoparticles obtained from solution combustion synthesis using urea as fuel and aqueous solutions of Na_2WO_4 , AgNO_3 and $\text{Bi}(\text{NO}_3)_3$ was already described. The sample consisted of crystalline AgBiW_2O_8 nanoparticles, with a BET surface area of $34 \text{ m}^2 \text{ g}^{-1}$ and E_g of 2.74 eV (indirect transition).¹⁵

Adding ethylene glycol to these solutions, hydrothermal synthesis (24 h at 190°C , in autoclave) produced crystalline greyish nanoparticles consisting of AgBiW_2O_8 , Bi_2WO_6 and Ag; i.e., a triphasic sample, HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$. The BET surface area of the calcined sample was $42 \text{ m}^2 \text{ g}^{-1}$. Figure 1 shows the XRD pattern exhibited by a calcined film of HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ nanoparticles deposited on glass. Comparison with the JCPDS database and using Rietveld refinement of X-Ray diffraction data (see Fig. S1), revealed that the sample prepared by HTS consisted of a mixture containing 35% of monoclinic AgBiW_2O_8 , 41% of orthorhombic Bi_2WO_6 and 20% of cubic Ag, with Ag_2WO_4 (~4%) adventitiously arising as a decomposition product from the thermal anneal. Interestingly, ethylene glycol, added to facilitate dissolution of the Bi precursor, acted as a reducing agent and induced the production of metallic Ag domains.¹¹

Figure 1. XRD pattern of HTS-AgBiW₂O₈/Bi₂WO₆/Ag film deposited on glass. The ICDD and ICSD reference patterns for AgBiW₂O₈, Bi₂WO₆, and Ag are also included.

Figure 2 shows the absorption spectrum (derived from UV-Vis DRS data) for the HTS-AgBiW₂O₈/Bi₂WO₆/Ag powder. Considering the already reported optical characteristics of SCS-AgBiW₂O₈,¹⁵ it can be concluded that both materials present an absorption edge around 455 nm, similar to the results previously reported in the literature for AgBiW₂O₈.¹⁴ Thus, both SCS-

Figure 2. Absorption spectrum from UV-Vis DRS data for HTS-AgBiW₂O₈/Bi₂WO₆/Ag nanoparticles.

AgBiW₂O₈ and HTS-AgBiW₂O₈/Bi₂WO₆/Ag samples exhibited considerable absorption in the visible range of the solar spectrum. However, since the HTS-AgBiW₂O₈/Bi₂WO₆/Ag particles consisted of a mixture of Ag and two different complex oxides, estimation of E_g from Kubelka-Munk analyses¹⁸ was not attempted for the data in Fig. 2. Furthermore, the hydrothermally synthesized oxide exhibited an additional band at ~500 nm (see Fig. 2), which can be assigned to surface plasmon resonance of metallic silver.¹² These Ag⁰ domains serve additionally to extend the visible light absorption properties to the sample.

The HTS-AgBiW₂O₈/Bi₂WO₆/Ag sample was also analyzed by HR-TEM (Fig. 3). Figure 3a shows a TEM micrograph of this nanocomposite sample, which consisted of irregular shaped nanoparticles of AgBiW₂O₈, Bi₂WO₆ and Ag, as revealed by the HRTEM image. The respective fast Fourier Transform (FFT) in Fig. 3b, showed epitaxial interface between the three phases. The lattice fringes indicated the interplanar distances to be 0.316 nm, 0.325 nm and 0.232 nm, in good agreement with the spacing of the corresponding (131) plane of the orthorhombic Bi₂WO₆, (220) plane of the monoclinic AgBiW₂O₈ component, and the (111) plane of the face-centered cubic Ag nanoparticles, respectively. The obtained lattice spacings were also entirely consistent with the above XRD results.

Figure 3. HTS-AgBiW₂O₈/Bi₂WO₆/Ag particles: TEM image (a) and HRTEM image with FFT patterns of each identified phase (b).

