Construction of a Z-Scheme Dictated WO$_{3-x}$/Ag/ZnCr LDH Synergistically Visible Light-Induced Photocatalyst towards Tetracycline Degradation and H$_2$ Evolution

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ABSTRACT: Herein, we have designed nonstoichiometric WO$_x$ coupled with ZnCr layered double hydroxide (LDH) nanosheet through Ag nanoparticle as the solid-state electron mediator to form WO$_{3-x}$/Ag/ZnCr LDH Z-scheme photocatalyst. The presence of oxygen defect levels in as-synthesized materials was confirmed by Raman, X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) analyses. The photocatalytic performance of the catalysts was investigated by the tetracycline degradation and H$_2$ energy production under visible light irradiation. The WO$_{3-x}$/Ag/ZnCr LDH ternary heterostructure exhibits superior activity toward tetracycline degradation and hydrogen evolution. The excellent photocatalytic performance of the catalyst was attributed to the synergistic effects among three species (WO$_{3-x}$, Ag, and ZnCr LDH) and the enhanced separation efficiency of photoinduced charge carriers through the Z-scheme WO$_{3-x}$/Ag/ZnCr LDH system. In addition, the created oxygen deficiency on WO$_{3-x}$ could improve the photocatalytic behavior of ZnCr LDH in heterostructure by delaying the recombination efficiency of photoexcited electron–hole pairs. Furthermore, the higher affinity of tetracycline at the oxygen defect levels of the photocatalyst supports the high rate of tetracycline degradation. The enhanced photocatalytic activity of the catalysts was further supported by PL spectra and photoelectrochemical studies (electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) plot). The present research opens up a new strategy for designing highly efficient visible light-induced Z-scheme-based photocatalysts with high population of active sites for energy and environmental applications in a sustainable manner.

INTRODUCTION

With increasing energy requirements and growing severity of environment issues, semiconducting materials-based photocatalysts have been found to draw intense attention as “green” and effective alternatives. In this contest, hydrogen is believed to produce high energy yield of about 141.9 mJ/kg and has been recognized as a cleaner, cheaper, and sustainable energy source with no greenhouse gas emission compared to conventional fuels.1−5

Moreover, environmental pollution associated with antibiotics is one of the most urgent issues to be solved. The most dangerous effect of the antibiotics is their multiresistant antibacterial properties and chemical stability. Tetracycline (TC) is one such widely used antibiotic due to its low absorptivity, so it gets released easily into the environment as unmetabolized compound. Occurrence of tetracycline in water bodies is now a subject of great concern. Traditional biological methods like biological filtration and conventional methods, including physical adsorption with chemical oxidation, are found ineffective for the elimination of antibiotic due to complexity and possible secondary pollution, while the visible light-induced photodegradation owing to its economic, energy-efficient strategy has been reported as suitable to dominate the bioavailability and sequestration of tetracycline.6−10

In this regard, a heterojunction is found to be an efficient photocatalyst with greater electron–hole separation. However, increments in charge separation take place while dampening the redox capability, due to the accumulation of photo-generated charge carriers on the band, resulting lower redox potentials, for which it is difficult to achieve simultaneously efficient electron–hole separation and high redox ability by designing a heterojunction composite photocatalyst. However, integration of semiconductors hybrid Z-scheme systems is found to be superior exhibiting efficient spatial separation of charge carriers and also maintaining the redox ability. Through Z-scheme, oxidation and reduction catalytic centers are more active to minimize the undesirable backreaction.11,12 Inspired by the natural photosynthesis and efficient charge separation through Z-scheme heterostructure photocatalysts, considerable interest has been devoted by researchers to introduce high redox capability. Z-scheme charge transfer started from opposite direction in water splitting mimicking photosynthesis of green plants, which was discovered by Bard in 1979.13 In a Z-scheme system, the photoexcited electron shifts from the CB.
position of photosystem II (PS II) to VB position of photosystem I (PS I), which gets trapped by the holes. As a result, electrons and holes are freely available on the conduction and valence bands of PS I and PS II, respectively, as they provide reacting sites for reduction and oxidation reactions to take place. So, it has enormous potential to be applied for water splitting reaction and environmental pollutant elimination. To date, a number of Z-scheme-based visible light photocatalytic systems have been reported, such as CeO2/BiO15, Cu/MoO3-x-C3N4,16 and LaFeO3-g-C3N4 possessing much better photocatalytic abilities than single photocatalysts.

In general, Z-schemes can be classified into two groups. One composed of charge transfer between two individual photocatalysts through a shuttle redox mediator [BiVO4/Ru-SrTiO3/Rh, with an electron shuttle [Co(bpy)3]+/[Co-(bpy)3]2+]18 but its photocatalytic activities become very poor due to its backward reaction. Another is all-solid-state Z-scheme photocatalytic system; selection of a solid electron mediator plays an important role in charge carrier transfer. According to energy band theory, the Fermi level of the mediator should remain in between the Fermi levels of PS I (photosystem I) and PS II (photosystem II). Otherwise, charge transfer is inhibited due to the formation of energy band barriers at the semiconductor–metal interfaces. Based on previously reported studies, it was found that solid electron mediators such as Au, Ag, and graphene are superior to other ionic redox shuttles. Moreover, these solid electron mediators are able to avoid the back reaction and can be recovered easily. In this respect, a solid-state metal semiconductor having low contact resistance can be used as an electron mediator, which speeds up the desirable specific carrier transfer process. Taking this into consideration, many studies have been conducted (TiO2-Au-Cds, LAVO2-Ag-BIVO4).

Among the various reported photocatalytic materials, layered materials like ZnCr layered double hydroxide (LDH) are found to be one of the best photocatalytic agents due to appropriate redox potential and tremendous light-harvesting capabilities. The ability of ZnCr LDH to absorb visible spectrum is associated with interelectronic excitation like metal-to-metal charge transfer (MMCT) through oxo-bridged bimetallic linkage. However, poor crystalline orientation, high recombination rates of electron–hole pairs, and slow charge carrier mobility greatly inhibit its application in practical photocatalysis. In this direction, Wu et al. fabricated O-doped carbon nitride/CoAl LDH through in situ growth method, which involves a direct Z-scheme charge transfer mechanism. Recently, WO3 has been regarded as a promising semiconducting material, with band gap energy values between 2.4 and 2.8 eV. Furthermore, it was extensively investigated for photocatalytic applications due to its intrinsic properties like easy synthesis, non-toxicity, steady physicochemical parameters, resistance to photocorrosiveness, and high oxidation potential of valence band that can oxidize H2O and −OH groups to obtain ‘OH. Moreover, the existence of oxygen vacancy in the case of non-stoichiometric WO3 also affects the surface properties of materials, as well as improves optical absorption, separation of photogenerated charge carriers, and electrical conductivity to behave as an efficient photocatalyst. Generally, the presence of oxygen defects not only delays the recombination process of photogenerated excitons by temporarily capturing charge carriers but also facilitates the adsorption of pollutant molecules onto the surface. The more oxidized VB potential of WO3 motivates the formation of Z-scheme-based photocatalyst system. In this context, a large number of WO3-based Z-scheme photocatalytic systems have been studied in the field of energy conversion and ecological cleanliness. For instance photocatalytic systems involving WO3 and LDH were also reported, such as WO3@NiFe-LDH and WO3/ZnCuGa LDH, by Fan et al. and Morikawa et al. separately for enhanced photoelectrochemical water splitting and photocatalytic conversion of carbon dioxide into methanol. Therefore, constructing the Z-scheme charge transfer heterogeneous system by coupling ZnCr LDH with nonstoichiometric WO3 by adjusting the electronic state is a promising way.

However, no LDH/WO3-based Z-scheme photocatalytic systems were reported. Therefore, WO3-LDH Z-scheme system is a new approach in the field of photocatalysis. Additionally, for improving the charge pair separation efficiency of WO3-coupled LDH heterostructure Z-scheme system, Ag has been inserted as a mediator due to its excellent electron conductivity. Owing to the presence of surface plasmon resonance (SPR) effect and induced electric field, Ag also plays an important role in the absorption of visible light and boosts the photogenerated charge transfer. In this periphery, many materials have been reported for photocatalytic application. In particular, Yuan et al. reported Ag2CO3/Au/WO3 photocatalysts toward organic pollutant degradation. With these motivations, in the present study, we rationally applied the SPR effect of metallic Ag as redox electron mediator in between WO3-x-ZnCr LDH heterostructure to design a Z-scheme WO3-x-Ag-ZnCr LDH photocatalyst. Among the photocatalysts, Ag nanoparticles (Ag NPs) were loaded onto the WO3 surface via photodeposition method, followed by the hybridization of Ag/WO3-x with LDH through simple facile in situ coprecipitation method. The photocatalytic behavior of the as-fabricated WO3-Ag-ZnCr LDH ternary heterostructure was investigated for TC degradation as a target recalcitrant pollutant and for H2 evolution. Upon excitation, the photoexcited charge carrier transfers from the CB band of WO3-x to Ag, which is basically due to development of Schottky barrier within the metal–semiconductor interface. The SPR effect and electric field will further transport the electrons of Ag to VB of ZnCr LDH, where the excited electron combines with holes. The defects created by surface oxygen vacancy in WO3-x and the existence of Ag as electron transfer conductor facilitate the charge pair separation efficiency and enhance the photocatalytic activity of ZnCr LDH. Eventually, based on the active species quenching experiment and H2 evolution results, Z-scheme photo-generated electron transfer mechanism has been proposed.

**RESULTS AND DISCUSSION**

The mechanism of the formation of WSASL1 ternary heterostructure involves mainly three steps. In the first step, we have tried to synthesize non-stoichiometric WO3 by hydrothermal effect followed by the calcination method. Under heat treatment, a number of W-O bonds break and oxygen atoms are removed from the surface to create oxygen deficiency along with reduction of W6+ to W5+. In the second step, Ag NPs get preferably attached to the oxygen deficient sites. In the case of stoichiometric WO3, the W atoms with 6+ oxidation state possess d0 configuration with no electrons acquired. Under heat treatment, a number of W-O bonds break and oxygen atoms are removed from the surface to create oxygen deficiency along with reduction of W6+ to W5+. In the second step, Ag NPs get preferably attached to the oxygen deficient sites.
available to reduce metal atoms. However, nonstoichiometric WO3 (WO3-x) makes available partially filled d-orbitals and provide active sites for reduction—deposition of Ag NPs. Due to the oxygen vacancy, the density of electrons around the W atom increases. Upon light irradiation, WO3-x leads to generation of photoinduced electron–hole pairs from 4f orbital of W atom near oxygen vacancy. At that same time, methanol act as a hole scavenger, trapping the holes to produce methoxy radicals, thus leaving the electrons to reduce the Ag NPs from AgNO3 solution compensating the electron effect of oxygen vacancy. Thus, Ag NPs are preferentially localized at defect sites. In the final step, the presence of Ag NPs in the WAS served more active sites, which are crucial to attach with LDH surface during in situ designing process. Usually, the presence of abundant hydroxyl groups on the surface of LDH materials is known to serve as an ideal support to load noble-metal nanoparticles via Ag–OH interfacial bond. Thus, hydroxyl groups provide a unique support for stabilizing Ag NPs. The surface of LDH built up a cooperative self-assembly between negatively charged −OH groups and slightly positively charged Ag NPs of WAS through covalent interaction resulting in deposition of Ag NPs as an interparticulate electron mediator. The WO3-x Ag NPs, and LDH contact interface favor easy flow of charge carriers through the Z-scheme mechanism in the heterostructure.

