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Enhanced kinetics of hole transfer and electrocatalytic processes during photocatalytic oxygen evolution by cocatalyst tuning

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ABSTRACT: Understanding photophysical and electrocatalytic processes during photocatalysis in a powder suspension is crucial for developing efficient solar energy conversion systems. We report a substantial enhancement by a factor of 3 in photocatalytic efficiency for the oxygen evolution reaction (OER) by adding trace amounts (~0.05 wt%) of noble metals (Rh or Ru) to a 2 wt% cobalt oxide-modified Ta$_3$N$_5$ photocatalyst particulate. The optimized system exhibited high quantum efficiencies (QEs) of up to 28 and 8.4% at 500 and 600 nm in 0.1 M Na$_2$SO$_4$ at pH 14. By isolating the electrochemical components to generate doped cobalt oxide electrodes, the electrocatalytic activity of cobalt oxide when doped with Ru or Rh was improved compared with cobalt oxide, as evidenced by the onset shift for electrochemical OER. Density functional theory (DFT) calculation shows that the effects of a second metal addition perturbs the electronic structure and redox properties in such a way that both hole transfer kinetics and electrocatalytic rates improve. Time resolved terahertz spectroscopy (TRTS) measurement provides evidence of long-lived electron populations (>1 ns; with mobilities $\mu_e$~0.1-3 cm$^2$/V·s$^{-1}$), which are not perturbed by the addition of CoO$_x$-related phases. Furthermore, we find that Ta$_3$N$_5$ phases alone suffer ultrafast hole trapping (within 10 ps); the CoO$_x$ and $M$-CoO$_x$ decorations most likely induce a kinetic competition between hole transfer toward the CoO$_x$-related phases and trapping in the Ta$_3$N$_5$ phase, which is consistent with the improved OER rates. The present work not only provides a novel way to improve electrocatalytic and photocatalytic performance but also gives additional tools and insight to understand the characteristics of photocatalysts that can be used in a suspension system.

KEYWORDS. Photocatalysis, Oxygen evolution reaction, Electrocatalysis, Time-resolved terahertz spectroscopy, Hole transfer kinetics, Tantalum nitride

Introduction

Direct conversion of solar energy to chemicals, particularly via photocatalytic water splitting to generate renewable hydrogen, has been a subject of research for decades. The main challenge lies in identifying materials suitable for efficient photocatalysis, i.e., with an optical response in the visible region, and energy levels compatible with chemical reduction and/or oxidation. These properties converge in Ta$_3$N$_5$, which can theoretically achieve a solar to hydrogen efficiency of approximately 17% using a single semiconductor; nevertheless, non-biased, overall efficient water splitting using this material has not been achieved. For efficient photocatalysis with the powder semiconductor, a solid-electrolyte interface is effectively utilized for charge separation, thereby directly inducing surface chemical redox reactions. One strategy to improve the photocatalytic activity of Ta$_3$N$_5$ is to decorate the surface with an oxygen evolution reaction (OER) electrocatalyst, being an essential component to achieve high efficiency. Previous work has demonstrated that the photocatalytic OER efficiency can be improved by one order of magnitude by the addition of CoO$_x$ cocatalyst on the Ta$_3$N$_5$ surface; when appropriate, heat treatment is applied to construct an intimate CoO$_x$-Ta$_3$N$_5$ interface. Generally, the role of the catalyst, which is commonly called a cocatalyst, on the semiconductor surface has been discussed as two-fold: 1) it improves the electrochemical performance by lowering overpotentials for the redox reactions (and resultant electron/hole consumption) and 2) effectively separates the excited charges by using a photocatalyst (semiconductor)-cocatalyst interface, exploiting the differences in Fermi levels between them.

