Enhanced Photocatalytic Hydrogen Evolution from Water Splitting on Ta$_2$O$_5$/SrZrO$_3$ Heterostructures Decorated with Cu$_x$O/RuO$_2$ Cocatalysts

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ABSTRACT: Photocatalytic H$_2$ generation by water splitting is a promising alternative for producing renewable fuels. This work synthesized a new type of Ta$_2$O$_5$/SrZrO$_3$ heterostructure with Ru and Cu (RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$) using solid-state chemistry methods to achieve a high H$_2$ production of 5164 μmol g$^{-1}$ h$^{-1}$ under simulated solar light, 39 times higher than that produced using SrZrO$_3$. The heterostructure performance is compared with other Ta$_2$O$_5$/SrZrO$_3$ heterostructures compositions loaded with RuO$_2$, Cu$_x$O, or Pt. Cu$_x$O is used to showcase the usage of less costly cocatalysts to produce H$_2$. The photocatalytic activity toward H$_2$ by the RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure remains the highest, followed by RuO$_2$/Ta$_2$O$_5$/SrZrO$_3$ > Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ > Pt/Ta$_2$O$_5$/SrZrO$_3$ > Ta$_2$O$_5$/SrZrO$_3$ > SrZrO$_3$. Band gap tunability and high optical absorbance in the visible region are more prominent for the heterostructures containing cocatalysts (RuO$_2$ or Cu$_x$O) and are even higher for the binary catalyst (RuO$_2$/Cu$_x$O). The presence of the binary catalyst is observed to impact the charge carrier transport in Ta$_2$O$_5$/SrZrO$_3$, improving the solar to hydrogen conversion efficiency. The results represent a valuable contribution to the design of SrZrO$_3$-based heterostructures for photocatalytic H$_2$ production by solar water splitting.

KEYWORDS: oxide heterostructure, photocatalyst, hydrogen evolution, band alignment, SrZrO$_3$.

1. INTRODUCTION

ABO$_3$ is an inorganic perovskite with a mixed metal oxide composition, where the A-element is an alkaline (earth) or a lanthanide, and the B-element is a transition metal. An example of ABO$_3$ is zirconate (AZrO$_3$)$_x$), known for its ferroelectric, piezoelectric, and photocatalytic properties.\(^1\)\(^2\) In photocatalysis, the H$_2$ production efficiency of AZrO$_3$ remains low due to its limited visible light absorption (E$_g$ > 4 eV) and poor carrier generation.\(^3\)\(^4\) Strategies to stimulate photocarrier generation as a means to improve H$_2$ water splitting under visible light are key for AZrO$_3$. A way forward is producing a semiconductor via cation replacement (A = Ba, Ca, Sr) in AZrO$_3$, followed by band alignment interfacing AZrO$_3$ with another semiconductor to form a heterostructure.\(^5\)\(^6\) First, cation replacement can be done by introducing Sr into AZrO$_3$ to form SrZrO$_3$, which has an orthorhombic crystal structure with a Pbnm space group.\(^10\)\(^11\) SrZrO$_3$ is an indirect band gap semiconductor. The valence band (VB) lies lower than the water oxidation potential, while the conduction band (CB) is located higher than the hydrogen reduction potential.\(^12\)

Photogenerated carriers through VB and CB can recombine, reaching the SrZrO$_3$ surface and induce the chemical transformation of 2H$_2$O into 2H$_2$ and O$_2$. However, due to its wide band gap (E$_g$ ~ 4 eV),\(^8\) SrZrO$_3$ requires UV light to photogenerate enough carriers to produce 50 μmol g$^{-1}$ h$^{-1}$.\(^6\) The H$_2$ production can be improved to reach 5310 μmol g$^{-1}$ h$^{-1}$ using UV light and electron donor species, such as Na$_2$S and Na$_2$SO$_3$.\(^7\) Although the addition of electron donor species is an option, the main challenge remains with the photocatalyst. An ideal catalyst should effectively promote charge transport and retain similar H$_2$ water-splitting performances under visible light.

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The heterostructure concept involves band alignment, which can be used to modulate charge transport. This can be done by incorporating Ta compounds, such as Ta$_2$O$_5$, and other tantalates, recognized as active photocatalysts for H$_2$ water splitting. The band gap structure in tantalum oxide consists of O 2p orbitals formed by the VB and the CB, with a d$^0$ electronic configuration that provides electron mobility access. Depending on the synthetic approach, the addition of Ta can lead to doping via SrZrO$_3$ substitution or yield Ta$_2$O$_5$, especially when treated at high temperatures. Notably, both Ta-substitution and Ta segregation can promote mobility access in photocatalysts. However, H$_2$ water splitting in tantalates has been mainly promoted with UV irradiation. From this aspect, the next desired step for Ta-containing SrZrO$_3$ catalysts is to retain charge transport properties under visible light.

Coupling a narrow band gap to a wide band gap semiconductor enhances light absorption in the visible spectrum. In essence, this entails band gap tunability via band alignment to reduce the recombination of photogenerated charges. Copper oxide can function as a narrow band gap p-type semiconductor (Cu$_2$O), or both, especially when Cu$_2$O and CuO species are combined (hereafter, Cu$_2$O). It could then be expected to improve the exchange of photocarriers when interfaced with wide-band semiconductors enabling high catalytic activity. Furthermore, interfacing Cu$_2$O with an oxide-based hydrogen evolution catalyst, such as RuO$_2$, is an attractive option to improve H$_2$ production during water splitting. The combination of Cu$_2$O and RuO$_2$ has been successfully applied in photocatalysts and is now proposed to improve the photocatalytic activity of Ta-containing SrZrO$_3$.

This work synthesized a novel SrZrO$_3$ heterostructure of mixed oxides (RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$) via solid-state chemistry. The functionality of the heterostructure is benchmarked during water splitting, achieving 5164 μmol g$^{-1}$ h$^{-1}$ of H$_2$. The photocatalytic performance of the heterostructure is compared with that of Ta$_2$O$_5$/SrZrO$_3$ loaded with RuO$_2$, Cu$_2$O, or RuO$_2$/Cu$_2$O to understand the role of each heterostructure component. The RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure is also compared with Pt, a more costly catalyst than Ru or Cu.

2. MATERIALS AND METHODS

2.1. Synthesis of Ta$_2$O$_5$/SrZrO$_3$ Photocatalysts. SrCO$_3$ (99%, Sigma-Aldrich 472018), ZrO$_2$ (99%, Merck 230693), and Ta$_2$O$_5$ (99%, Sigma-Aldrich 303518) were ground in an agate mortar for 10 min, adding 0.1 mL of acetone as a dispersant. Ta$_2$O$_5$ amounts added were 0.8, 1.6, 2.4, 3, and 3.9 wt %. The homogenized mixture was placed in a platinum crucible and then thermally treated for 12 h at 1100 °C in air, with a 3 °C/min$^{-1}$ heating rate.