The crystal and phase purities of the as-synthesized material (LDH, WO3-x, WAS, WSL1, and WSASL1) were analyzed by XRD study, as shown in Figure 1a. Bragg reflections of neat LDH can be indexed as hexagonal lattice having R3m space group with rhombohedral symmetry. The intense dihedral hydration peaks provide a unique support for stabilizing Ag NPs. The surface of LDH built up a cooperative self-assembly between negatively charged −OH groups and slightly positively charged Ag NPs of WAS through covalent interaction resulting in deposition of Ag NPs as an interparticulate electron mediator. The WO3-x Ag NPs, and LDH contact interface favor easy flow of charge carriers through the Z-scheme mechanism in the heterostructure.

The XRD results signify that the structure and crystallinity of the materials with a relative vapor pressure range of 0.1–0.9 P0/Ps. The XRD pattern of WO3-x indicates the hexagonal phase (JCPDS no. 75-2187). The characteristic diffraction peaks observed at 2θ values of 14.0, 22.8, 24.4, 26.9, 28.2, 36.3, 50.0, and 55.3° were attributed to the (100), (001), (110), (101), (200), (201), (220), and (202) basal planes, respectively. Their lattice parameters were found to be a = b = 0.78 nm and c = 0.39 nm. In addition, two less intense peaks were observed at 2θ values of 17.7° (111) and 38.7° (003) for orthorhombic phase of WO3-x crystals. Meanwhile, it is worth noting that the diffraction peak intensity of the WO3-x was shrunk after the formation of heterostructure between LDH and WO3-x indicating the synergistic effect between the two components. In WSL1 and WSASL1 nanohybrids, due to low concentration of LDH, three peaks [(003), (006), and (113)] of LDH were noted. In particular, the (006) plane of LDH (23.3°) coincides with the (110) plane of WO3-x (22.8°) and a broad peak was observed nearer 2θ value. Interestingly, there was no shift in the diffraction peak locations of WO3-x and LDH suggesting that LDH simply gets attached onto the surface of WO3-x instead of covalently bonded into the lattice crystal. Furthermore, it was found that the introduction of metallic Ag NPs into WSL1 material (WSASL1) had no remarkable impact on their crystalline structure. This can be attributed to low doping amount of Ag NPs in the WSL1 binary heterostructure, as well as overlapping of the diffraction peak of WO3-x at 2θ = 38.7° with the characterization peak of metallic Ag [(111), 38.1°]. The XRD results signify that the structure and crystallinity of WO3-x were maintained in both WSL1 and WSASL1 materials resulting in superphotocatalytic performance. Conclusively, the above technique endorses the coexistence of three species (WO3-x, LDH, and Ag) in the WSASL1 ternary heterostructure photocatalysts having polycrystalline structure.

The specific surface area and pore size distribution of as-prepared photocatalysts (WO3-x, WSL1, and WSASL1) were analyzed by the N2 adsorption–desorption technique. As depicted in Figure 1b, the entire isotherms curve can be classified as type IV, suggesting the existence of mesopores in the materials with a relative vapor pressure range of 0.1–0.9 P/P0. The adsorption at high P/P0 represents a feature of H3 loop type. The specific surface areas and the corresponding pore size data of the catalysts estimated by the Brunauer, Emmett, Teller (BET) and Barrett, Joyner, Halenda (BJH) methods are listed in Table 1. The inserted pore size distribution curve resulted from an analyzed desorption branch
of isotherm. According to our previous study, the neat LDH showed the surface area of 28.7 m²/g with the pore size and pore volumes of 1.64 nm and 0.04 cm³/g, respectively. The BET specific surface areas of the synthesized WO₃₋ₓ and W5A5L1 heterostructures were found to be 32.6 and 36.4 m²/g, respectively. These results reveal that the formation of heterostructure between WO₃₋ₓ, Ag, and LDH increases the specific surface area of the prepared ternary WSASLA photocatalyst compared to both the parent materials (LDH and WO₃₋ₓ) and provided a large number of reaction sites for enhanced photocatalytic activity.

The surface morphologies of LDH, WO₃₋ₓ, and W5A5L1 heterostructure were investigated by the SEM technique. The SEM image of LDH (Figure 2a) displayed huge clusters of flaky sheets. This material is composed of large crystal nanosheets, which effortlessly gather in cohesive force. Additionally, the crystal surface of the LDH was relatively smooth, suggesting no other particles on it. As revealed in Figure 2b, some of the particles of WO₃₋ₓ are capsule-like and many of them are spherical-shaped. The capsule-like structures of WO₃₋ₓ are found to have average length and diameter around 144 and 26 nm, respectively, whereas the spherical structure is found to be 90 nm in diameter. To further establish the emergence of LDH and Ag NPs on the surface of WO₃₋ₓ heterostructure, TEM analyses of LDH and W5A5L1 were carried out. As shown in Figure 2c, the TEM micro images evidently show the formation of LDH consisting of plate like nanosheets of nanomeric range. After the construction of ternary heterostructure, the Ag NPs and LDH nanoplates were coated on the WO₃₋ₓ surface (Figure 2d). Some capsule-like and spherical particles were observed for WO₃₋ₓ, which is in good agreement with SEM results. As a consequence of Ag NPs and LDH loading, a few small spherical particles were assembled and adhered on WO₃₋ₓ surface without aggregation, and LDH nanoplates were uniformly distributed on the WAS surface indicating the formation of hierarchical WSASL1 ternary heterostructure. Most of Ag NPs were not visible due to deposition of LDHs on Ag NPs in WO₃₋ₓ surface. The absence of isolated Ag NPs and LDH nanoplates further disclosed the strong interaction between LDH, Ag NPs, and WO₃₋ₓ. Furthermore, the structural orientation of WO₃₋ₓ and LDH particles was not changed after the formation of ternary heterostructure. The bright- and dark-field images of WSASL1 ternary heterostructure are shown in Figure 2e,f. The bright and dark areas in the micrographs indicate WO₃₋ₓ and LDH, respectively, whereas the Ag NPs are assigned by more shining particles. As a result, the dark- and bright-field images further corroborate the presence of three types of components in WSASL1 ternary heterostructure. Moreover, High-resolution transmission electron microscopy (HRTEM) image was taken to give more information regarding the internal structure and interface of WO₃₋ₓ, LDH, and Ag NPs in the heterostructure. Figure 2g signifies the well-resolved periodic lattice fringes of hexagonal WO₃₋ₓ with interplanar distances of 0.389 and 0.33 nm, indexed as (001) and (200) zone axes, respectively. Furthermore, remarkably circular nanoparticles on the edge of the WO₃₋ₓ appeared with 0.23 nm interplanar spacing, representing the (111) basal plane of cubic Ag NPs. The crystal lattice spacing of 0.14 nm fringe corresponding to the (113) plane of rhombohedral LDH nanoplates were found near Ag NPs. Notably, there exists well-defined heterointerfacial contact between three components with Ag NPs present at the interface along with its lattice fringes strongly connected to the lattice fringes of WO₃₋ₓ and LDH. The second fact is probably due to the diffusion of photoinduced electron on the interface of WS1L during the photodeposition of Ag NPs. As a result, it can be said that Ag NPs serve as an electron conduction mediator between WO₃₋ₓ and LDH in the heterostructure photocatalyst. Moreover the selected area electron diffraction (SAED) patterns of ternary heterostructure (WSASL1) confirmed the polycrystalline nature of the material. As displayed in Figure 2h, the solid smooth concentric ring patterns are analogous to the crystallographic planes of WO₃₋ₓ, Ag, and LDH in the WSASL1. In energy-dispersive X-ray (EDX) image, Zn, Cr, W, Ag, C, and O elements could be detected (Figure S1), which again

| samples | surface area (m²/g) | mean pore diameter (nm) | pore volume (cm³/g) |
|---------|---------------------|-------------------------|--------------------|
| LDH     | 28.7                | 1.64                    | 0.04               |
| WO₃₋ₓ   | 32.6                | 8.76                    | 0.072              |
| W5A5L1  | 36.4                | 7.74                    | 0.070              |

Figure 2. SEM images of (a) LDH and (b) WO₃₋ₓ; TEM images of (c) LDH and (d) W5A5L1; (e, f) bright- and dark-field images of WSASL1; (g) HRTEM images [selected area presenting lattice fringes of LDH, WO₃₋ₓ and Ag NPs]; and (h) SAED pattern of WSASL1 heterostructure.
evidenced that W5A5L1 heterostructure was successfully synthesized without any impurities. The HRTEM and SAED outcomes are well consistent with XRD results, and the TEM morphological advantage of W5ASL1 supports a “sandwich”-like heterostructured material having superior efficiency for photocatalytic application owing to the synergistic interaction.

Figure 3. (a) FTIR and (b) Raman images of as-synthesized materials.

Figure 4. High-resolution deconvoluted XPS images of WSASL1: (a) C 1s, (b) Zn 2p, (c) Cr 2p, (d) W 4f, (e) O 2p, (f) Ag 3d, and (g) survey spectra.
The FT-IR spectra were implemented to determine the nature of the grafted functional groups present in the materials. The structures of LDH and WO$_{3-x}$ and the impact of the coupling between three components were investigated and are displayed in Figure 3a. In the case of LDH, a broad band was observed at around wavenumbers of 3220–3600 cm$^{-1}$ for −OH stretching vibration mode. Mainly the −OH group was bonded with the metal centers of brucite layers present in the intergallery space of LDH, while the asymmetric and symmetric stretching vibration modes of intercalated CO$_3^{2-}$ anion centered at 1370 and 1493 cm$^{-1}$, respectively. The characteristic peaks at 1590–1640 cm$^{-1}$ can be attributed to H$_2$O bonded through oxygen atoms (H−O−H bending vibration) in all as-synthesized photocatalysts. These peaks imply the subsistence of adsorbed H$_2$O and −OH compounds in the materials. In addition, the lattice metal vibrations (Zn/Cr−O, Zn−O−Cr, Zn/Cr−OH) were found at lower wavenumber of about 500–700 cm$^{-1}$ for LDH, but in the cases of WSL1 and WSASL1, those bands were not clearly visible due to low concentration of LDH. For pure WO$_3$, three distinctive absorption bands at 754, 819, and 932 cm$^{-1}$ can be observed, where the first two were endorsed to the W−O−W/O−W−O interbridging stretching vibration and the third peak corresponding to W=O terminal stretching. Due to low wt % loading of Ag NPs, no vibration modes appeared in WAS and WSASL1 photocatalysts. In comparison to bare WO$_{3-x}$, the intensities of O−W−O stretching vibration peaks in both binary (WAS and WSL1) and ternary heterostructures (WSASL1) became weaker along with its position slightly shifted. In addition, the broadness of −OH stretching band deceased in the cases of WSL1 and WSASL1 relative to LDH. Therefore, the FTIR results provide additional proofs for successful coupling between LDH, WO$_{3-x}$, and Ag NPs in WSASL1 ternary heterostructure.