The materials with high rates in electrochemical reactions are naturally considered to be good cocatalysts because fast redox kinetics is strongly correlated with fast carrier consumptions, thus avoiding its recombination. In other words, for slow redox kinetics, deleterious charge recombination is expected. In previous works on electrocatalytic OER, CoO$_x$ has been considered...
to be an effective catalyst.\textsuperscript{30-32} Recently, the combination of CoO\(_x\) and a noble metal (M-CoO\(_x\)), such as an Au-CoO\(_x\) electrode, has drastically improved its performance, compared with that of its mono-metallic counterpart.\textsuperscript{30} Because of its electron negativity, Au may serve as an electron sink, facilitating the oxidation of Co\(_3^+\) and Co\(_{11}^+\) to Co\(_{0}^\circ\) and increasing the availability of the active sites for OER.\textsuperscript{30} In situ Raman spectroscopy during the electrochemical OER supports this scenario; it has been demonstrated that the population of Co\(_3^+\) states is promoted in the presence of Au, which explains the higher current density on the Au-CoO\(_x\) sample.\textsuperscript{30} Furthermore, a very recent work by Tae et al. strongly suggest that CoO\(_x\) redox potential was effectively perturbed by IrO\(_x\), as inferred from operando X-ray absorption spectroscopy, giving one of the lowest overpotentials of OER ever reported (−0.19 V at 10 mA cm\(^{-2}\)).\textsuperscript{33} Other noble metals, such as Rh, Pt, Ru, Pd, and Ir, were also shown to have a similar impact, suggesting a common underlying mechanism governing the improved performance of M-CoO\(_x\) in OER efficiency.\textsuperscript{30-32}

The second role of the cocatalyst is presumed to be the charge separation at the metal (oxide)-semiconductor interface. In fact, in photoelectrochemical OER using a CoO\(_x\)/BaTaO\(_x\)N system, the addition of RhO\(_x\) has been found to significantly improve the photocurrent and lower the onset potential.\textsuperscript{34} It was speculated that there is a synergistic effect between RhO\(_x\) and CoO\(_x\), where Rh (i.e., in the form of RhO\(_x\)) forms highly oxidized Rh\(^{4+}\), which promotes effective hole extraction from the bulk Ba-TaO\(_x\)N.\textsuperscript{35} To investigate the charge separation on the catalyst-semiconductor interface, time-resolved spectroscopy has often been used. Transient absorption spectroscopy (TAS) at the microsecond to second time scale, with low excitation densities on Fe\(_3O_4\) and TiO\(_2\) photoanodes, revealed an increase in photogenerated holes’ lifetime when adding a cocatalyst.\textsuperscript{35-37}

In this work, we present a comprehensive study regarding the nature of enhanced photocatalytic OER on Ru and Rh co-loaded CoO\(_x\)/Ta\(_2\)N\(_x\) particulate. The electrocatalytic activity of M-doped-cobalt oxide (M/CoO\(_x\)) is interrogated by isolating the electrochemical components to generate doped cobalt oxide electrodes. When doped with Rh or Ru, the electrocatalytic activity of cobalt oxide is significantly improved, as evidenced by the onset potential. Time resolved terahertz spectroscopy (TRTS) measurement provides evidence of long-lived electron populations (>1 ns; with mobilities \(\mu_e\) ~0.1-3 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), which are not perturbed by adding Co\(_x\)-related phases. Furthermore, we find that Ta\(_2\)N\(_x\) phases alone suffer ultrafast hole trapping (within 10 ps): the CoO\(_x\) and M/CoO\(_x\) decorations most likely cause a kinetic competition between hole transfer toward the CoO\(_x\)-related phases and trapping at the Ta\(_2\)N\(_x\) phase (which could be linked with the observed OER improvement). We conclude that the origin of improved photocatalytic OER of CoO\(_x\) by doping is two-fold: improved hole transfer kinetics from the semiconductor (Ta\(_2\)N\(_x\)) to doped CoO\(_x\) and improved electrocatalytic performance. Both improvements are associated with work function tuning, as shown by the density functional theory (DFT) calculations.