2.2. RuO$_2$, Cu$_2$O, and Pt Cocatalyst Deposition. RuCl$_3$ (Sigma-Aldrich 208523), CuCl$_2$ (Sigma-Aldrich 222011), and H$_2$PtCl$_6$ (Sigma-Aldrich 520896) were impregnated into the Ta$_2$O$_5$/SrZrO$_3$ photocatalysts. The final weight percentages were 0, 0.13, 0.5, 1.0, 1.3, and 1.5 wt %. The samples were kept in solution at 80 °C for 4 h under constant stirring. The samples were dried at 80 °C. The obtained powders were annealed in an air atmosphere at 400 °C for 2 h. For Pt deposition, H$_2$PtCl$_6$ was added to a Ta$_2$O$_5$/SrZrO$_3$ suspension in propanol. The powder was centrifuged and also dried at 80 °C for 4 h.

2.3. TEM, Energy-Dispersive X-ray Spectrometry, and EELS. Scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectrometry (EDXS), and EELS were carried out using a Cs-corrected microscope JEOL ARM 200CF equipped with an JEOL SSD EDX spectrometer and a Gatan Dual EELS Quantum spectrometer-imaging filter. The operational voltage was 200 kV. The photocatalyst powders were dispersed in ethanol and were deposited over different carbon-coated Au, Cu, and Ni grids before the inspection.

2.4. X-ray Diffraction. The structural characterization was performed with X-ray diffraction (XRD) in a θ–2θ arrangement, employing a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA with CuKα radiation (λ = 1.5406 Å), from 10 to 70 °(2θ).

2.5. Chemical Analysis by XPS. For the X-ray photoelectron spectroscopy (XPS) measurements, a Quantera SXM (Physical Electronics) was used. The X-rays were Al Kα, monochromatic at 1486.6 eV with a beam size of 200 μm. The binding energies were corrected according to the C 1s peak (284.8 eV). Samples were located on millimetric-sized indium cups, forming a pellet for sample homogeneity. In every sample, three different areas were probed with an area size of 600 × 300 μm$^2$.

2.6. Optical Characterization. The optical properties were analyzed using a UV–vis-NIR spectrophotometer (Cary 5000) in the diffuse reflectance mode. The band gap was calculated with the Tauc method, which involves plotting (αhν)$^{1/2}$ versus (hν). The value of the exponent n denotes the nature of the sample transition, the value is 2, considering indirect allowed transitions. A linear region was used to extrapolate to the X-axis intercept to find the band gap values. Photoluminescence spectra were collected in an Agilent Cary Eclipse spectrophotometer using a 254 nm excitation. Prior to UV–vis-NIR or PL, the samples were sieved and pelletized.

2.7. Photocatalytic Characterization. The photocatalytic measurements were carried out in a three-electrode quartz cell connected to a potentiostat from AUTOLAB. Pt was used as a counter electrode and Ag/AgCl (3 M KCl) as a reference electrode. The working electrode was fabricated by depositing the photocatalyst over an ITO substrate. For this process, 2 mg/mL of the photocatalyst suspension in ethanol was deposited using a spin coater at 2000 rpm. The samples were dried at 80 °C for 10 min. Once dried, the samples are immersed in 0.5 M Na$_2$SO$_4$ and used as an electrolyte. Electrochemical impedance spectroscopy (EIS) measurements for obtaining Mott Schottky plots were performed under dark conditions in a potential range of 0.8 to −0.8 V vs. Ag/AgCl at a frequency of 100 kHz–100 MHz and an AC perturbation of 10 mV.
The potential versus Ag/AgCl, $E_{Ag/AgCl}$, was converted to reversible hydrogen electrode potential, $E_{H2E}$, using the Nernst equation. For the photocurrent response experiment, a constant potential of 0.3 V vs. Ag/AgCl is applied. The electrode was illuminated with a solar simulator (Xe lamp 100 mW/cm$^2$) for 300 s, and the photocurrent was obtained considering the electrode area (1 cm$^2$).

### 2.8. Photocatalytic H$_2$ Evolution

The photocatalytic experiments were performed in a Pyrex reactor of 250 mL. In a typical experiment, 0.1 g of the photocatalyst was dispersed in 200 mL of deionized water. Before each experiment, the reactor was purged with $N_2$ for 30 min and irradiated with a wide range UV–vis xenon lamp (simulated solar light). The photocatalyst was stimulated with irradiation between 400 and 900 nm at 100 mW/cm$^2$ in demineralized water. The oxygen and hydrogen products were analyzed using a gas chromatograph (Thermo Scientific) coupled with a thermal conductivity detector. No buffer or electrolyzer was added during the reaction, and the starting pH was 7. No external potential was applied during photocatalytic experiments.

The solar to hydrogen conversion efficiency (STH) was estimated from eq 1:

$$\text{%STH} = \left( \frac{\text{mmol} \text{ H}_2 \text{/s}}{\text{P}_{\text{total}} \text{ (mW/cm}^2\text{)}} \times \Delta \text{Area (cm}^2\text{)} \right) \times 100$$

The quantum efficiency (QE) was calculated with eq 2:

$$\text{QE} = \frac{2N_{H_2}}{N_{hv}} \times 100$$

#### 2.9. Computational Methods

Periodic DFT calculations using the projected augmented wave (PAW) formalism were performed with the Vienna Ab Initio Simulation Package (VASP). The revised Perdew–Burke–Ernzerhof for solids (PBEsol) were selected for cell-optimization as it reduces PBE’s tendency to overestimate unit cell parameters. The one-electron Kohn–Sham orbitals were expanded on a plane-wave basis with a kinetic energy cutoff for the plane waves of 800 eV (PBEsol calculations). PAW potentials were employed to describe the interaction between the valence electrons and the core electrons. Reciprocal space integration over the Brillouin zone was approximated with finite sampling using Monkhorst–Pack k-point grids of $7 \times 7 \times 7$. The bulk unit cell of SrZrO$_3$ was optimized until the largest force on all atomic coordinates became smaller than 0.01 eV/Å. Furthermore, the convergence criterion for the self-consistent electric field (SCF) problem was set to $10^{-6}$ eV for all optimizations, and the symmetry group was preserved throughout all simulations. The unit cell volume was kept fixed at different cell volumes, followed by a constant volume cell optimization to verify the strain effect on the band gap. The unit cell of both structures was scaled proportionally to investigate the strain effect on the band gap. The unit cell volume was kept fixed at different cell volumes, followed by a constant volume cell optimization to verify the strain effect on the band gap. The unit cell of both structures was scaled proportionally to investigate the strain effect on the band gap.