Raman spectroscopy is found to be an effective, highly sensible, and nondestructive characterization tool that has been carried out to explore the phase transition, bond vibration, and presence of oxygen defect sites. Figure 3b represents the Raman spectra of LDH (inserted), WO$_3$, WO$_{3-x}$, and WSL1. It was observed that WO$_3$ exhibits four highly intense and one weak Raman peaks encountered at wavenumbers of 265, 324, 717, 811, and 952 cm$^{-1}$. The peaks positioned at 717 and 811 cm$^{-1}$ were ascribed to the O−W−O stretching bonds, while the O=W−O bending modes of bridging oxygen atom were located in the lower-frequency region of 265−324 cm$^{-1}$. Additionally, the less intense Raman peak centered at 952 cm$^{-1}$ was related to terminal W=O stretching mode. In case of pristine LDH (inserted), two characteristic Raman bands appeared at 487 and 510 cm$^{-1}$ signifying the brucite sheets of LDH. In addition, other two strong bands at 1062 and 152 cm$^{-1}$ were found corresponding to symmetric stretching and translation vibration modes of intercalated CO$_3^{2-}$ anion. From pictorial Raman graph, after annealing, in the cases of WO$_{3-x}$ and WSL1 ternary heterostructures, similar Raman bands were detected with slight shifting toward lower frequency. The peak intensities of polarized bands were found to be less intense and broader compared to WO$_3$, which confirms the existence of oxygen vacancy in WO$_{3-x}$. Furthermore, in the case of WSASL1 photocatalyst, a wider and less intense band was observed in addition to WO$_{3-x}$, suggesting the subsistence of lattice imperfections resulting in more oxygen voids. The calculation process can effectively remove surface-adsorbed water species and affects the lattice structure of WO$_3$ crystal, which results in the introduction of oxygen defect sites. The dipole moment of the W−O bond is directly proportional to the electronegativity difference of the W and O atoms. When some oxygen atoms have been removed from WO$_3$ lattice, the instantaneous dipole moment of the W−O bond is weaker, revealing the lower absorption peak intensity. The Raman bands for LDH and Ag were not observed in WSASL1 material due to the presence of low concentration of Ag NPs and LDH. In particular, the terminal W=O stretching band was prominently noted and shifted toward more lower wavelength (905 cm$^{-1}$) than WO$_3$ and WO$_{3-x}$, which shows that the W=O bond was strongly affected by different chemical environments (LDH and Ag NPs) and resulted in higher oxygen vacancy in WSASL1 heterostructure. X-ray photoelectron spectroscopy (XPS) analysis provides evidence for elemental constitution, electronic environment, and chemical state of the as-synthesized materials. The XPS images of WSASL1 ternary heterostructure are shown in Figure 4. The photoelectron peaks of C, O, Zn, Cr, W, and Ag elements were noted in the survey spectrum of WSASL1 (Figure 4g) endorsing the formation of heterostructure. Using CASAXPS and Origin software, high-resolution XPS images of the individual elements were successfully deconvoluted and analyzed. According to our previous study, in pure ZnCr LDH (Figure S2), the XPS profiles of C 1s showed binding energies of 284.9 and 288.8 eV. Moreover, Zn 2p and Cr 2p spectra displayed four distinct peaks (Zn 2p$_{3/2}$, Zn 2p$_{1/2}$, Cr 2p$_{3/2}$, and Cr 2p$_{1/2}$) at binding energies of 1022.0, 1045.0, 577.7, and 587.1 eV, respectively. But in the present study (WSASL1), two peaks of C 1s spectrum appeared at binding energies of 284.9 and 287.7 eV due to reference carbon and the presence of intercalated carbonate ion of LDH in WSASL1 heterostructure, respectively (Figure 4a). As shown in Figure 4b for the Zn 2p, two fitted spin−orbit doublet (Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$) peaks were found at 1021.7 and 1044.8 eV, respectively, indicating the typically high-spin Zn$^{2+}$ state. The Cr 2p (Figure 4c) displayed three peaks at 573.88, 577.5, and 586.93 eV corresponding to metallic traces Cr$^{0}$, Cr 2p$_{3/2}$, and Cr 2p$_{1/2}$ spin state, due to Cr$^{3+}$ oxidized state. The Zn$^{2+}$ and Cr$^{3+}$ species proved the existence of Zn(OH)$_2$, and Cr(OH)$_3$ in WSASL1. In particular, to pure LDH, a blue shift in binding energy was observed for C 1s, Zn 2p, and Cr 2p in the WSASL1 heterostructure. According to the reported value, the binding energies of W4f$_{1/2}$ in W$^{5+}$ and W$^{6+}$ were located at 34.22 and 35.43 eV, respectively, whereas the binding energies at 36.12 and 37.53 were ascribed to the W 4f$_{1/2}$ spin orbit of W$^{5+}$ and W$^{6+}$ oxidation states, respectively. As shown in Figure 4d, the W 4f spectrum of WSASL1 heterostructure showed a red shift in comparison to the above-reported value. Moreover, two additional peaks related to W$^{5+}$ shifted a lower electron volt value with small area, indicating the existence of surface defects and nonstoichiometric oxygen vacancy in the heterostructure. The relative concentration of W$^{5+}$ to W$^{6+}$ was approximately determined by using the included area of every peak in the W 4f spectrum through the above equation (eq 1) and was estimated to be 13.5%, which further support to establish the presence of surface defects and oxygen deficiency of WO$_{3-x}$ in WSASL1. These oxygen deficiencies present in WSASL1 participate and determine the photocatalytic activity of tungsten oxide-based systems. The high-resolution O 1s
spectra of neat LDH (Figure S2) showed two distinct peaks at binding energies of 531.5 and 532.3 eV, attributed to the surface hydroxyl group of brucite layer and intercalated carbonated anion, respectively. In contrast to WSA1L1, three peaks of O 1s spectra (OI, OII, and OIII) appeared with slight positive shifting in binding energy (Figure 4e). Basically, the less intense peak located at 530.6 eV (OI) was due to the lattice oxygen in the M–O–M bond (M=W, Zn, and Cr). The intermediate binding energy peak (OII) at 532.0 eV was assigned to the −OH group, and OIII with higher binding energy (533.5 eV) revealed the carbonated oxygen and chemisorbed water molecule. Furthermore, the most intense OII peak was observed by the oxygen ions adsorbed in the oxygen lacking area for maintaining the charge equilibrium or the −OH groups caused by the surface activity. The upshifted binding energy of the O 1s state further proved the chemical environment of O atom associated with deformation mode of W–O and O–O bonds due to oxygen vacancy in WSA1L1 heterostructure. As in Figure 4f, the Ag 3d peaks (3d_{3/2} and 3d_{5/2}) in WSA1L1 were located at 367.4 and 373.4 eV, respectively, suggesting Ag²⁺, which remained unaltered as in previously reported bare Ag/WO₃−ₓ. From the above XPS analysis, a negative shifting binding energy of Zn, Cr, and C and a positive shifting binding energy of W were observed in the case of WSA1L1. Generally, the upshift of binding energies suggests lower electron clouds and the downshift reveals to larger electron mass on the photocatalyst surface, which indicates that the shift of electrons is from WO₃−ₓ to LDH surface. However, the binding energies of Ag as electron mediator between WO₃−ₓ and LDH remained unchanged in this system because the shifting of electron from WO₃−ₓ to LDH surface through metallic Ag results in charge equilibrium. It can be concluded that the reduction in electron concentration around WO₃−ₓ results in the SPR effect. The improved light absorption is significantly due to oxygen vacancy state between the conduction band (CB) and valence band (VB) in the WO₃−ₓ band structure, which is in good agreement with Raman and XPS results. The deficiency of surface oxygen promotes the charge pair transfer and results in enhanced photoactivity. After the immobilization of Ag NPs onto the surface of WO₃−ₓ, the resulted WAS material possessed both a characteristic absorption of WO₃−ₓ and the surface plasmon resonance (SPR) band at 500−600 nm, which can be attributed to the spatially confined electrons in Ag NPs. In contrast to pure WO₃−ₓ, the band gap absorption edge in the WAS catalyst shifted toward longer wavelength and exhibited a superior visible light absorption. Additionally, the introduction of WO₃−ₓ into the LDH (WSL1) significantly increased photoresponse behavior of both LDH and WO₃−ₓ. In the case of WSL1, the d–d transition band of LDH positioned at 570 nm, merged with SPR band of Ag NPs, and exhibited a notably stronger spectrum, extending from the UV−visible to near-infrared region compared to parent and binary heterostructure materials. It may be due to the deposition of metallic Ag NPs on the crystal facet WO₃−ₓ resulting in the SPR effect. The improved light absorption is consistent with the outcomes of photoactivity, suggesting a synergetic effect in the ternary system (LDH, WO₃−ₓ, and Ag). The highest absorption strength of WSA1L1 represents