The same material was also subjected to XPS analyses (Fig. 4). Results obtained from powder samples indicate a defect-rich structure, with significant amount of atoms in less positive oxidation states than expected for a stoichiometric compound (binding energies and ratio of different oxidation states are shown in Table S1). The W 4f core-level spectrum (Fig. 4a) showed 4f_{7/2} peaks at 35.6 and 36.8 eV suggesting a significant presence of tungsten atoms at oxidation states lower than the expected W⁶⁺ species.^{19,20} This profile could indicate the existence of defects in the crystalline structure, such as oxygen vacancies and Frenkel defects, which would allow the presence of W⁵⁺ states. The Ag 3d_{5/2} peaks around 368.0 and 369.0 eV (Fig. 4b) confirmed the presence of metallic silver domains along with the expected Ag⁺ species, respectively.^{12,21} The curves obtained at the Bi 4f binding energy regime (Fig. 4c), which consist of multiple overlapped peaks in the 157-160 eV range, indicated the presence of multiple oxidation states. As the expected oxidation state for bismuth was 3+ in these compounds, and the synthetic medium provided a reductive environment, the existence of bismuth in the 5+ oxidation state could be ruled out.

Although a small difference of 0.9 eV could be expected for the binding energy of Bi 4f electrons in Bi_2WO_6 and AgBiW_2O_8 , the two main overlapped signals (159.1 and 160.3 eV) may be attributed to bismuth atoms in the same oxidation state as in the case of FeBiO_3 where Bi-O-Bi and Fe-O-Bi bonds provide distinct binding energies for Bi^{3+} .²² As the Aurivillius phase presents Bi-O-Bi layers in its structure, substitution of bismuth atoms by silver (possessing similar ionic radius) may be responsible for the observed shift in binding energy. Interestingly, the deconvolution of Bi 4f peaks also provided a small signal at even lower binding energy (157.7 eV), hypothesized first to be Bi^{2+} cations and confirmed by photoluminescence experiments, discussed below. The O 1s spectrum (Fig. 4d) contained 3 peaks (530.4, 531.8 and 533.9 eV), which can be ascribed to tungsten-oxygen bonds,²⁰ surface hydroxyl groups²³ (as expected for a defect-rich structure), and C-O bonds from adventitious hydrocarbons adsorbed on the oxide surface,²⁴ respectively. Table S1 contains further (quantitative) details from the XPS analyses.

Figure 4. XPS analyses of HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ in: (a) W 4f, (b) Ag 3d, (c) Bi 4f and (d) O 1s binding energy regimes (fitted profiles are shown as a red line).

Photoemission spectroscopy measurements also provided further insights on the electronic structure of HTS-AgBiW₂O₈/Bi₂WO₆/Ag; as shown in Fig. 5, the photoluminescence (PL) spectrum consisted of three (structured) emission bands ranging over the whole visible region. The broad band centered at ~465 nm can be assigned to intrinsic emission from charge transfer transition between the conduction band (mainly composed of W 5d orbitals) to the valence band, (composed of Bi 6s and O 2p orbitals); see, for example, Refs. 25-27. The band centered at ~535 nm can be assigned to defect centers that may arise from the insertion of oxygen in interstitial positions with concomitant silver substitution (Frenkel-type defects).²⁵ The third major band observed at longer wavelengths with peak at ~620 nm is assigned to the intrinsic emission of Bi²⁺, as in the case of bismuth-activated M²⁺BPO₅,²⁸ which corroborates with the hypothesis from XPS analyses (Fig. 4c above). The reduction of Bi³⁺ may be related to the use of ethylene glycol for the synthesis of HTS-AgBiW₂O₈/Bi₂WO₆/Ag (see above).

Figure 5. Photoluminescence spectrum of HTS-AgBiW₂O₈/Bi₂WO₆/Ag. $\lambda_{\text{exc}}=375$ nm.

Electrochemical and photoelectrochemical (PEC) properties of Ag-Bi-W oxide electrodes.

Thin films of nanoparticles of the two Ag-Bi-W based oxides, with geometrical area of 1 cm², were deposited on different substrates from aqueous suspensions containing PEG followed by thermal treatment. The average amount of immobilized particles on the substrates corresponded to (1.5 ± 0.2) mg cm⁻²; usually, deposition of TiO₂ particles on glass-FTO using this methodology corresponded to smaller values, (1.2 ± 0.2) mg cm⁻².¹⁷ Representative SEM images for these films are shown in Fig. S2. Comparison of these images revealed similar morphology; films of both these materials, consisted of interconnected sub-micrometric agglomerates of nano-sized primary particles.