### 3. RESULTS AND DISCUSSION

A SrZrO$_3$ heterostructure of mixed oxides (RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$) synthesized via solid-state chemistry has been produced. The synergy between the RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure components is investigated structurally, chemically, and optically. The application of the RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure is assessed during photocatalytic water splitting and contrasted with other SrZrO$_3$ compositions to select the most suitable heterostructure that yields the highest H$_2$ efficiency. The results are then correlated to the charge transport in RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$. Finally, a mechanism is proposed to shed light on charge transfer in the RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure.

#### 3.1. RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ Heterostructure Synthesis

##### 3.1.1. Structural Analysis of the RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ Heterostructure

STEM and EDXS analyses are assessed to unveil the morphology of the heterostructure components. First, the characterization of SrZrO$_3$ is examined (Figure 1), followed by a discussion on the higher-order heterostructures, such as RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ (Figure 2). In Figure 1a, the morphology of SrZrO$_3$ consists of agglomerated particles of ten to hundreds of nanometer sizes with a uniform distribution of chemical elements Sr, Zr, and O. The crystal structure of SrZrO$_3$ is visualized along the [1 0 0] zone axis in Figure 1bc that corresponds to the perovskite orthorhombic phase. An atomic model of the SrZrO$_3$ structure is depicted in Figure 1d. The identification and orientation of the crystal lattice planes are extracted from the fast Fourier transform (FFT) shown in Figure 1e.

In Figure 2a, the STEM-EDXS maps of 0.1%RuO$_2$/1%Cu$_2$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure show the distribution of Sr, Zr, and O, corresponding to the SrZrO$_3$ nanocrystallite formation. The Ru EDXS signal map indicated the growth of nanorods characterized in detail in Figures S1 and S2. The composition of the nanorods is RuO$_2$ (Figures S1 and S2), and they are distributed at various locations over the heterostructure, ranging in size from 10 to 30 nm in width and 100 to 200 nm in length. In the case of Cu, the overlapping signals of Cu Ka 8.04 with Ta L$_\alpha$ 8.140 and Hf L$_\alpha$ 7.898 present as an impurity from the synthesis precursor turned the EDXS mapping problematic for small quantities. However, when the amount of Cu is significant, it is possible to detect Cu among the SrZrO$_3$ nanocrystallites (see Figure S3). The Cu morphology is found not as distinctive as the RuO$_2$ nanorods but rather in the form of agglomerates, in a mixture state of CuO and Cu$_2$O according to EELS observations (Figure S3d).

The distribution of Ta is observed in various parts of the SrZrO$_3$ nanocrystallites: (i) dispersed over the SrZrO$_3$ nanocrystallites and (ii) accumulated in selected regions (Figures 2a and S4). A closer look at RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$ revealed that Ta segregated between the grains, as seen in the HAADF image in Figure 2b (see also Figure S4b). This can be distinguished by the higher contrast observed at the grain boundaries, corresponding to an accumulation of Ta (a higher Z = 73 element compared to Sr = 38 and Zr = 40). A similar observation in Figure 2c revealed Ta at the surface of the SrZrO$_3$ nanocrystallites (see also Figure S4d). To verify our hypothesis (and discard the presence of Hf Z = 72), EDXS and EELS are carried out in these distinct regions (Figure S4). The Ta O$_{2.3}$ edge was detected when collecting the EELS signal from the high contrast region in the HAADF image (Figure S4d); likewise, by performing EDXS in a similar area, the presence of the Ta L$_\alpha$ 8.140 peak was observed in the spectra (as shown Figure S4c). This detailed examination revealed that when Ta accumulates preferentially more in some grains than in others, it segregates at the grain boundaries and decorates the nanocrystallite surface. In addition, Ta is found forming clusters around the crystallites as seen in Figure 2d and confirmed by the Ta O$_{2.3}$ edge in the EELS signal in Figure 2e.
3.1.2. Chemical Species at the Surface of the RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ Heterostructure.

The elemental compositions and chemical environments of RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ and comparative and control samples are investigated with XPS. Figure 3 shows the XPS spectra of (a1−d1) Sr 3d, (a2−d2) Zr 3d, (a3−d3) Ta 4d, and (a4−d4) O 1s. The analyzed samples are displayed per row. In this case, (a1−a4) SrZrO$_3$, (b1−b4) 3%Ta$_2$O$_5$/SrZrO$_3$, (c1−c4) 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$, and (d1−d4) 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$. Irrespective of the sample structure, the Sr 3d and Zr 3d core level XPS spectra show almost superimposable envelopes. The position of the Sr 3d$_{5/2}$, Sr 3d$_{3/2}$, Zr 3d$_{5/2}$, and Zr 3d$_{3/2}$ components located at 132.9, 134.7, 181.2, and 183.6 eV, respectively, indicate Sr$^{2+}$ and Zr$^{4+}$ in a SrZrO$_3$ environment (Table S1).$^{7,38}$ The specific area ratios (2/3) and spin−orbit splitting values for Sr 3d (1.8 eV) and Zr 3d (2.4 eV) suggest no secondary phase. For Ta 4d (a3−d3), unsurprisingly, the pure SrZrO$_3$ sample (a3) shows no Ta presence. The Ta 4d envelopes of the three other samples are identical and show two main contributions at 229.2 eV (Ta 4d$_{5/2}$) and 241.6 eV (Ta 4d$_{3/2}$) assigned to Ta$^{5+}$ in Ta$_2$O$_5$.$^{39−41}$ A less-resolved contribution is also observed at lower binding energies (ca. 224.3 eV) and is attributed to Ta 4d$_{5/2}$ of hydrated Ta species. Finally, the O 1s core-level XPS spectra (a4−d4) display broad envelopes that can be fitted with three components. The first contribution at lower binding energies, ca. 529.2 eV, is assigned to O$^{2−}$ in metal oxides (i.e., SrZrO$_3$, Cu$_x$O, and RuO$_2$). The contribution at 531.2 eV is
attributed to oxygen adsorbed in SrZrO$_3$, while the contribution at the highest binding energies, ca. 532.6 eV, could be associated with O−H. It can be concluded that there is no significant difference in the chemical environments of Sr, Zr, Ta, and O species for SrZrO$_3$, 3%Ta$_2$O$_5$/SrZrO$_3$, 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$, and 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$.