**Figure 5. UV−vis diffuse reflectance spectra of (a) LDH, (b) WO₃, WO₃−ₓ, WAS, WSL1 and WSA1L1.**

The highest absorption strength of WSA1L1 represents the optical response of the as-synthesized materials (LDH, WO₃, WO₃−ₓ, WAS, WSL1, and WSA1L1). As shown in Figure 5a, the optical absorption shoulders of pure LDH were located in the UV−visible range of light. An inherent optical band positioned in the UV region due to the ligand−metal charge transfer (LMCT) spectra arises from the transition between 2p orbital of O to 4s and 3d orbitals of the Zn and Cr, respectively. The metal−metal charge transfer (MMCT) band appeared at 270−320 nm, due to the transition between Cr 3d t₂₉ and Zn 4s orbital. These absorption spectra were mainly originated from the crystal field splitting of the bimetallic oxo-bridged linkage in the LDH system. The 4A₂g → 4T₁g(F) and 4A₂g → 4T₂g(F) d−d transitions of Cr³⁺ ion (d⁵ configuration) were related to the absorption peaks at 410 and 570 nm, respectively, in the visible light region. As depicted in Figure 5d, the WO₃ exhibits an absorption edge at 470 nm, and there is considerably no absorption in longer wavelength, i.e., visible light region from 460 to 800 nm, whereas WO₃−ₓ displayed wide absorption spectrum from 440 nm to the NIR region with an absorption edge at 494 nm. This intrinsic absorption suggests the presence of newly created energy levels due to oxygen vacancy state between the conduction band (CB) and valence band (VB) in the WO₃−ₓ band structure, which is in good agreement with Raman and XPS results. The deficiency of surface oxygen promotes the charge pair transfer and results in enhanced photoactivity. After the immobilization of Ag NPs onto the surface of WO₃−ₓ, the resulted WAS material possessed both a characteristic absorption of WO₃−ₓ and the surface plasmon resonance (SPR) band at 500−600 nm, which can be attributed to the spatially confined electrons in Ag NPs. In contrast to pure WO₃−ₓ, the band gap absorption edge in the WAS catalyst shifted toward longer wavelength and exhibited a superior visible light absorption. Additionally, the introduction of WO₃−ₓ into the LDH (WSL1) significantly increased photoresponse behavior of both LDH and WO₃−ₓ. In the case of WSL1, the d−d transition band of LDH positioned at 570 nm, merged with SPR band of Ag NPs, and exhibited a notably stronger spectrum, extending from the UV−visible to near-infrared region compared to parent and binary heterostructure materials. It may be due to the deposition of metallic Ag NPs on the crystal facet WO₃−ₓ resulting in the SPR effect. The improved light absorption is consistent with the outcomes of photoactivity, suggesting a synergetic effect in the ternary system (LDH, WO₃−ₓ, and Ag). The highest absorption strength of WSA1L1 represents
maximum production of electron–hole pairs, which participate in the photocatalytic reaction.

To understand the origin of improved photoactivity in the heterostructure system, it is highly essential to find out the potential energy diagram of the nanohybrids. To calculate the relative band edge potential of each bare material in this W5A5L1 heterostructure, the optical band gap energy and flat band potentials of LDH and WO3−X were estimated. As in Figure S3a,b, by extrapolation, the linear portion of curve to the photoenergy axis gives the band gap energy based on the Tauc equation (eq 2)

\[
(\alpha \nu)^{1/n} = A(\nu - E_g)
\]

where \( \alpha, h, \nu, A, \) and \( E_g \) are the absorption coefficients, Planck’s constant, light frequency, proportionality constant, and band gap energy, respectively. The transition properties of photocatalyst depend on \( n \). The pure LDH showed direct allowed transition having \( E_g \) of 2.5 eV, and similarly, a 2.7 eV band gap was obtained in the case of WO3−X considering indirect allowed transition. To determine the flat band (\( V_{fb} \)) potential, the following MS equation (eq 3) was used. The \( V_{fb} \) potential at electrode/electrolyte interface can be evaluated from the MS plot.

\[
\frac{1}{C^2} = \left( \frac{2}{\epsilon \epsilon_0 N_d} \right) \left( V_a - V_{fb} - \frac{kT}{e} \right)
\]

where \( \epsilon \) is the dielectric constant, \( V_a \) is the applied potential, \( N_d \) is the electron donor density, \( V_{fb} \) is the flat band potential, \( \epsilon_0 \) is the permittivity of vacuum, \( C \) is the space charge layers capacitance, \( e \) is the electron charge, \( T \) is the temperature, and \( k \) is the Boltzmann constant. \( V_{fb} \) was calculated by considering the x intercept of a linear fit to the Mott–Schottky plot, whereas \( 1/C^2 \) is the function of applied potential (\( V_a \)). As shown in Figure S3c,d, both LDH and WO3−X electrodes display positive slopes, suggesting n-type nature of the semiconductors, where main charge carriers are electrons. The \( V_{fb} \) values of LDH and WO3−X were found to be –0.7 and 0.18 V versus Ag/AgCl, respectively. According to the literature, the CB potential of n-type semiconductor-based metal oxide was 0–0.1 V higher than its \( V_{fb} \). Therefore, the CB potential of WO3−X was calculated to be 0.7 V versus NHE, but in the case of LDH, it was assumed that the flat band potential is equal to CB potential, i.e., –0.08 V versus NHE. By taking the optical band gap energy and CB potential, the VB positions of both LDH and WO3−X were calculated to be 2.42 and 3.2 V versus NHE, respectively.

To investigate the separation and transport effectiveness of photoinduced charge carriers, photoluminescence (PL) spectra, EIS plot, and photocurrent density over WO3−X, LDH, WAS, WSL1, ASWSL1, and W5A5L1 photocatalysts were explored. Particularly, PL spectroscopy is a very powerful technique to quantify the impurity level and directly connected to the dynamic behavior of photoinduced charge carriers like transfer, separation, and capture. The PL signal is a consequence of free electron–hole pairs recombination. Generally speaking, the lifetime of photogenerated charge carriers is high for weaker PL spectra. Figure 6a represents the PL emission spectra of all of the samples at an excited wavelength of 330 nm. A strong emission peak at 420–450 nm in LDH was attributed to the radiative recombination of localized surface trapped charge pairs, and the existence of weak band at 470 nm was attributed to the band-to-band emission peak of LDH. Additionally, a less intense band at

Figure 6. (a) PL spectra, (b) EIS images, (c) Bode plot, and (d) LSV plot.
around 500 nm was due to the surface defect sites in the LDH material. In addition, the less intense emission peak at 468 nm in WO$_{3-x}$ material was ascribed to the localized states of band gap along with the presence of oxygen vacancies and due to indirect band-to-band transition. In the case of WAS, the photogenerated electrons get transferred from the CB of WO$_3$ to Ag NPs, which acts as electron trapping center and helps to improve the charge separation due to matched energy band structures. This also arises from the charge transfer between the O 2p orbital of WO$_{3-x}$ and the vacant d orbital of Ag NPs. This leads to lower PL intensity compared to neat LDH and WO$_{3-x}$. However, after the heterostructure formation between LDH and WO$_{3-x}$, the luminous peak intensity of the WSL1 is lower than that of both parent and WAS materials, which confirm the reducing recombination rate of the photoinduced charge pairs to some extent. Furthermore, in ASWSL1 and WSASL1 ternary heterostructures, the PL intensity significantly drops compared to WSL1 photocatalyst demonstrating a lower fluorescence associated with delayed annihilation rate of photoinduced electron–hole pairs. Again, between the two ternary heterostructures, i.e., ASWSL1 and WSASL1, the Ag-mediated system (WSASL1) displayed a reduced PL intensity. It was earlier reported, while the noble-metal nanoparticle act as mediators between two semiconductors, resulting in an interior direct pathway, which efficiently transports the photogenerated charge pairs.

Conclusively, the presence of Ag NPs as an electron conduction mediator and oxygen vacancy in this WSASL1 ternary heterostructure can efficiently prolong the lifetime of the photoexcited electrons that can involve in the photocatalytic reaction in place of emissive recombination. Further, to investigate the charge transfer resistance, diffusion, conductivity, and separation capability of photogenerated charge pairs in the electrode–electrolyte interfacial region, EIS measurements were carried out. EIS analysis represents the Nyquist plots, which basically consist of a semicircle in the high-frequency region (conductive loop), suggesting the interfacial charge migration resistance and diffusion of charge within the space charge layer. The other part is a straight line in the low-frequency region (inductive loop) related to the ion diffusion resistance called the Warburg resistance. Figure 6b shows the Nyquist plots of WO$_{3-x}$–LDH, WAS, WSL1, and WSASL1 heterostructure under visible light irradiation. The magnitudes of the resistance in the cases of pure WO$_{3-x}$–LDH, WAS, WSL1, and WSASL1 obtained from the X-intercepts of the semicircles are found to be 79, 73, 69, 62, and 49 Ω, respectively. The smallest diameter of arc was provided by WSL1 electrode than both parent and WAS material resulting in the minimum charge transfer resistance and more effective separation of electron–hole pairs at the solid–solid interfacial. Additionally, after the formation of heterostructure between LDH and WO$_{3-x}$, more number of oxygen vacancies were introduced in the material, which increases the electrical conductivity and retards the recombination of charge pairs. Furthermore, compared to WSL1 binary heterostructure, WSASL1 ternary heterostructure showed a remarkably reduced semicircle. This implies that the existence of Ag NPs lowered the hurdle for the electron–hole migration and favors the faster separation and transportation efficiency of photogenerated charge pairs during the photocatalytic reaction process, facilitating the enhancement of the photocatalytic behavior. To determine the lifetime ($\tau_n$) of photoinduced electron or for how much time the excited electrons are accessible for participating the photocatalytic reaction, a Bode phase plot is drawn. Figure 6c shows the Bode phase plot of LDH, WSL1, and WSASL1 photocatalysts. In the Bode phase image, the peak shifting from the higher frequency area to the lower frequency area indicates a quick transport process of light-induced electrons. The life span of injected electron from the photoelectrode to electrolyte solution is related to this frequency and it can be easily calculated by using the following expression (eq 4):

$$\tau_n = \frac{1}{2nf_{\text{max}}}$$

The $f_{\text{max}}$ of the WSASL1 photoelectrode was calculated to be 96.26 μs, which is greater than WSL1 binary hybrid (68 μs) and neat LDH material (26.33 μs). The highest lifetime of WSASL1 suggests lower recombination and faster migration of photogenerated charge pairs, facilitating enhanced photocatalytic activity.