**Experimental and theoretical methods**

**Photocatalyst synthesis**

Ta\(_2\)N\(_x\) particles were prepared from commercially available crystalline Ta\(_2\)O\(_x\) (≥99.99% metal basis, <5 microns, Sigma–Aldrich) by applying direct NH\(_3\) nitridation under high temperature, as reported elsewhere.\textsuperscript{7,22-24} In a typical experiment, a total of 0.5 g Ta\(_2\)O\(_x\) was wrapped with quartz wool and placed into a tube furnace. The tube furnace was initially purged with N\(_2\) before the introduction of NH\(_3\) flow at room temperature. The nitridation was conducted at 900 °C, with a heating rate of 5 °C min\(^{-1}\) and was held at this temperature for 15 h under an NH\(_3\) flow of 200 mL min\(^{-1}\). The sample was allowed to cool to room temperature inside a tube furnace under NH\(_3\) flow. Cobalt deposition onto the Ta\(_2\)N\(_x\) was conducted using the wet-impregnation method.\textsuperscript{22-23} A known amount of Co(NO\(_3\))\(_2\)-6H\(_2\)O (Aldrich, 99%) and 0.1 g Ta\(_2\)N\(_x\) were suspended in 5 mL H\(_2\)O and sonicated for 5 minutes. The suspension was then subjected to evaporation to remove water under a slight vacuum at 70 mbar for 30 minutes, followed by 50 mbar for 30 minutes. Subsequently, the resulting powder was subjected to heat treatment at 700 °C for 1 h under 200 mL min\(^{-1}\) NH\(_3\) flow. In a similar manner, the cooling process inside the tube furnace was conducted under NH\(_3\) flow. A noble metal cocatalyst (Rh or Ru) was subsequently deposited onto the Co-impregnated Ta\(_2\)N\(_x\) (hereafter, CoO\(_x\)/Ta\(_2\)N\(_x\)) by applying a similar method of wet impregnation, with or without subsequent reduction at 400 °C for 1 h under a H\(_2\) flow. The chemicals used for noble metal precursors were Na\(_2\)RhCl\(_6\)-6H\(_2\)O and RuCl\(_3\)-3H\(_2\)O and were of analytical grade (Aldrich, 99.99% trace metal basis). For TRTS measurements, SiO\(_x\) supported M/CoO\(_x\) samples were prepared in an identical procedure. Nonporous spherical SiO\(_x\) (COSMO 30, JGC Catalysts and Chemicals Ltd.) was selected because of similar surface area as Ta\(_2\)N\(_x\) (10 m\(^2\) g\(^{-1}\)).

The diffuse reflectance spectra, surface oxidation state, and morphology of CoO\(_x\)/Ta\(_2\)N\(_x\) and M-CoO\(_x\)/Ta\(_2\)N\(_x\) were characterized; the details are presented in Supporting Information (section S1.1).

**Photocatalytic reaction**

The photocatalytic reactions were performed in a recirculating batch reactor connected to a gas chromatography (GC) unit equipped with a vacuum line.\textsuperscript{6,23,24} The reactant solution was maintained at room temperature by using a flow of cooling water during the reaction. Before irradiation, the reaction vessel was degassed several times to remove air, followed by the introduction of 100 torr of Ar gas into the photocatalytic system. A Xe lamp (CERMAX PE300-BF, 300-W) was used as a light source, and the irradiation wavelength was controlled with a combination of a cold mirror and a water filter (350 < \(\lambda\) < 800 nm). A cut-off filter (HOYA L 42) was used with the aforementioned light source (420 < \(\lambda\) < 800 nm). The homogeneity of the solution during the reaction was maintained by agitation with a magnetic stirrer. The gases evolved were analyzed by using GC (Bruker 450 GC, TCD, Ar gas, molecular sieve 13X). All the samples were tested for photocatalytic OER using 0.1 M Na\(_2\)S\(_2\)O\(_3\) as the sacrificial electron acceptor. This strong electron acceptor facilitates the electron consumption process to conduct, in turn, the hole consumption process, i.e., OER, as the kinetically relevant step. (Similar concept to rate determining step (rds): However, the photocatalytic process has parallel reaction pathways (e.g., reduction and oxidation), so this term, i.e., rds, does not apply because it indicates an elementary step that pins the overall rate within sequential elementary reactions.) In a typical experiment, a known amount of Na\(_2\)S\(_2\)O\(_3\) was dissolved in 100 mL H\(_2\)O and the pH was adjusted with a NaOH solution. Then, a 50-mg sample was suspended in a corresponding solution and sonicated for 5 min.