The Cu 2p and Ru 3p core-level XPS spectra of the heterostructure samples containing Cu and Ru, that is, 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ (Figure 4a1,a2) and 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ (Figure 4b1,b2), are presented in Figure 4. Although the spectra have a low signal-to-noise ratio, the Cu 2p and Ru 3p peaks still provide valuable information. It should be noted that Ru 3d is not reported due to the elemental overlap with C, as observed in Figure S5. In Figures 4a1,b1, two contributions in the form of 932.7 and 934.2 eV peaks assigned to Cu$_2$O and CuO are observed. In this set of samples, the additional contribution at 942.4 eV is assigned to Cu 2p$_{3/2}$ satellites. The coexistence of the Cu$^+$ and Cu$^{2+}$ oxidation states is corroborated by the Cu LMM spectrum (Figure S5). The presence of the Cu$_2$O and CuO phases is observed even after the water-splitting reaction (Figure S5). The presence of Cu$^+$ and Cu$^{2+}$ also agrees with EELS measurement (Figure S3). XPS confirms the presence of Ru in the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure (Figure 4b2). The binding energy of Ru 3p$_{3/2}$ of ca. 463.0 eV agrees with the presence of Ru$^{4+}$ in RuO$_2$ (Table S1). The chemical information, elemental composition, and chemical environments are summarized in Tables 1 and S1. The chemical environment of Sr and Zr and the Sr/Zr ratio are notably constant for all the studied heterostructures and unaltered even after the photocatalytic test (Figure S5 and Table S1). However, a small reduction in Ta, Cu, and Ru is found after the photocatalytic water splitting for the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure (Table 1).

3.1.3. Optical Properties of the RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ Heterostructure Components. The light absorption and charge photogeneration properties of the heterostructure components are shown in Figure 5. Figures 5a,b displays the UV−vis and photoluminescence spectra for various Ta$_2$O$_5$
loadings. The inset in Figure 5a shows the Tauc plots estimated from the UV−vis spectra. Band gap for Ta$_2$O$_5$/SrZrO$_3$ has been found between 3.85 and 4 eV. A redshift to lower energies is observed for the highest Ta$_2$O$_5$-loaded samples. A reduction in the absorption band near a wavelength (λ) of 250 nm is seen in the UV−vis spectrum for 3 wt % Ta$_2$O$_5$, probably due to the participation of Ta 5d orbitals affecting the CB. It should be mentioned that such an effect can promote charge separation, resulting in a significant benefit for a photocatalytic process. The results are in good agreement with photoluminescent (PL) measurements in Figure 5b, indicating a reduction in charge recombination for 3%Ta$_2$O$_5$/SrZrO$_3$.

Light absorption in the visible range increases with Cu$_x$O and RuO$_2$ in 3%Ta$_2$O$_5$/SrZrO$_3$ (Figure 5c). The results show a considerable increase in light absorption for the 0.1%RuO$_2$/1% Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure, which is more significant than those for 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ and 1% RuO$_2$/3%Ta$_2$O$_5$/SrZrO$_3$. Therefore, it can be argued that the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure reduces further charge recombination, as shown in Figure 5d. The results in Figure 5d suggest that by controlling RuO$_2$/Cu$_x$O ratios, visible light absorption can be optimized to maintain the photocatalytic rate high.

It should be noted that in Figure 5d, the PL spectrum of 3%Ta$_2$O$_5$/SrZrO$_3$ overlaps with the 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ spectrum. Both spectra are also comparable to that of 1%RuO$_2$/3%Ta$_2$O$_5$/SrZrO$_3$.

3.1.4. Structural Characterization. Structural characterization with XRD for Ta$_2$O$_5$/SrZrO$_3$ and RuO$_2$/Cu$_x$O/Ta$_2$O$_5$/SrZrO$_3$ heterostructure are assessed to understand how Ta$_2$O$_5$ and RuO$_2$/Cu$_x$O loadings affect the optical properties as shown in Figure 5. The synthesized SrZrO$_3$ exhibits a highly crystalline pattern (Figure 6a1) and corresponds to the orthorhombic phase (JCPDS/ 44−0161). The other SrZrO$_3$ samples with various Ta$_2$O$_5$ loadings in Figure 6a2−a4 retain the SrZrO$_3$ phase. No distinct Ta$_2$O$_5$ peaks have been identified. Interestingly, from the diffractogram in Figure 6b, a peak shift from 30.75 to 30.90° in 2θ is observed. A slight shift to higher 2θ theta values is pronounced for large Ta$_2$O$_5$ loadings in Figure 6b2−b4. The shift has been suggested to be

Figure 4. XPS spectra of Cu 2p and Ru 3p in Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ (a1−a2) and in 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ (b1−b2).

Table 1. Sr/Zr Ratio and Elemental Composition of Different SrZrO$_3$-Based Catalysts, Including the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ Heterostructure

| sample                        | Sr/Zr (at. %) | Ta (at. %) | Cu (at. %) | Ru (at. %) |
|-------------------------------|---------------|------------|------------|------------|
| SrZrO$_3$                     | 1.11          | (at. %)    | (at. %)    | (at. %)    |
| 3%Ta$_2$O$_5$/SrZrO$_3$       | 1.35          | 1.1        |            |            |
| 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ | 1.48         | 1.0        | 0.35       |            |
| 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ | 1.31       | 1.5        | 0.37       | 0.4        |
| 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$* | 1.27           | 0.6        | 0.2        | 0.2        |

*Values reported in atomic percent (at.%). (*) at. % after photocatalytic water splitting.
a substitution effect from Ta\textsuperscript{5+} (0.64 Å) and Zr\textsuperscript{4+} (0.72 Å) in the crystalline structure of SrZrO\textsubscript{3}, distorting the lattice.

From the XRD results of Ta\textsubscript{2}O\textsubscript{5}/SrZrO\textsubscript{3}, a reduction in the cell volume is found. The results are in agreement with band gap changes to higher energy in Figure 5a. Our attributions are supported by density functional theory in Figure 7, in which the band gap is studied as a function of the unit cell volume. In this case, the unit cell of both the Pnma and Pnmb SrZrO\textsubscript{3} (Figure 5).

Figure 5. (a) UV–vis diffuse reflectance spectra and Tauc plots (inset). (b) Photoluminescence spectra for various Ta\textsubscript{2}O\textsubscript{5} loadings from (a). (c) UV–vis diffuse reflectance spectra and Tauc plots (inset) for various heterostructure constructions. (d) Photoluminescence spectra of the synthesized heterostructures from (c).