In addition, photocurrent densities of as-prepared photocatalysts (LDH, WO$_{3-x}$, WAS, WSL1, and WSASL1) were determined by LSV measurements under visible light illumination (Figure 6d). It has been demonstrated that photocurrent is initiated from the transfer of photoexcited electrons under the circumstances of light irradiation, whereas the holes move to the electrode–electrolyte interfacial region, thus getting the separation and transportation of photogenerated charge carriers. The order of photocurrent response over photocatalysts is WO$_{3-x}$ (0.5 mA/cm$^2$) < LDH (1.2 mA/cm$^2$) < WAS (1.5 mA/cm$^2$) < WSL1 (3.1 mA/cm$^2$) < WSASL1 (4.7 mA/cm$^2$). It was observed that WSL1 exhibits higher photocurrent density than neat WO$_{3-x}$ LDH, and WAS materials. Heterostructure between WO$_{3-x}$ and LDH serves as a shallow electron donor to increase the photocurrent generation. As reported earlier, the presence of oxygen vacancies in WO$_{3-x}$ results in inter-band-gap states below the CB minimum provides more charge carriers to enhance the lifetime of photoelectron, by the trapping of electrons/hole within shallow defective sites. This increase in charge separation and transportation ability with the external applied voltage is mainly due to expanded surface charge layer. The increased lifetime would allow holes in the VB to migrate toward the electrode/electrolyte interface to favor photocatalytic oxidation reactions. Moreover, in comparison to WSL1, WSASL1 ternary heterostructure exhibits greater photocurrent density and showed almost 9 and 4 times higher photocurrent than pure WO$_{3-x}$ and LDH, respectively. Furthermore, WSASL1 also shows a significant cationic shift in onset potential. These results clearly indicate effective reduction in the rate of recombination of charge carriers through Ag NPs as a mediator that offers lowest resistance supporting excellent photocatalytic performance. Furthermore, the transient photocurrent–time curves of LDH, WO$_{3-x}$, and WSASL1 were plotted by several light on–off runs. It is well known that the photocurrent is produced primarily due to the diffusion of collective photogenerated electrons to the back contact, and simultaneously the photoinduced holes are consumed by the holes acceptor in the electrolyte. As displayed in Figure S4, the photocurrent increased quickly in the presence of light irradiation and remains constant at a relatively high value. By contrast, when light illumination was cut off, the current suddenly decreased to steady state. Moreove, it is clearly seen that the photocurrent density of WSASL1 was
greater than both pure materials (LDH and WO$_3$−$X$). This implies that the ternary heterostructure has a lower recombination rate of charge pairs under light irradiation conditions and a more efficient electron−hole separation through the LDH, Ag, and WO$_3$−$X$ interface. It should be noted that the LSV and transient photocurrent results are well consistent with PL and EIS data of different samples and supports the synergistic interaction between WO$_3$−$X$, LDH, and Ag NPs in W5A5L1 heterostructure contributing to the significantly improved photocatalytic performances toward TC degradation and H$_2$ evolution.

**Photocatalytic Activity.** To examine the photocatalytic performance of the as-synthesized photocatalyst under visible light illumination (λ ≥ 420), a typical antibiotic TC was selected as the target pollutant. The weight ratio between WO$_3$−$X$ and LDH was varied followed by loading of different wt % of Ag NPs. Figure S5a shows the photocatalytic performance of as-prepared WO$_3$−$X$, LDH, W5L1, and W1L5 toward TC degradation. The pure WO$_3$−$X$ showed a higher TC degradation efficiency (19%) than WO$_3$ (12%). It suggests the surface oxygen vacancy facilitates the separation efficiency of photon-induced charge pairs. Meanwhile, it was observed that neat LDH shows just 51% of TC removal. Once the WO$_3$−$X$ was hybridized with LDH, the degradation efficiency was found to increase with the maximum content of WO$_3$−$X$ compared to bare LDH. The subsistence of oxygen defect in WO$_3$−$X$ not only suppresses the electron−hole recombination by temporarily trapping the photogenerated charges in binary heterostructure but also favors adsorption of reactant substrates on the top surface of photocatalyst, resulting in enhanced TC degradation. The removal efficiencies of various binary heterostructures follow the order: W1L1 (64%) < W5L1 (77%) > W1L5 (59%). This can be demonstrated by the following two reasons: (1) the optimized amount of WO$_3$−$X$ results utmost harvest of incident light and (2) the created heterostructure formation between WO$_3$−$X$ and LDH and the presence of oxygen void promote the charge carrier transfer efficiency at the surface of the photocatalyst. But the increased LDH content (W1L5) acts as the recombination centers of heterostructure and suppresses the electron−hole channelization. Hence, we have considered the optimal binary system W5L1 for further study.

To again develop the photocatalytic performance of the WO$_3$−$X$/LDH binary heterostructure, metallic Ag NPs were introduced onto the most favorable W5L1 photocatalysts to generate the ternary WO$_3$−$X$/Ag/LDH heterostructure. As displayed in Figure S5b when the study was carried out with varying wt % of Ag NPs (3, 5, 7, and 9 wt %), 5 wt % Ag NPs were found efficient. The Ag-based ternary heterostructure follows the degradation order: W5A3L1 (86.5%) < W5A5L1 (92%) > W5A7L1 (82.3%) > W5A9L1 (79%). This result suggests that the optimum concentration of Ag NPs acts as an electron bridge and passageway to promote the electron migration ability of LDH and WO$_3$−$X$. A surplus amount of metallic Ag NP results agglomerated and acted as the recombination hub with ensuing the reduction of TC degradation. The output of photocatalytic experiment implies that both WO$_3$−$X$ and Ag NPs contents played key roles for the eventual photocatalytic degradation activity.
More precisely, the photocatalytic TC removals of the as-fabricated materials (WO3, WO3-x, LDH, WAS, WSL1, and WSASL1) are summarized in Figure 7a. A negligible removal of TC concentration was found in the blank experiment, which was performed in the absence of photocatalysts, demonstrating insignificant TC degradation in self-photolysis reaction. The degradation rate of TC over the photocatalysts was found to be in the order: W5A5L1 (92%) > W5L1 (77%) > WAS (59.2%) > LDH (51%) > WO3-x (19.7%) > WO3 (12%). Compared to pure LDH and WO3-x, the WAS, WSL1, and WSASL1 exhibit better TC degradation. Importantly, WSASL1 ternary heterostructure achieved the highest TC degradation and reached 92% in 90 min. In addition, the concentration of TC for 15 min time interval was also studied to predict the reaction kinetics using the WSASL1 photocatalyst. The UV-visible absorbance spectra (Figure 7b) of TC show two major peaks centered at 357 and 275 nm corresponding to the E2 absorption bands of the benzene ring. The aromatic B peaks centered at 357 and 275 nm corresponding to the E2−D rings are diminished 275 nm shoulder peak further con

**Scheme 1. Proposed Photocatalytic TC Degradation Pathways in the WSASL1 Heterostructure**

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literature. First, the TC-HCl is deprotonated, to generate the fragmentation molecular ion with 445.60 m/z value. (i) In degradation pathway I, the hydrogenation occurred at the carbonyl group of TC and generated a product TC1 (m/z = 446.89). In addition to the degradation of TC1, it leads to the formation of TC2 (m/z = 279.49) through the cleavage of carbon carbon single bond or dislodging of hydroxy group. In this pathway, the aromatic ring is broken and the naphthol ring of TC remains unchanged during the degradation process. Further by losing the water and methanol group, the TC2 is converted to TC3 (m/z = 241.82). (ii) Pathway II mainly involves the detachments of N-methyl group. The loss of two N-methyl groups is followed by the degradation of TC to TC4 (m/z = 433.31) and from TC4 to TC5 (m/z = 417.36), respectively. Then, the resulting molecular ion (TC5) was fragmented to TC6 with m/z = 403.36 via cleavage of methyl group. (iii) In pathway III, the deamination reaction of TC generates to TC7 (m/z = 405.1), followed by fragmentation of TC 7 into TC8 (m/z = 306.43) through the loss of dimethylamino group followed by dehydroxylation, deethylation, addition reaction, and breakage of benzene rings. Then, TC 8 was converted to TC 9 (m/z = 274.59) via carbonation reaction. Finally, TC3 and TC9 intermediate products were mineralized into small inorganic materials like NH4+, NO3−, H2O, and CO2.

The mineralizing properties were found to be an important factor in analyzing the photocatalytic abilities of semiconductor-based photocatalyst. The mineralization of tetracycline was evaluated by WSASL1 photocatalyst at regular interval by performing TOC measurement. The degree of mineralization in terms of total organic carbon was estimated by the following equation:

\[
\text{percentage of mineralization} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0}
\]

where TOC0 and TOCt are the total organic carbon of the test solution before and after irradiation of light, respectively. Figure 7 demonstrates the amount of mineralization with respect to time interval. From Figure 7, it was observed that the mineralization efficiency reached about 69% in 120 min of reaction. The obtained result suggests that TC has been oxidized to CO2, H2O, and other intermediate molecules, which have been verified and well explained in LC-MS section.

According to the Langmuir–Hinshelwood model, the kinetics of TC degradation in the presence of photocatalysts was determined, as shown in Figure 7d. TC decomposition over the synthesized parent, binary and ternary materials ascertainment the pseudo-first-order kinetics model and represented as follows (eq 6):

\[
\ln \left( \frac{C_0}{C} \right) = k_{\text{app}} t
\]

where \(C_0\) is the original concentration of the TC solution, the concentration of TC solution after reaction is denoted as \(C\), \(k_{\text{app}}\) (min\(^{-1}\)) represents the apparent rate constant of the reaction system, and \(t\) is time. The graph of \(\ln(C_0/C)\) versus time reveals a straight line with slope \(k_{\text{app}}\) calculated through linear fitting of the regression curve. Additionally, by using the following equation (eq 7), \(t_{1/2}\) was estimated. Basically, \(t_{1/2}\) is the time required to decompose TC into half of its original concentration.
Table S1 summarizes the apparent rate constant ($k_{app}$), half-life time ($t_{1/2}$), and correlation coefficient factor ($R^2$) of TC degradation reaction. The highest value of $k_{app}$ ($288.5 \times 10^{-4}$ min$^{-1}$) with the lowest $t_{1/2}$ ($24 \times 10^{-4}$ min) was found in the case of W5L1A5, which is about 10.8, 3.4, and 1.6 times higher compared to pure LDH, WO$_3$−X, and W5L1 photocatalysts. This phenomenon explains that the introduction of Ag NPs as the “carriers transport bridge” obviously hampers the recombination efficiency of charge carriers in WSL1A5 ternary heterostructure.

In the photocatalytic degradation, pH is an important parameter for treatment of antibiotic in water bodies. Figure S8a displays the photocatalytic response of WSASL1 toward TC degradation at various pH values (2, 3, 4.5, 6.5, 8.5, and 10). It was reported that TC is amphoteric in nature, and its three functional groups represent the three pKa values of 9.69, 7.68, and 3.30 (Figure S8c). The photocatalytic stability of TC in distilled water is considerably affected by the pH of the solution. Therefore, its molecular conformations are different in various pH values: the protonated form of TC (TCH$_3^+$) exists at pH < 3.3, neutral form (TCH$_2^0$) lies between pH 3.3 and 7.7, and the monoanionic form (TC$^-$) is stable above pH 7.7. Meanwhile, the pH at zero point charge (PZC) of WSASL1 photocatalyst was calculated by drift method and found to be 7 (Figure S8b). As we know, at pH < PZC value, the surface of WSASL1 is positively charged and becomes negative when pH > PZC value. The TC degradation efficiency (95.3%) is highest at pH 4.5, shown in Figure S8a, which explains that in weak acidic environment, H$^+$ could easily react with O$_2^-$ active species to produce OH$, which was one of the reactive species taking part in TC degradation process. However, in strong acidic medium, a repulsive force was developed among the protonated forms of TC (TCH$_3^+$) and positive surface of photocatalyst, which results in decrease of degradation activity (pH 2 = 71.5% and pH 3 = 88%). Moreover, at higher pH (8.5 and 10), the H$^+$ concentration gets lowered and inhibits OH$^-$ formation. Additionally, the adsorption of TC on WSASL1 surface was obstructed in alkaline medium because both the anionic form (TC$^-$) and negatively charged catalyst surface repel each other and lead to the reduced photodegradation performance of TC, i.e., 55.1 and 39% at pH 8.5 and 10, respectively.