The electrochemical properties of the electrodes were investigated in supporting electrolyte aqueous solutions (neutral pH) by cyclic voltammetry. In such media and under ambient illumination (i.e., "dark"), the rest potential (V_{rest}) varied from 0.1 to 0.2 V (vs. Ag/AgCl). In aqueous NaClO₄ solution, when the applied potential was scanned from V_{rest} to -0.3 V, the electrodes exhibited stable and reproducible current-potential profiles and, for potential values $E_V < V_{\text{rest}}$, the cathodic current was intensified by irradiation, as will be discussed below.

However, as can be observed in Fig. 6a, for potentials $E_V > V_{\text{rest}}$, the voltammograms of a SCS- AgBiW_2O_8 electrode exhibited an anodic peak at ca. 0.4 V and, for the reverse sweep, a cathodic peak at ~ 0.2 V; also, the waves decreased in amplitude with potential cycling. Analogous results were obtained for the HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ electrode (Fig. 6b); however, the anodic and cathodic current peaks were respectively observed at ~ 0.2 V and ~ 0.1 V instead.

These features can be assigned to redox process within silver oxides, as well as intercalated silver species^{29, 30} that may be present at the layered AgBiW_2O_8 structure. Also, the peaks were sharper in the HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ case, indicating faster kinetics for this internal process when compared to the SCS- AgBiW_2O_8 electrode. These could be attributed to the Ag metallic domains and to the higher tunneling current, as a consequence of a lower energy barrier height³⁰ (as expected from the presence of Bi_2WO_6 , which presents a lower conduction band minimum than AgBiW_2O_8). The alternate possibility that these redox signatures arise from

Figure 6. The four initial cyclic voltammograms (20 mVs^{-1}) of SCS- AgBiW_2O_8 (a) and HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ (b) porous films (1 cm^2) deposited on glass-FTO in aqueous NaClO_4 solution, in ambient illumination ("dark"). Pt wire and $\text{Ag}/\text{AgCl}/\text{KCl}$ (saturated) were used as counter and reference electrodes, respectively.

metallic Ag domains can be ruled out since these are present for both the SCS and HTS samples (c.f., Figs. 6a and b)

To further compare the Ag-Bi-W based oxides against the Ag-deficient counterpart, namely, Bi_2WO_6 , experiments were performed using aqueous solutions containing dissolved O_2 , methylviologen dichloride or silver (I) ions as electron acceptors. Figure 7a shows the voltammograms registered in O_2 -saturated NaClO_4 aqueous solution (20 mVs^{-1}). From 0.1 to -0.3 V , the Bi_2WO_6 electrode exhibited identical voltammograms and *negligible* current flow in the dark and under irradiation. On the other hand, the cathodic current exhibited by the SCS- AgBiW_2O_8 electrode in the dark indicates its high proclivity towards the oxygen reduction reaction. This trend is also corroborated by comparing the cyclic voltammograms obtained in N_2 - and O_2 -saturated solutions (Fig. S3).

Figure 7. Electrochemical and PEC behavior of SCS- Bi_2WO_6 , SCS- AgBiW_2O_8 , and HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ in aqueous solutions containing electron acceptor species, in the dark or under irradiation: cyclic voltammograms (20 mVs^{-1}) in O_2 saturated NaClO_4 solution (a) and photocurrent transients at -0.3 V (vs. Ag/AgCl) in O_2 saturated NaClO_4 solution (b) or in Na_2SO_4 solution with methylviologen dichloride (c). Data taken for the substrate glass-

FTO also included for comparison in Fig. 7b. In Figs. 7b and c, the black, green, and blue traces have been off-set (from the zero current point) for clarity.

The cathodic current was intensified by irradiation, suggesting that SCS-AgBiW₂O₈ behaves as a p-type semiconductor electrode for $E_{\text{bias}} < V_{\text{rest}}$.³¹ Cathodic photocurrents could also be observed in the chronoamperograms obtained for electrodes of Ag-Bi-W based oxides under intermittent irradiation and polarization at -0.3 V in O₂ saturated NaClO₄ aqueous solution (Fig. 7b) as well as in Na₂SO₄ aqueous solution containing methyl viologen dichloride (Fig. 7c). As expected and as a control, the PEC properties of the underlying glass-FTO substrate were negligible (see, for example, Fig. 7b) under these conditions.