Figure 6. (a) XRD patterns of (1) SrZrO\textsubscript{3} and SrZrO\textsubscript{3} with various Ta\textsubscript{2}O\textsubscript{5} loadings, i.e., (2) 0.8%, (3) 1.6%, and (4) 3%. The 0.1%RuO\textsubscript{2}/1%Cu\textsubscript{x}O/3%Ta\textsubscript{2}O\textsubscript{5}/SrZrO\textsubscript{3} heterostructure is presented in (5). (b) Enlarged region of XRD patterns between 2θ = 30–32°.

a substitution effect from Ta\textsuperscript{5+} (0.64 Å) and Zr\textsuperscript{4+} (0.72 Å) in the crystalline structure of SrZrO\textsubscript{3}, distorting the lattice.

From the XRD results of Ta\textsubscript{2}O\textsubscript{5}/SrZrO\textsubscript{3}, a reduction in the cell volume is found. The results are in agreement with band gap changes to higher energy in Figure 5a. Our attributions are supported by density functional theory in Figure 7, in which the band gap is studied as a function of the unit cell volume. In this case, the unit cell of both the Pnma and Pnmb SrZrO\textsubscript{3}.
structures are scaled proportionally to investigate the effect of strain on the band gap. Via subsequent constant volume optimization at PBEsol, it is possible to verify the strain effect on the band gap. At the PBEsol level of theory, the band gap for both SrZrO₃ structures increases when applying compressive strain and decreases with tensile strain. Furthermore, a rigorous evaluation of the band gap using the hybrid functional of Heyd–Scuseria–Ernzerhof (HSE06) is employed. It has been found that the HSE06 functional is superior in localizing valence electrons of transition metals (e.g., those in Cu 3d orbitals) more correctly than (semi)local density functionals. An experimental band gap close to 5.6 eV for single SrZrO₃ crystals is typical, and HSE06 predicts theoretical band gaps of about ~5.0 eV, which is in line with the HSE06-calculated band gaps of 5.09 eV (Pnma) and 5.11 eV (Pmnb) in Figure 7. For all unit cell volumes, it is clear that the HSE06 calculated band gaps are higher than those obtained from PBEsol. However, the trend remains the same. The results suggest that strain effects may originate from the presence of Ta₂O₅ after the synthesis procedure. Ta in SrZrO₃ induces compressive strain on the lattice, leading to lower unit cell volumes. Computationally, it has been found that compressive strain increases the band gap, while tensile strain leads to lower band gaps, as in low-loaded SrZrO₃ (Figure 5a). The effect is primarily due to (i) Zr²⁺ substitution by Ta⁵⁺ or (ii) strain effects on SrZrO₃ caused by segregated Ta₂O₅, both leading to a broader band gap.

In the case of 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure, the presence of RuO₂, CuO, or their combination RuO₂/CuO leads to broader photosorption over a larger part of the visible spectrum (Figure 5c). The rationale behind this is that these oxides have lower band gaps compared to Ta₂O₅/SrZrO₃ (Figure 5a). The measured UV–vis diffuse reflectance spectra (Figure 5c) of the RuO₂/CuO bi-catalyst in 3%Ta₂O₅/SrZrO₃ help to extend the heterostructure absorption edge into the visible range. A small shift is found for the 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure in Figure 6b (2θ = 30.80), particularly when compared to 3%Ta₂O₅/SrZrO₃ in Figure 6b. The results indicate that 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ has a smaller reduction in the cell volume than 3%Ta₂O₅/SrZrO₃. This 2θ shift agrees with the estimated band gap of 3.6 eV of the 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure in Figure 5c. Although there is a band gap difference of 0.4 eV between heterostructures with or without a bicatalyst, the role of Ta is imminent, either substituting Zr⁴⁺ or compressive strain in the SrZrO₃ lattice (Figure 7). It should be mentioned that no peak characteristics of RuO₂, CuO, or Cu₂O have been found in the XRD pattern, possibly due to the low cocatalyst amounts used (lower than 5%).

In short, a detailed analysis of the heterostructure components and the effect of Ta₂O₅ in SrZrO₃ has been carried out optically (Figure 5a). Ta₂O₅ has a positive effect by lowering charge recombination, as indicated by the photoluminescent measurements in Figure 5b. The effect of Ta₂O₅ in the SrZrO₃ structure leads to band gap tunability and has been studied further in Figures 6 and 7. The results show that the role of tantalum is imminent, by either substituting Zr⁴⁺ or introducing compressive strain in the SrZrO₃ lattice. Lattice constraints in SrZrO₃ due to the presence of Ta are not observed in TEM, pointing toward shallow Ta⁴⁺ doping. Although this lattice effect is not seen locally in Figure 2, the XRD pattern in Figure 6b reveals cell volume contraction for Ta₂O₅/SrZrO₃. Therefore, Ta-substitution or ejected strain in SrZrO₃ should not be disregarded in Ta₂O₅/SrZrO₃ and 0.1% RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructures. The chemical composition of the 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure consisting of RuO₂ and CuO contributes to extending the light absorption in the visible region (Figure 5c), promoting high photocatalytic activity, demonstrated in the next section.

3.2. Heterostructure Synergy to Promote Photocatalytic Water Splitting. The photocatalytic activity for SrZrO₃ is evaluated for various Ta₂O₅ loadings in Figure 8a (i.e., 0.8, 1.6, 2.4, 3, and 3.9 wt %). H₂ production under simulated solar light for SrZrO₃ is 132 μmol g⁻¹ h⁻¹, increasing the H₂ production rate to 1297 μmol g⁻¹ h⁻¹ as Ta₂O₅ reaches 3 wt % (hereafter, 3% Ta₂O₅). The higher catalytic activity is attributed to Ta₂O₅ improving charge transport at the SrZrO₃ interface. In this sense, Ta₂O₅ can provide a large number of states, where electrons might be trapped, reducing hole–electron recombinations. For still larger Ta₂O₅ loadings (i.e., 3.9 wt %), the H₂ evolution activity reduces to 959 μmol g⁻¹ h⁻¹. The results indicate that Ta₂O₅ loadings can also affect the overall catalyst performance. It can then be hypothesized that there is a trade-off between charge mobility and trapped states for different Ta₂O₅ loadings. From the results, Ta₂O₅ in SrZrO₃ is maintained fixed to 3 wt %, as it shows the highest amount of H₂ produced in Figure 8a. It should be noted that during experiments shown in Figure 8a, the production of O₂ has not been observed.