To give evidence in support of photodegradation mechanism and to examine the predominant active radical species, trapping experiments were carried out under visible light illumination over LDH, WO$_3$−X, and WSASL1 photocatalysts. The three typical sacrificial agents BQ, EDTA, and IPA were employed for trapping the O$_2^-$, h$, and OH$^-$ radicals, respectively, as the changes in photocatalytic efficiency could depend on the actions of various active species in the TC degradation reaction. Figure 8a highlights the major loss of TC degradation rate (29.3%) over WSASL1 ternary heterostructure by the addition of BQ and implies that O$_2^-$ is the main active species. However, when IPA was introduced into the reaction system, a moderate concentration (46.3%) of TC gets decomposed, which confirms the OH$^-$ radical playing a relatively important role in photodegradation process. Moreover, TC removal efficiency slightly inhibited by the quenching of h$, and degradation was found to be 69%, which indicates...
that involvement of h+ in photocatalytic reaction is partly significant. In the case of LDH, the same trend of active species participation in TC degradation was observed as in WSAFL1. With the addition of EDTA, the photocatalytic degradation process over WO3-x material was almost nil, which only resulted in 5.6% TC removal efficiency, suggesting h+ as the chief reaction species. Furthermore, the degradation process was moderately affected by the presence of IPA, signifying that *OH has also some contribution in the TC removal process. On the other hand, the presence of BQ does not change the photocatalytic performance considerably for WO3-x system, which indicates that *O2- is an inactive radical species. Accordingly, it can be preliminary concluded that, in the case of pure LDH and WSAFL1 ternary heterostructure, the active species participate in the order *O2- > *OH > h+, whereas h+ and *OH were dominant reactive species for WO3-x material. To further provide evidence for the formation of *O2- and *OH, the NBT transformation and TAOH photoluminescence technique have been performed, and the result is displayed in Figure 8b,c. The absence of peak at 259 eV in the UV–vis absorption spectra of NBT transformation over LDH and WSAFL1 suggests that the formation of *O2- contradicts with WO3-x because the CB edge of LDH (0.08 V vs NHE) is extra negative than the oxygen reduction potential [E0 (O2/H2O, 0.046 eV vs NHE)]76 whereas the CB potential of WO3-x (0.7 V vs NHE) is more positive, so it could not produce *OH. Moreover, a less intense absorbance spectrum was observed for WSAFL1 and a larger percentage of NBT transformation occurred, resulting in the formation of maximum *O2- in WSAFL1 heterostructure. After the construction of ternary heterostructure (WSAFL1) with band coupling, the electrons move from higher CB of LDH to lower CB of WO3-x, resulting in more accumulation of electron on the CB of WO3-x but that electron could not react with O2 to generate *O2-. Therefore, the maximum proportion of electrons is supposed to reside at CB of LDH in WSAFL1 ternary heterostructure to produce more effective *O2- radicals. This fact evidences a Z-scheme charge transfer pathway between them. On the other hand, the increased TAOH photoluminescence spectra of WSAFL1 suggest that heterostructure material produced more fluorescent product (2-hydroxyterephthalic acid) revealing the generation of higher-concentration *OH radicals.

To ascertain the charge transfer mechanism, photocatalytic H2 evolution was also studied over as-fabricated LDH, WO3-x, WSL1, and WSAFL1 materials under visible light irradiation (λ ≥ 420) by using methanol as the electron supplier. As shown in Figure 9a, the neat WO3-x showed no H2 evolution due to its positive CB potential.25 However, pristine LDH showed 717 μmol H2 generation. Meanwhile, when WO3-x was coupled with LDH, it displayed enhanced H2 evolution (1002 μmol) compared to pure LDH. In addition, Ag NPs (5 wt %) deposited on the surface of WSL1 material and the ternary catalysts (ASWSFL1) exhibited obviously improved photoactivity toward H2 evolution (1103 μmol) compared to binary and parent materials signifying the co-catalytic function of Ag NPs. Furthermore, WSAFL1 displayed superior H2 evolution (1175 μmol) to ASWSFL1 material and also 1.6 and 1.2 times that of the pure LDH and WSL1 samples, respectively. It was previously reported that when noble-metal nanoparticles work as mediators on the interface of type II heterostructures, an interior direct pathway is produced that efficiently separates and transports the charge carrier. PL spectra also support the above fact. This photocactivity ascertains a Z-scheme photocatalytic mechanism between LDH, WO3-x, and Ag NPs. Actually, sacrificial agents play a decisive role in H2 evolution because they act as electron donors and consume the photogenerated holes during photocatalytic reaction. To study the effect of various sacrificial agents on the rate of H2 evolution, water reduction reactions were carried out under the same condition by using different scavengers (TEOA, methanol, lactic acid, and Na2S with Na2SO3) (Figure 9b). The rate of H2 evolution is mainly dependent on oxidation potential values of various sacrificial agents. However, along with oxidation potential, permittivity and chain length of organic sacrificial agents are also equally important. It has been found that methanol acts as the most suitable sacrificial agent among all. It should be noted that, by using 10% methanol solution as the sacrificial agent, H2 is produced according to the following reactions (eqs 8–10) of methanol conversion

CH3OH + h+ → HCHO + H2

HCHO + H2O + h+ → HCOOH + H2

HCOOH + h+ → CO2 + H2

Moreover, methanol was oxidized to CO2 and then transformed to CO. The existence of oxygen defects in WSAFL1 heterostructure greatly enhances the interaction between CO
and catalyst surface through the electron backdonation from the surface of W5+ to the \( \pi^* \) molecular orbital of CO.\textsuperscript{77,78,16}

Such remarkably improved photocatalytic performance toward TC degradation and H\(_2\) evolution over W5A5L1 was mainly ascribed to the intimate contact and synergetic effect between WO\(_3\)\(^-\)X, LDH, and Ag NPs with the suitable band edge potentials. The Ag NPs (act as the charge communication bridge) enhanced the separation and transfer efficiencies of photoinduced charge carriers at the W5L1 interface. The loading amounts of Ag NPs and WO\(_3\)\(^-\)X in composites play a remarkable role in their photocatalytic activity. Moreover, the lowest PL intensity, highest photocurrent density, and reduced EIS Nyquist arc also supported the superior photocatalytic performance in the case of W5A5L1 heterostructure.

Comparison studies of the photocatalytic H\(_2\) evolution and TC degradation activity over various LDH- and WO\(_3\)-based composites are tabulated (Tables 2 and 3).

Table 2. Values of H\(_2\) Evolution by Different LDH- and WO\(_3\)-Modified Nanocomposites

| photocatalyst                  | reaction condition (visible light source and sacrificial agents) | H\(_2\) evolution (\(\mu\)mol g\(^{-1}\) h\(^{-1}\)) | ref |
|-------------------------------|------------------------------------------------------------------|-----------------------------------------------|-----|
| CdSe/ZnCr LDH                 | 300 W Xe lamp (\(\lambda \geq 420\)), 0.1 M Na\(_2\)S and 0.1 M Na\(_2\)SO\(_3\) | 2196                                         | 79  |
| RGO/La\(_2\)Ti\(_3\)O\(_7\)/NiFe LDH | AM 1.5, 10 vol % TEOA                                           | 532                                          | 80  |
| g-C\(_3\)N\(_4\)/NiFe LDH      | 125 W Hg (\(\lambda \geq 420\)), 10 vol % methanol              | 3720                                         | 201 |
| CHLDH30                      | 125 W Hg (\(\lambda \geq 420\)), 10 vol % methanol              | 27875                                        | 22  |
| Au/CaFe\(_2\)O\(_4\)/CoAl LDH  | 150 W Xe (\(\lambda \geq 420\)), 10 vol % methanol              | 1179                                         | 82  |
| WO\(_3\)/g-C\(_3\)N\(_4\)       | 300 W Xe (\(\lambda \geq 420\)), 10 vol % TEOA                  | 3120                                         | 83  |
| WO\(_3\)/g-C\(_3\)N\(_4\)/Ni(OH)\(_x\) | 300 W Xe (\(\lambda \geq 400\)), 15 vol % TEOA                  | 576                                          | 84  |
| WASA1L (present research)     | 150 W Xe (\(\lambda \geq 420\)), 10 vol % methanol              | 29375                                        |     |

Table 3. Rate of TC Degradation by Different LDH- and WO\(_3\)-Modified Nanocomposites

| photocatalysts                  | reaction condition (visible light source, TC concentration, catalyst dosage and time period) | TC degradation efficiency (%) | ref |
|--------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------|-----|
| C\(_{0.33}\)W\(_3\)/Ni Al LDH   | 500 W Xe (\(\lambda \geq 420\)), 50 mL of 30 mg/L TC solution, 50 mg, 270 min                   | 92                            | 85  |
| WO\(_3\)/AgI                    | 300 W Xe (\(\lambda \geq 420\)), 40 mL of 35 mg/L TC solution, 40 mg, 60 min                   | 75                            | 6   |
| WO\(_3\)/Ag/g-C\(_3\)N\(_4\)     | XG500 W Xe (\(\lambda \geq 420\)), 300 mL of 10 mg/L TC solution, 100 mg, 40 min              | <95                           | 86  |
| Ag\(_3\)VO\(_4\)/WO\(_3\)       | 300 W Xe (\(\lambda \geq 420\)), 100 mL of 10 mg/L TC solution, 50 mg, 30 min                  | 71                            | 87  |
| NaTaO\(_3@WO_3\)               | 500 W Xe (\(\lambda \geq 420\)), 100 mL of 20 mg/L TC solution, 25 mg, 120 min                 | 69                            | 88  |
| WASA1L (present research)       | 250 W Xe (\(\lambda \geq 420\)), 20 mL of 40 mg/L TC solution, 20 mg, 90 min                  | 92                            |     |

Scheme 2. Schematic Illustration of the Proposed Reaction Mechanism in the (a) Ag/WO\(_3\)\(^-\)X/LDH Heterostructure and (b) WO\(_3\)\(^-\)X/Ag/LDH-Based Reaction Systems toward TC Degradation and H\(_2\) Evolution under Visible Light Irradiation

and catalyst surface through the electron backdonation from the surface of W\(_5^+\) to the \( \pi^* \) molecular orbital of CO.\textsuperscript{77,78,16}

Such remarkably improved photocatalytic performance toward TC degradation and H\(_2\) evolution over WASA1L was mainly ascribed to the intimate contact and synergetic effect between WO\(_3\)\(^-\)X, LDH, and Ag NPs with the suitable band edge potentials. The Ag NPs (act as the charge communication bridge) enhanced the separation and transfer efficiencies of photoinduced charge carriers at the WSL1 interface. The loading amounts of Ag NPs and WO\(_3\)\(^-\)X in composites play a remarkable role in their photocatalytic activity. Moreover, the lowest PL intensity, highest photocurrent density, and reduced EIS Nyquist arc also supported the superior photocatalytic performance in the case of WASA1L heterostructure. Comparison studies of the photocatalytic H\(_2\) evolution and TC degradation activity over various LDH- and WO\(_3\)-based composites are tabulated (Tables 2 and 3).