**Electrochemical measurement**
Co was electrochemically deposited onto Ni foam (NF) of a 1 cm × 1 cm geometric surface by chronopotentiometry. NF was immersed in a deposition bath containing 0.5 mM cobalt nitrate (Co(NO$_3$)$_2$, Sigma-Aldrich, 99.999%). A constant current of ~10 mA was applied for 1 h at 298 K. Rh and Ru were placed by chronopotentiometry onto the Co supported on NF, a bare NF, a Co plate and a Ni plate. A metal precursor solution containing 0.5 mM of Rh (hexachlororhodide, Sigma-Aldrich) or Ru (Ruthenium chloride hydrate, Sigma-Aldrich). Constant currents (NF: ~1 mA, others: ~0.3 mA) were applied for 1 h. All the electrochemical deposition was carried out in 3-electrode configuration, with a Pt wire and Hg/HgSO$_4$ (sat. K$_2$SO$_4$) as counter and reference electrodes, respectively. Anodic polarization over the prepared electrodes was performed at 298 K with a scan rate of ~1 mV s$^{-1}$ using a research grade potentiotstat system (VMP3) purchased from BioLogic Science Instruments.

For all measurements, a Pt wire and Hg/HgO (sat. 1 M NaOH) were used as counter and reference electrodes, respectively. Solution resistances were measured by impedance spectroscopy performed at 100 kHz with 10 mV amplitude at 298 K.

**Time-resolved THz spectroscopy**

We used optical pump–THz probe spectroscopy to investigate the charge carrier dynamics on M/CoO$_x$/Ta$_2$N$_5$ nanocomposites. In these types of measurements, the nanocomposite is photoexcited by an ultrashort (~100 fs) laser pulse at wavelengths of 400 nm and 800 nm. Subsequently, a freely propagating THz pulse interrogates the conductivity of the generated free charge carriers in the frequency range 0.4–2 THz (2.8–800 meV). The evolution of the carrier conductivity is then measured with a time resolution down to ~100 fs. The technique, owing to its low probing frequency, resolves the motion of carriers at a ~10 nm length scale. Consequently, it enables direct monitoring of carrier transport dynamics in nanostructured systems.

Our optical pump-THz probe (OPTP) setup was driven by ultrashort laser pulses with a temporal length ~40 fs, pulse energy ~1 mJ, mean wavelength of 800 nm and repetition rate of 1 kHz, generated by a Ti:sapphire amplified laser system (Spitfire ACE by Spectra-Physics). Part of the laser power (~20%) was used for THz generation and detection: THz pulses were generated via nonlinear mixing in a (110) oriented 1 mm thick ZnTe crystal. The generated THz pulses were focused onto the sample using parabolic mirrors. The transmitted THz pulses were focused onto a sensor consisting of a 1 mm thick (110) oriented ZnTe crystal. The THz pulses were detected in a phase-sensitive fashion using the electro-optic effect. The larger part of the laser power was used for photoexcitation as is or frequency-doubled by second harmonic generation in a BBO crystal. The size of the photoexcited part of the sample was always much larger than the spot size of the THz beam on the sample. The pump fluence of the photoexcitation was 50–200 μJ cm$^{-2}$ at wavelengths of 400 and 800 nm. During the measurements, the samples were placed into an N$_2$ purged box to avoid any possible photo-oxidation.