The H₂ production is further improved by incorporating various RuO₂/CuO loadings to 3%Ta₂O₅/SrZrO₃. Insights on the kinetics of H₂ evolution on RuO₂/CuO heterostructures are presented in Figure 8b. The results reveal that the H₂ production in the first 3 h shows a linear tendency. After this time, the production rate is diminished, showing a plateau effect, which several authors correlate to limitations in the surface area and the available active sites on the photocatalyst. However, we should not disregard possible elemental losses after the reaction (Table 1). We also assess potential changes in the chemical environment and crystalline structure in 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ with XPS and XRD after the reaction (Figures S5 and S6 and Table S1). In this case, no significant changes are observed; only the Ta at

Figure 7. Simulation of the band gap decrement as a function of the unit cell volume. Unit cells of Pnma and Pmnb symmetry groups are optimized at chosen unit cell volumes between 0.94⁴, 0.95⁵, 1.05⁶ and 1.06⁶ of their optimized cell volume, that is, 277.3 and 274.2 Å³ respectively.
% reduces nearly 2-fold at the surface (Table 1), possibly explaining the changes in Figure 8b after 3 h. The cumulative H₂ production is presented in Figure 8c. Figure 8c shows that 0.1%RuO₂/1%CuₓO is the ideal ratio, yielding a H₂ production rate of 5164 μmol g⁻¹ h⁻¹, which is even higher than those of several cocatalysts (e.g., RuO₂, CuₓO, and Pt) and other zirconates and perovskite heterostructures as shown in Figure 8e and Table S2. The photocatalytic activity of 0.1%RuO₂/1%CuₓO has also been estimated to support our attributions. In this case, the H₂ production rate remains approximately 184 lower (28 μmol g⁻¹ h⁻¹) than the H₂ rate obtained for 0.1%RuO₂/1%CuₓO coupled to the 3%Ta₂O₅/SrZrO₃ heterostructure (5164 μmol g⁻¹ h⁻¹). The experiments indicate that charge transfer through the different heterostructure components is improved by adding 0.1%RuO₂/1%CuₓO to 3% Ta₂O₅/SrZrO₃. The photocatalytic activity for 0.1%RuO₂/1%CuₓO is also attributed to the strong electronic coupling with Ta₂O₅/SrZrO₃.

The H₂ production rate for the RuO₂/1%CuₓO/3%Ta₂O₅/SrZrO₃ heterostructure of varied RuO₂ contents and other heterostructures of lower-order with CuₓO, RuO₂, and Pt (Figure 8c) is contrasted with the O₂ production rate to demonstrate the overall water-splitting process (Figure 8d). The trends for the O₂ production rates in Figure 8d are compared to those in Figure 8c. The results show an O₂ to H₂ ratio of 1:2 for the RuO₂/CuₓO/3%Ta₂O₅/SrZrO₃ heterostructure. Similar ratios for lower-order heterostructures decorated with RuO₂, CuₓO, and Pt cocatalysts can be seen in Figure 8e. Among the results, it should be noted that the O₂ production rate for the 0.1%RuO₂/1%CuₓO/3%Ta₂O₅/SrZrO₃ prevails as the highest without evident chemical changes after reaction (Figures S5 and S6, and Table S1). Overall, the results suggest the favorable effect of the cocatalyst and bicatalyst on promoting the kinetics of O₂ evolution. Although the 0.1%RuO₂/1%CuₓO/3%Ta₂O₅/SrZrO₃ heterostructure prevails the highest, it is essential to reflect on the

Figure 8. (a) H₂ production rates under simulated solar light for Ta₂O₅/SrZrO₃ with various Ta₂O₅ loadings. (b) Kinetic curves of the H₂ evolution vs time for RuO₂/1%CuₓO/3%Ta₂O₅/SrZrO₃ with various RuO₂ loadings. (c) H₂ and (d) O₂ production rates for RuO₂/1%CuₓO/3% Ta₂O₅/SrZrO₃ with various RuO₂ loadings. (e) H₂ and (f) O₂ production rates in 3%Ta₂O₅/SrZrO₃ loaded with CuₓO, RuO₂, and Pt cocatalyst.
results from CuO, RuO₂, and Pt carefully (Figure 8e). In this case, various loadings have been assessed (i.e., 0.1, 0.3, 0.5, 1.3, and 1.5 wt %) for the three RuO₂, CuO, and Pt cocatalysts, as shown in Figure 8e. We compare 3%Ta₂O₅/SrZrO₃ (1297 μmol g⁻¹ h⁻¹) with 1 wt % RuO₂. A nearly 3-fold increase (4986 μmol g⁻¹ h⁻¹) is achieved. As for the catalyst with 1 wt % CuO, a 2-fold increase (3282 μmol g⁻¹ h⁻¹) has been found. For Pt, a very low loading of ca. 0.1 wt % is required to obtain an activity close to 2744 μmol g⁻¹ h⁻¹, which is comparable to that of either 0.5 wt % CuO or 0.5 wt % RuO₂. However, the H₂ evolution activity of Pt decreases substantially comparable to that of catalysts with RuO₂ and CuO loadings (i.e., 0.1 wt %). In all cases, a high cocatalyst content does not necessarily improve the production of H₂ due to parasitic recombination losses as the amount of either CuO increases, that is, (>1 wt %), RuO₂ (>1 wt %), or Pt (>0.1 wt %). Additionally, high loadings can also promote the formation of large metal (metal oxide) particles or aggregates detrimental to the overall catalytic activity during water splitting. Overall, the photocatalytic activity of 0.1 wt % CuO and 0.1 wt % RuO₂ can be attributed to the strong electronic coupling with Ta₂O₅/SrZrO₃ where hole–electron recombination might be reduced. To support our attribution, the photocatalytic activity of RuO₂ and CuO has been measured. The H₂ production rate for RuO₂ and CuO remains low, ca. 14 and 26 μmol g⁻¹ h⁻¹. This indicates that Ta₂O₅/SrZrO₃ provides the necessary transfer of charges to RuO₂ or CuO, reaching the solid–liquid interface to promote H₂ water splitting. To this end, an important aspect to highlight is the reduction of the use of noble catalysts such as Ru or Pt without compromising photocatalytic activity. Even if Ru is a less costly catalyst than Pt, Ru usage can be reduced when combined with other catalysts, such as CuO. Therefore, the photocatalytic performance of binary cocatalysts composed of RuO₂/CuO has also been assessed. Various RuO₂ loadings, that is, 0.01 wt % (0.01%RuO₂) and 1 wt % (1%RuO₂), are incorporated to 1%CuO/Ta₂O₅/SrZrO₃ (Figure 8c,d). The QE at λ = 420 nm and the photocatalysts’ STH are calculated according to eqs 1 and 2 to compare our heterostructures with other systems. The efficiencies obtained are summarized in Table 2. The QE and STH of performances than 1%RuO₂/3%Ta₂O₅/SrZrO₃. The estimated QE and STH values of 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ are 41 and 0.40%, which are competitive with either QE or STH values from other photocatalysts and other perovskite heterostructures of high order (Table S2). For example, this is the case of the SrTiO₃-based photocatalyst with a QE of 30% at λ = 360 nm. Compared to bare and decorated SrZrO₃ with Ni, Cu, Fe, and Co, our 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure surpasses the known STH values by nearly 4-fold.