Compiling the results of two applications, a probable mechanistic pathway over heterostructure-based photocatalytic reaction has been proposed and is demonstrated in Scheme 2. In accordance with MS and Tauc plot, CB edge positions of LDH and WO\(_3\)\(^-\)X were found to be -0.08 and 0.7 V, respectively, and the corresponding VB potentials were calculated to be 2.42 and 3.2 V vs NHE scale. Considering the band alignments of LDH and WO\(_3\)\(^-\)X there may exist two typical ways for migration and separation of charge pairs, such as conventional type II heterojunction (double charge transfer) and Z-scheme-type mechanism, shown in Scheme 1a,b, respectively. Zeng et al. and Veldurthi et al. also predicted these two classes of charge transport mechanism over LaVO\(_4\)-Ag-BiVO\(_4\) and BiVO\(_4\)-Ag-CuO, respectively.\textsuperscript{1,7} In this regard, if
W5A5L1 belongs to conventional type II heterojunction (Scheme 2a), with illumination of visible light, LDH would consume the utmost radiation and get excited to generate electrons and hole. The journey of light-induced electrons will start from the CB of LDH to CB of WO$_3^{-x}$, revealing the decrease of electron reduction ability. To manage the electron neutrality, the holes jumped from more positive VB to less positive VB potential, as a result of which maximum holes are accumulated on the VB of LDH. This transport approach makes some donation to the spatial segregation of the photogenerated charge pairs, and the gathered electrons situated at the top of CB position of WO$_3^{-x}$ are not capable of reducing O$_2$ to *O$_2^-$ owing to the more positive CB potential than $E_0$ [(O$_2$/HO$_2^{-} = -0.046$ eV vs NHE )].$^{76}$ However, according to the scavenger experiments and NBT analysis results, the *O$_2^-$ radical was the predominant active species in TC photodegradation process and a high concentration of *O$_2^-$ moieties was generated in the case of W5A5L1 heterostructure than neat LDH. Moreover, due the positive CB potential of WO$_{3-x}$ (0.7 V vs NHE), the photoexcited electrons in the CB of WO$_{3-x}$ were also not able to reduce H$_2$O for producing H$_2$ gas. Nevertheless, the results of present photocatalytic performances toward TC degradation and H$_2$ evolution tests disagree with the traditional heterojunction mechanism. For that reason, the photocatalytic hydrogen evolution and *O$_2^-$ generation for TC degradation can only be possible through the Z-scheme mechanism. In addition, the interfacial charge migration of binary heterostructure was further promoted by incorporating metallic Ag NPs. The former metallic Ag NPs can consume a significant quantity of radiation from the visible light source due to its SPR phenomenon, which is helpful for enhancing absorption of visible light. Second, the function of Ag NPs as an electron transport via duct plays a significant role in the creation of Z-scheme charge conduction mechanism. After the irradiation of visible light to the W5A5L1 photocatalyst, both the LDH and WO$_{3-x}$ can be excited and generate photoinduced electrons and holes in the CB and VB positions, respectively. Then, weak reductive electrons in CB of WO$_{3-x}$ get transferred to metallic Ag through the Schottky barrier [owing to the CB potential of WO$_{3-x}$ (0.7 V vs NHE) and a relatively negative potential with respect to the Fermi level of metallic Ag (i.e., 0.8 eV)].$^{7}$ Simultaneously, the weak oxidative holes in VB of LDH move to metallic Ag as the VB of LDH (2.42 V vs NHE) is far positive in comparison to the Fermi level of metallic Ag.$^{26}$ Consequently, the energetic electrons with strong reducing ability get accumulated on the CB of LDH, which have the potential to stride above the energy barrier for reducing H$_2$O into H$_2$ gas and generation of *O$_2^-$ used for TC degradation. At the same time, the strong oxidizability photoinduced holes are gathered at the VB of WO$_{3-x}$ and funneled to be trapped by the scavenging reagent. In addition, the most positive VB potential of WO$_{3-x}$ than $E_0$ (OH$^-$/*OH = 1.99) was found suitable for production of *OH through reaction of H$_2$O with the powerful oxidized hole. According to the quenching experiment, *OH radical was one
of the active species for photocatalytic TC degradation. Therefore, the $^\cdot$OH radical reacts with TC and produces some oxidizing product. The detailed TC mechanism is illustrated by eqs 11–20. Hence, it can be said that the WSASL1 heterostructure clearly establishes a solid-state Z-scheme mechanism and supports the assurance for realizing this photocatalytic process. It should be noted that this kind of charge migration pathway can not only speed up the transfer and isolation tendency of photogenerated charge carriers but also maintain strong redox capacity for superior photocatalytic activities toward degradation of antibiotic as TC and H$_2$ evolution. Moreover, the large electroconductivity of the metallic Ag NPs enhances the quenching rate of the photoinduced electron–hole pairs consecutively at the interfacial phase, which suppresses the annihilation of charge carriers in LDH and WO$_3$–x and finally attains Z-scheme transfer pathway.

$$\text{LDH} + h\nu \rightarrow \text{LDH}(e_{\text{CB}}^- + h_{\text{VB}}^+)$$ (11)

$$\text{WO}_3$–x + h$\nu \rightarrow \text{WO}_3$–x( e$_{\text{CB}}^-$ + h$_{\text{VB}}^+$) (12)

$$\text{LDH}(h_{\text{VB}}^+) \rightleftharpoons \text{WO}_3$–x( e$_{\text{CB}}^-$) (13)

$$\text{LDH}(e_{\text{CB}}^-) + O_2 \rightarrow O_2^- + \text{LDH}$$ (14)

$$\text{LDH}(e_{\text{CB}}^-) + O_2^- + 2H^+ \rightarrow H_2O_2$$ (15)

$$H_2O_2 + \text{LDH}(e_{\text{CB}}^-) \rightarrow OH + OH^-$$ (16)

$$\text{OH} + \text{TC} \rightarrow \text{degraded product}$$ (17)

$$\text{LDH}(e_{\text{CB}}^-) + H_2O \rightarrow H_2 \text{ gas evolution}$$ (18)

$$\text{WO}_3$–x( h$_{\text{VB}}^+$) + OH$^-$ → OH + WO$_3$–x (19)

$$\text{OH} + \text{TC} \rightarrow \text{degraded product}$$ (20)

Recyclability and reusability of semiconducting materials are important in the field of photocatalytic application. In the present study, reusability properties of the prepared WSASL1 photocatalyst were reevaluated toward TC degradation and H$_2$ evolution for at least four cycle runs, as depicted in Figure 10a,b. After each reaction process, the photocatalysts were separated from the suspension by centrifugation, cleaned with distilled water, and then dried in an oven for further use. From Figure 10a, it was observed that TC degradation by the photocatalyst was found to be constant up to two consecutive cycles and thereafter slightly decreased in each photocatalytic run. The decrease in degradation rate can be related to the loss of photocatalyst during recovery process. A similar process was adapted to check the reusability and stability of the photocatalyst toward H$_2$ evolution. The figure describes that hydrogen evolution by the photocatalyst was found to be regular up to the third run and after that it decreases. So, it can be concluded that the photocatalyst is steady enough for repeated use. Moreover, to determine the structural and optical stabilities of the material, XRD and UV–vis DRS studies of the WSASL1 heterostructure were carried out after the fourth run of TC degradation. As seen in Figure 10c, the XRD plot of the used catalyst shows no considerable change in comparison to fresh catalyst, where only a little less intense peak was observed in the case of used WSASL1 photocatalyst. Moreover, as shown in Figure 10d, the absorbance peak intensity and visible light-harvesting capabilities were slightly reduced after four consecutive cycles of TC degradation under visible light illumination. The recycling experiment results exemplify that the WSASL1 ternary heterostructure could maintain brilliant photocatalytic performance even after four repetitive runs, which indicates its superior photostability and reusability for the management of antibiotic decomposition and H$_2$ evolution.

## CONCLUSIONS

In conclusion, unique oxygen-deficient Ag-deposited WO$_3$–x nanocapsules coupled with Zn/Cr LDH, a Z-scheme photocatalyst, were synthesized by the hydrothermal method, followed by photodeposition and in situ coprecipitation technique. The ternary heterostructure shows excellent visible light-driven H$_2$ evolution (29 °375 μmol g$^{-1}$ h$^{-1}$) and TC removal (92% in 90 min) with high stability. An interfacial internal electric field-induced direct Z-scheme charge transfer mechanism under visible light, in the presence of Ag as an electron mediator, strongly enhances the photocatalytic performance. The EIS, photocurrent response, and PL intensity results support efficient charge separation through Z-scheme with Ag NPs as an electron intermediary. Ag NPs at the solid–solid interface function as an electron conduction bridge and play an important work in the formation of Z-scheme charge transfer mechanism. This strategy by the introduction of oxygen vacancies of WO$_3$–x not only contributes to increase the adsorption of antibiotic on the surface of catalysts but also increases the lifetime of photoinduced charge carriers through Z-scheme mechanism on coupling with LDH. The results of this work open up a new avenue in designing Z-scheme photocatalytic system for challenging the desires of future energy and environmental issues.

## EXPERIMENTAL SECTION

**Materials.** Na$_2$WO$_4$·2H$_2$O, NaCl, HCl, AgNO$_3$, CH$_3$OH, Zn(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·6H$_2$O, NaOH, Na$_3$CO$_3$, tetracycline, EDTA, benzoquinone, isopropl alcohol, terephthalic acid, NBT, TEOA, lactic acid, Na$_2$S, and Na$_2$SO$_3$ were procured from Sigma-Aldrich and Merck. All chemicals used in the current research work were of pure analytical grade and directly used in the experimental method and analysis procedure.

**Preparation of WO$_3$–x.** The nanoparticle of WO$_3$ was synthesized by the hydrothermal procedure. Before hydrothermal treatment, 1 g of Na$_2$WO$_4$·2H$_2$O and 0.2 g of NaCl were dissolved in 30 mL of deionized water and the mixture solution was continuously stirred for 6 h. Then, the pH of the solution was adjusted to 2 by dropwise addition of concentrated HCl and the solution mixture was stirred for further 3 h. After completion of the stirring period, the solution mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After hydrothermal treatment, the as-obtained product was washed with double-distilled water and dried in a vacuum oven at room temperature. The product was further annealed at 350 °C for 2 h.