The photoelectrochemical properties of Bi₂WO₆ electrodes were already reported.^{32,33} Depending on the film thickness and porosity, under polychromatic irradiation in aqueous Na₂SO₄ solution, Bi₂WO₆ electrodes exhibited anodic photocurrent ranging from 1 to 20 μAcm^{-2} in potentiodynamic scans from 0 to 1.0 V (vs SCE). For monochromatic irradiation, the Bi₂WO₆ electrodes exhibited photoactivity for wavelengths up to 450 nm, with the highest photocurrent values for incident photons with ca. 340 nm (1.2 % IPCE). Thus, electrodes of this n-type semiconductor have been used as photoanodes for photocatalytic oxidation of organic pollutants in aqueous media.

However, upon a detailed review of the literature, we believe that this is the first description of the electrochemical properties of AgBiW₂O₈ electrodes. The p-type behavior, resulting from an increased mobility of positive charge carriers in the semiconductor, can be associated with metal ion vacancies or oxygen excess.^{34,35} The VB could also be modulated by Ag 4d states, considering the reported band structure and partial density-of-states calculated by density functional theory.¹⁵ From calculations based on a wolframite AgBiW₂O₈ lattice (considered the most stable among other possible monoclinic structures), it was proposed that the conduction band minimum could be associated with W 5d and the Bi 6p levels.¹⁵ Also, the upper part of the wolframite AgBiW₂O₈ VB would be dominated by Ag 4d contribution, while the O 2p contribution for the top of VB would not be significant.¹⁵ Thus, the VB modulation by Ag 4d states could increase the hole mobility for irradiated AgBiW₂O₈ electrodes under cathodic polarization; these holes would move toward the bulk to reach the external circuit while photoelectrons would be driven to the electrode surface and react with electron acceptors such as O₂, methylviologen or silver (I) ions.

Since these Ag-Bi-W-based oxides behaved as p-type semiconductor electrodes under cathodic polarization, they could be used as photocathodes for O₂ reduction (ORR) and for the CO₂ reduction reaction (CO₂RR). Thus, in preliminary experiments, band gap irradiation improved the production of formate from CO₂RR using HTS-AgBiW₂O₈/Bi₂WO₆/Ag as photocathode in CO₂-saturated acetonitrile containing trihexyltetra-decylphosphonium 1,2,4-triazolide, [P_{6,6,6,14}][1,2,4-Triz] (a superbasic ionic liquid that interacts with CO₂).^{36, 37} Further, for a *photocatalytic* system consisted of a TiO₂ photoanode and a HTS-AgBiW₂O₈/Bi₂WO₆/Ag photocathode, preliminary results revealed that the hydrogen peroxide produced from light assisted ORR enhanced the efficiency for photocatalytic removal of the amoxycillin antibiotic from aqueous solution. Clearly, these p-type Ag-Bi-W-based oxides can be considered as promising photocathodes for solar fuels generation and environmental remediation scenarios.

Conclusions

Complex oxides derived from Ag, Bi, and W were derived by two variant preparation approaches. While solution combustion synthesis (SCS) afforded nanoparticle powders of AgBiW_2O_8 and Bi_2WO_6 , the hydrothermal synthesis (HTS) procedure, yielded, interestingly enough, a tri-phasic material composed of AgBiW_2O_8 , Bi_2WO_6 , and Ag nanoparticles. That these nanoparticles were in electronic contact was well substantiated by the variety of characterization probes deployed in this study. The presence of embedded Ag nanoparticles in the sample matrix had a positive optoelectronic effect stemming from surface plasmon resonance. While it is tempting to speculate that p-n semiconductor nano-junctions were also present in the matrix because AgBiW_2O_8 behaved as a p-type semiconductor (as established in this study) and Bi_2WO_6 is an n-type semiconductor, further studies would be needed, beyond the scope of this study, to address this possibility. The high defect density in the HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$ samples (as shown by the XPS and PL data), also calls for further optimization efforts before practical applications of these oxides for solar fuel generation are considered. Finally, further studies addressing the PEC stability of the oxides generated in this study, would be needed.

SUPPORTING INFORMATION

Rietveld refinement of XRD data for HTS- $\text{AgBiW}_2\text{O}_8/\text{Bi}_2\text{WO}_6/\text{Ag}$, XPS peak deconvolution, SEM data, and additional electrochemical measurements,

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