After assessing the overall water-splitting performance of the heterostructures, it is clear that the 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ composition has the highest H₂ or O₂ production rate and STH. Regarding QE, 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ has the highest among the synthesized SrZrO₃ heterostructures. The QE (Table 2) of 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ is comparable to, if not better, than other QE values reported for perovskite heterostructures shown in Table S2.

The next step is to understand the effect of the heterostructure component during charge transfer to provide a plausible picture of the water-splitting mechanism.

### 3.3. Donor Density and Charge Transfer Resistance in the RuO₂/CuO/Ta₂O₅/SrZrO₃ Heterostructure.

EIS is used to obtain information on the conductivity type, flat band potential, and donor density in the photocatalysts through the Mott Schottky plots (Figure 9a). The samples exhibit a positive slope, evidencing the n-type conductivity. The donor density, Nₐ, has an inverse relationship with the capacitance through the Mott–Schottky formula, eq 3.

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_A} \left( V - V_{FB} - \frac{k_B T}{e} \right)
\]

where C is the differential capacitance, εₑ is the dielectric constant of SrZrO₃ (εₑ = 60), ε₀ is the vacuum permittivity, e is the electron charge, Nₐ is the donor density, A is the active electrode area, V is the applied potential, V_{FB} is the flat band potential, T is the temperature (in kelvin), and k_B is the Boltzmann constant. The donor density is estimated using the Mott–Schottky plot slope, and a value of 60 is estimated for the dielectric constant of SrZrO₃. These values are summarized in Table 3.

In Table 3 and Figure 9a, the donor density of SrZrO₃ is affected by the incorporation of Ta₂O₅ and the different co-catalysts. The addition of Ta₂O₅ increased the donor density from 6.37 × 10¹⁵ to 3.59 × 10¹⁶ cm⁻³. The donor density can be further improved with cocatalyst incorporation. For example, 1%CuO/3%Ta₂O₅/SrZrO₃ has a donor density of 3.78 − 4.26 × 10¹⁶ cm⁻³, and 1%RuO₂/3%Ta₂O₅/SrZrO₃ has a similar donor density of ca. 4.26 × 10¹⁶ cm⁻³. Remarkably, the bicatalyst (0.1%RuO₂/1%CuO) surpasses the obtained values for 1%CuO and 1%RuO₂ with a donor density of ca. 5.02 × 10¹⁷ cm⁻³. This confirms our observations in Figure 8 and indicates that the photocatalytic activity of 3%Ta₂O₅/SrZrO₃ can be enhanced using 0.1%RuO₂/1%CuO. Donor density mobility in the 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ heterostructure can be associated with a reduction in charge recombination (Figure 5).

To this end, transient photocurrent measurements are evaluated under simulated solar light (100 mW cm⁻²) to understand the photocatalyst response in Figure 9b. 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃ promoted the higher photocurrents.

| Table 2. Solar to Hydrogen Efficiency, STH, and Quantum Efficiency, QE, Obtained from the Experimental Results in Figure 8 |
|---------------------------------|-----------------|-----------------|
| Material                        | STH (%)         | QE (%) at 420 nm |
| SrZrO₃                          | 0.01            | 1.0             |
| 3%Ta₂O₅/SrZrO₃                  | 0.10            | 10              |
| 1%RuO₂/3%Ta₂O₅/SrZrO₃           | 0.39            | 39              |
| 1%CuO/3%Ta₂O₅/SrZrO₃            | 0.26            | 26              |
| 0.1%Pt/3%Ta₂O₅/SrZrO₃           | 0.24            | 24              |
| 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃    | 0.26            | 26              |
| 0.01%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃  | 0.50            | 50              |

SrZrO₃ are at the lowest end of the photocatalysts. The incorporation of 3%Ta₂O₅/SrZrO₃ increases the QE and STH. Among the heterostructures containing either RuO₂ or CuO, 1%RuO₂/3%Ta₂O₅/SrZrO₃ has superior performance, even better than the Pt cocatalyst. However, the RuO₂ content is relatively high compared to 0.1%RuO₂/1%CuO/3%Ta₂O₅/SrZrO₃, which shows a similar if not even better QE and STH.

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to response associated with charge carrier separation in this heterostructure. This higher photocurrent is also attributed to the increase in light absorption. Light absorption around 250 nm or higher is improved, as shown in Figure 5c. Hence, one can assume that photogeneration of electrons and holes occurs more efficiently at the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ interface than in other photocatalysts, as shown in Table 2.

For insights into the reaction kinetics, impedance analyses are carried out. The semicircle in the impedance spectra in the Nyquist plots (Figure 10) shows the charge transfer resistance. The diameter of the semicircle describes the reaction kinetics. A smaller diameter implies faster reaction kinetics. Figure 10 also shows the corresponding equivalent circuit, where $R_s$ is the resistance associated with the electric connection, electrolyte, and substrate. $R_1$ is the charge transference resistance in the electrode–electrolyte interface, and CPE is the constant phase element (Table 4). 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ shows the smallest diameter among the other heterostructures and control (e.g., SrZrO$_3$). This high-order heterostructure also exhibits the lowest $R_1$ (ca. 1.97640 × 10$^5$ Ω), which indicates enhanced charge transport in the heterostructure when 0.1%RuO$_2$/1%Cu$_x$O and 3%Ta$_2$O$_5$/SrZrO$_3$ are combined. Through this comparison, it is possible to show the beneficial effect on the charge transport kinetics of the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure. It should be noted that the prepared electrodes show relatively high charge transfer resistance values due to the physical form of the catalyst, that is, the powder form. Low charge transfer resistance values are expected for denser layers, such as thin films.