**Preparation of Binary WO$_3$–x/Ag Heterostructure.** A photodeposition procedure was followed to anchor metallic Ag nanoparticles (NPs) on the prepared WO$_3$–x. In a typical experiment, AgNO$_3$ and methanol as an electron acceptor were used for the deposition of noble-metal NPs. Initially, a known amount of WO$_3$–x powder (0.5 g) was dispersed in 30 mL of...
distilled water followed by the addition of 3.7 mL of AgNO₃ solution (10 g/L). Simultaneously, methanol (3 mL) was poured into the above solution. Photodeposition of metallic Ag upon WO₃-x surface was achieved by irradiating the entire suspension under visible light with continuous stirring for 3 h. A 250 W medium-pressure Hg lamp with a UV cutoff window (BS-02, Germany) equipped with a 250 mL of TC (40 ppm) along with 20 mg of catalyst was taken in analyzing the degradation of a colorless antibiotic like adsorption (420 nm). Before being exposed to light illumination to establish the irradiation chamber, the reaction mixture was magnetically stirred for 30 min. Then, the sample solution was irradiated in visible light for 30 min. After completion of reaction, the obtained precipitate was filtered and washed several times using distilled water to eliminate the additional dissolved ions. Finally, the product was dried at 80 °C in a vacuum oven. The nanocomposites were prepared by varying the weight ratio between WO₃ and ZnCr LDH, i.e., 1:1, 1:5, and 5:1, which are labeled as W1L1, W1L5, and W5L1, respectively. After evaluation of photocatalytic activity, the optimum weight ratio was obtained. Then, WAg (3%)L1 (W5A3L1), WAg (5%)L1 (W5A5L1), WAg (7%)L1 (W5A7L1), and WAg (9%)L1 (W5A9L1) were synthesized. Again the photocatalytic activities were tested for as-synthesized materials (W5A3L1, W5A5L1, W5A7L1, and W5A9L1), after which an optimum amount of Ag NPs was loaded on the surface WSL1 binary heterostructure to construct the ASWSL1 material for comparison study. Pure ZnCr LDH sample (LDH) was also prepared under the same circumstances without support of WO₃-x and WO₃-x/Ag.

**Preparation of Ternary WO₃ Ag/ZnCr LDH Heterostructure.** In situ coprecipitation process has been employed to prepare WO₃-x/ZnCr LDH or WO₃-x/Ag/ZnCr LDH heterostructure. In a typical experiment, a known amount of WO₃-x or WO₃-x/Ag was dispersed into 30 mL of double-distilled water. After well dispersion of WO₃-x or WO₃-x/Ag heterostructure, an aqueous solution of Zn(NO₃)₂·6H₂O (12 mM) and Cr(NO₃)₃·6H₂O (6 mM) with 2:1 molar ratio was slowly dropped to the above dispersed solution; the reaction was allowed to reach pH 7–8 controlled by slow addition of 1 M Na₂CO₃ and 1 M NaOH. The reaction system was stirred for 24 h. After completion of reaction, the obtained precipitate was filtered and washed several times using distilled water to eliminate the additional dissolved ions. Finally, the product was dried at 80 °C in a vacuum oven. The nanocomposites were prepared by varying the weight ratio between WO₃ and ZnCr LDH, i.e., 1:1, 1:5, and 5:1, which are labeled as W1L1, W1L5, and W5L1, respectively. After evaluation of photocatalytic activity, the optimum weight ratio was obtained. Then, WAg (3%)L1 (W5A3L1), WAg (5%)L1 (W5A5L1), WAg (7%)L1 (W5A7L1), and WAg (9%)L1 (W5A9L1) were synthesized. Again the photocatalytic activities were tested for as-synthesized materials (W5A3L1, W5A5L1, W5A7L1, and W5A9L1), after which an optimum amount of Ag NPs was loaded on the surface WSL1 binary heterostructure to construct the ASWSL1 material for comparison study. Pure ZnCr LDH sample (LDH) was also prepared under the same circumstances without support of WO₃-x and WO₃-x/Ag.

**Photocatalytic Experimental Procedure.** The photocatalytic capabilities of the prepared samples were evaluated by analyzing the degradation of a colorless antibiotic like tetracycline (TC) under visible light irradiation. In detail, 20 mL of TC (40 ppm) along with 20 mg of catalyst was taken in an irradiation chamber (BS-02, Germany) equipped with a 250 W medium-pressure Hg lamp with a UV cutoff filter (λ ≥ 420 nm). Before being exposed to light illumination to establish the adsorption-desorption equilibrium between catalyst and TC molecules, the above solution was stirred in the dark for 30 min. Then, the sample solution was irradiated in visible light for 60 min with steady-state stirring. Additionally, for an in-depth understanding of the TC degradation pathway, kinetics study was performed. During the photocatalytic reaction at 15 min interval of time, the remaining TC concentration present in the supernatant of each sample solution was measured by a UV–vis spectrophotometer at the characteristic absorption peak of 357 nm. A control experiment was performed following the same procedure without catalyst under visible light illumination. Moreover, trapping experiment was performed to determine the role of active species in photocatalytic antibiotic degradation, which is produced during the reaction process. Various scavenging agents like isopropyl alcohol (IPA), p-benzoquinone (BQ), and ethylene diaminetetraacetic acid disodium (EDTA) were used to trap relative species like hydroxyl (OH•), super oxide (O₂•−), and hole (h+), respectively. All scavengers (1 mM) were dispersed in the catalyst/TC mixture solution and exposed to visible light for 1 h. Furthermore, to confirm the generation of active species like O₂•− and OH• in the photocatalysis process, nitroblue tetrazolium (NBT, 5 × 10⁻⁵ mol L⁻¹) and terephthalic acid (TA, 5 × 10⁻⁴ M) in NaOH solution tests were conducted, respectively. These experiments were conducted by following the above-mentioned procedures. Here, instead of TC solution, NBT and TA solutions were used and irradiated by visible light for 30 min. Then, the concentrations of NBT (200–350 nm) and TA (at 330 nm of excitation wavelength) in the filtrate solutions were recorded by using a spectrophotometer and spectrophotometer, respectively. The intermediates formation during the TC degradation was analyzed by liquid chromatography–mass spectrometry (LC-MS) system (TSG Quantum Access MAX Triple Quadrupole Mass Spectrometer, Thermo Fisher Scientific). The photocatalytic TC degradation efficiency over all photocatalysts was estimated by the following expression (eq 20):

\[
\text{degradation efficiency(\%)} = \left(1 - \frac{C}{C_0}\right) \times 100
\]

where \(C_0\) is the initial concentration of the TC solution, and after the photocatalytic reaction, the TC concentration was denoted as \(C\).

Along with TC degradation, the photocatalytic performance of the as-prepared samples was also examined toward H₂ evolution under visible light illumination in a batch reactor at ambient temperature and vacuum pressure. In a typical experiment, 0.02 g of catalyst was dispersed in 20 mL of 10 % CH₃OH aqueous solution as a hole quencher and the suspension was magnetically stirred to avoid the particle settlement at reactor bottom. Before the light illumination, N₂ gas was purged for 30 min to remove all dissolved gases from the suspension and to create inert condition for the reaction process. For visible light source, a 150 W xenon arc lamp was used. The UV region present in the light was discarded by using 1 M NaNO₂ solution as a UV filter (λ ≥ 420 nm). The produced gas was collected by downward displacement technique and analyzed by a gas chromatograph (GC-17A) equipped with a 5 Å molecular sieves column and a thermal conductivity detector (TCD). The experiments were repeated thrice and then the mean value was calculated for consideration. The apparent conversion efficiency for photocatalytic H₂ evolution (1175 μmol/2h) was calculated to be 9.41% by using the following formula (eq 21).

\[
\text{apparent conversion efficiency} = \frac{\text{stored chemical energy}}{\text{incident light intensity}} \times 100
\]
Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to determine the internal morphology and microstructures of the samples. Both TEM and HRTEM were executed by Philips TECNAI G2 instrument with a high voltage of 200 kV. Similarly, the surface morphology and topology of the samples were measured by scanning electron microscopy (SEM) using Hitachi S-3400N with a low voltage of 5 kV. The presence of functional groups within the photocatalysts was confirmed by using JASCO FTIR-4600 spectrometer with KBr pellet as a reference sample. To investigate the Raman polarization spectra, a Renishaw InVia Raman spectrometer was used. More information about elemental environment, oxidation states, and elemental composition were confirmed by XPS measurements taken by a Kartos Axis Ultra X-ray photoelectron spectrometer consisting of charge neutralizer and Al Kα monochromatized X-ray source. The 1s peak of carbon atom was considered for reference peak. The optical properties of the as-synthesized photocatalysts were evaluated by a UV–vis JASCO 750 instrument using BaSO₄ as reference. A JASCO-FP-8300 fluorescence spectrometer was used to investigate the photoluminescence characteristics. All of the photoelectrochemical characterizations were performed by IVIUMnSTAT electrochemical workstation equipped with a 300 W xenon lamp as a visible light source. The electrochemical workstation consists of a conventional Pyrex electrochemical cell having a three-electrode system such as reference electrode (Ag/AgCl electrode), counter electrode (Pt electrode), and working electrode [prepared using fluorine-doped tin oxide (FTO) by electrophoresis deposition (Pt electrode)], and working electrode [prepared using fluorine-doped tin oxide (FTO) by electrophoresis deposition method]. Na₂SO₄ (0.1 M, pH = 6.8) electrolyte solution was used for measuring the electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) plots and transient photocurrent response, whereas to study the Mott–Schottky (MS) plot, 0.5 M Na₂SO₄ (pH = 7.2) solution was adopted as electrolyte. The EIS analysis was executed from frequency of 10⁶ to 10¹ Hz with applying 0 biases under visible light irradiation at open-circuit potential. By applying the potential from 0 to 1.5 V with a scan rate of 10 mV/s, the LSV plots were performed and 0.2 V was implemented for measuring the transient photocurrent response under visible light irradiation. The MS plot was measured at a frequency of 500 Hz.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01146.

EDS pattern of WSASL1; high-resolution deconvoluted XPS images of LDH; Tauc and MS plots of LDH and WO₃; transient photocurrent response of photocatalyst; TC degradation; LC-MS data of WSASL1; TOC removal percentage of TC over WSASL1; k₅⁺ and t₁/₂ values of as-prepared catalysts; photocatalytic degradation of TC with different pH values; PZC plot of WSASL1; and molecular structure of TC (PDF)

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**Notes**

The authors declare no competing financial interest.

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