### 3.4. Charge Transfer Mechanism

Mott–Schottky plots are used to estimate the flat band potential (Figure S7 and Table S3) by extrapolating the x-axis intercept of the linear plot ($1/C^2$ vs $E$). A positive slope is characteristic of n-type semiconductors, and a negative slope is representative of p-type semiconductors. Note that the Fermi level and the majority charge carrier band (CB ($E_{CB}$) for n-type and VB ($E_{VB}$) for p-type) can vary approximately ±0.1 V versus NHE.$^{61,64,65}$ Therefore, it is safe to say that the band energy diagram is estimated using the Mott–Schottky and the

![Figure 9](#) (a) Mott–Schottky plots (dark conditions, 10 kHz) and (b) photocurrent response of the photocatalysts at 0.3 V versus Ag/AgCl.

### Table 3. Summary of the Donor Density Values Calculated from the Mott–Schottky Plots; The Results of This Table are Derived From Figure 9a

| photocatalyst                  | $N_d$ (cm$^{-3}$) |
|-------------------------------|------------------|
| SrZrO$_3$                     | 6.37 × 10$^{15}$ |
| 3%Ta$_2$O$_5$/SrZrO$_3$       | 3.59 × 10$^{16}$ |
| 1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ | 3.78 × 10$^{16}$ |
| 1%RuO$_2$/3%Ta$_2$O$_5$/SrZrO$_3$ | 4.26 × 10$^{16}$ |
| 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ | 5.02 × 10$^{17}$ |

**Table 4. EIS Parameters from the Equivalent Circuit Fitting of Nyquist Plots of SrZrO$_3$-Based Electrodes Measured in 0.5 M Na$_2$SO$_4$**

| sample                  | $R_s$ (Ω) | $R_1$ (Ω) | CPE1 (F) |
|-------------------------|-----------|-----------|----------|
| SrZrO$_3$               | 252.5     | 3.9 × 10$^{6}$ | 0.97     |
| 3%Ta$_2$O$_5$/SrZrO$_3$ | 125.1     | 2.3 × 10$^{6}$ | 0.95     |
| 1%Cu$_x$O/3%Ta/SrZrO$_3$| 64.2      | 2.0 × 10$^{6}$ | 0.97     |
| 1%RuO$_2$/3%Ta/SrZrO$_3$| 61.3      | 1.4 × 10$^{6}$ | 0.97     |
| 0.1%RuO$_2$/1%Cu$_x$O/3%Ta/SrZrO$_3$ | 59.4 | 1.9 × 10$^5$ | 0.97     |

SrZrO$_3$ shows the smallest diameter among the other heterostructures and control (e.g., SrZrO$_3$). This high-order heterostructure also exhibits the lowest $R_1$ (ca. 1.97640 × 10$^5$ Ω), which indicates enhanced charge transport in the heterostructure when 0.1%RuO$_2$/1%Cu$_x$O and 3%Ta$_2$O$_5$/SrZrO$_3$ are combined. Through this comparison, it is possible to show the beneficial effect on the charge transport kinetics of the 0.1%RuO$_2$/1%Cu$_x$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure. It should be noted that the prepared electrodes show relatively high charge transfer resistance values due to the physical form of the catalyst, that is, the powder form. Low charge transfer resistance values are expected for denser layers, such as thin films.$^{63}$
semiconductor band gap ($E_g$) values. These values are used in eq 4. Note that the $E_g$ values for SrZrO$_3$ and 3%Ta$_2$O$_5$/SrZrO$_3$ are based on Figure 5. The band gaps of RuO$_2$, Cu$_2$O, Cu$_3$O, and Ta$_2$O$_5$ are taken from the literature.66—69 It should also be noted that the same values are used to construct SrZrO$_3$-based heterostructures containing either Ta$_2$O$_5$, RuO$_2$, or Cu$_2$O shown in Figure S8. The results from Table S3 are used to understand the charge transfer mechanism (Figure 11).

$$E_{CB} = E_{VB} - E_g$$  \hspace{1cm} (4)

The charge transfer mechanism in Figure 11 is proposed for the 0.1%RuO$_2$/1%Cu$_2$O/3%Ta$_2$O$_5$/SrZrO$_3$ heterostructure to elucidate the possible charge pathways that led to high photocatalytic water splitting shown in Figure 8. It should be noted that other mechanisms might involve during charge transfer (e.g., Figure S9), but the mechanism in Figure 11 might be the most plausible one. The structural, morphological, chemical, optical, and electrochemical characterization results are used to derive our proposition (Figure 11). In this heterostructure, electrons are transferred from tantalum-doped strontium zirconate to Ta$_2$O$_5$ and Cu$_2$O to overcome the evolution of H$_2$. Meanwhile, the electrons in Cu$_2$O move toward the RuO$_2$ CB. After that, these electrons recombine with Cu$_2$O holes. RuO$_2$ holes are transferred to CuO$_2$, performing the O$_2$ evolution reaction. Holes in Ta$_2$O$_5$ move to tantalum-doped strontium zirconate, where they carry out O$_2$ evolution reactions (Figure 8). For other heterostructures, the possible mechanism is presented in Figure S8.

4. CONCLUSIONS

SrZrO$_3$-based heterostructures of mixed oxides are synthesized. The highest H$_2$ production is ca. 5164 μmol g$^{-1}$ h$^{-1}$ for 0.1% RuO$_2$/1%Cu$_2$O/3%Ta$_2$O$_5$/SrZrO$_3$ which is comparable if not even higher than that of SrZrO$_3$ and reported QE values for other perovskite heterostructures. In-depth structural analysis revealed the presence of Ta$_2$O$_5$ in SrZrO$_3$. Ta$_2$O$_5$ has been found segregating at the surface and grain boundaries of SrZrO$_3$, which improved the photocatalytic activity in SrZrO$_3$. Yet, the photocatalytic activity of Ta$_2$O$_5$/SrZrO$_3$ is further improved with RuO$_2$ or Cu$_2$O as a cocatalyst or RuO$_2$/Cu$_2$O as a binary catalyst. An optimum activity for the RuO$_2$/Cu$_2$O heterostructure components has been found, surpassing RuO$_2$ or Pt activity. DFT, structural, optical, and electrochemical characterization generates insights on band gap tunability for the different heterostructure components and demonstrates enhanced charge transfer for RuO$_2$/Cu$_2$O/Ta$_2$O$_5$/SrZrO$_3$. The results are valuable in demonstrating that SrZrO$_3$-based heterostructure can harvest visible light to improve the hydrogen evolution reaction.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c02520.

Materials and methods for the synthesis of photocatalysts; analysis conditions employed in the characterization techniques of the physicochemical properties of the materials (XRD, SEM, TEM, XPS, UV–vis, photoluminescence, and EIS); DFT calculations; calculation details of the energy band diagram; characterization of the best photocatalyst after reaction; and supplementary microscopy images of the materials (PDF).

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Notes
The authors declare no competing financial interest.

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