**Theoretical method**

All theoretical calculations were performed using the Vienna Ab initio Software Package (VASP)

<table>
<thead>
<tr>
<th>39–41</th>
<th>version 5.3.5. DFT was used with the PBE GGA functional. 42 Cobalt oxides are known to be strongly correlated materials. Even hybrid functionals that are popular for semiconductors fail to reproduce the electronic structure of this family of compounds. 43 For that reason, the Hubbard Hamiltonian (noted +U) was added in the calculations. This approach has proven its reliability for several metal oxides, including cobalt oxides. 41–46 More precisely, the formalism proposed by Dudarev et al. 47 was used, along with the following U-J values: 3.5 eV for Co, 3.0 eV for Ru and 3.3 eV for Rh, based on previous works. 47–49</th>
</tr>
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<tr>
<td>40</td>
<td>The convergence criterion for the SCF cycles was fixed at 10$^{-8}$ eV per unit cell. The E$_{\text{cut-off}}$ value, defining the basis set size, was fixed at 400 eV. The k-points sampling was done with a 3$x$3$x$1 Monkhorst-Pack grid for slab calculations and 12$x$12$x$12 grid for the bulk calculation. The core electrons were described by using the projector-augmented plane wave (PAW) approach. The convergence criterion for geometry optimization was 0.01 eV Å$^{-1}$ for the forces.</td>
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<tr>
<td>41</td>
<td>All slabs were 2$x$2 supercells of the primitive surface cell. A thickness of five layers (containing five Co planes) was used, based on the work of Bajdich et al. 42 During the geometry relaxation of the surface, only the atoms were allowed to relax, and the cell parameters were fixed for the ones determined on the bulk CoOOH. Charge analyses were performed using the Bader scheme based on electron density using the software developed by Henkelman et al. 50 For each system, several spin states were investigated to find the most stable one. The low spin (LS) and high spin (HS) labeling were based on analyses of the magnetic moment projected on atoms.</td>
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<td>42</td>
<td>Bajdich et al. proved that the active phase of cobalt oxide at the potential and pH of the OER is the CoOOH phase by using thermodynamic experimental or computed (using DFT) data. 51 Furthermore, they also showed that two surfaces are stable at the working condition of the OER, namely, the (01-12) O-terminated and the (10-14) OH-terminated surfaces. However, the most active surface is the (10-14) surface, leading to an overpotential for the OER, estimated as half of the one of the (01-12) surface. For these reasons, the calculations were performed on the (10-14) surface of CoOOH. On this surface, the oxidation state of Co is +III (low spin state). The influence of Rh(III) doping was determined by substituting one Co of the surface with Rh. The influence of Ru(IV) and Rh(IV) doping was determined by substituting one Co of the surface with Ru or Rh and by removing one top H atom to allow the increase in oxidation state compared with Co. This corresponds to a 25% substitution of the Co surface atoms. To be consistent within this manuscript, notation of the Co sample is kept to be CoO$_x$, for DFT calculation section.</td>
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| 43 | The thermodynamic potential necessary to split water molecules, corresponding to the half reaction (1), is 1.23 V vs. RHE. In practice, a higher potential is always needed to overcome kinetic and thermodynamic barriers. The difference between the real potential and the ideal one is called the overpotential (η).

$$2\text{H}_2\text{O} \rightarrow 2\text{OH}^-
+ \text{OH}^-
+ \text{H}^+ + 4\text{e}^-$$  

(1)

The overpotential has two origins: kinetic barriers (related to transition state energies) and thermodynamic barriers (related to the stability of the intermediates). For OER on CoO$_x$, the active sites are believed to be adsorbed O, OH and OOH groups on a surface vacancy (denoted by *). The following equations resume the elementary steps of the OER:

$$\text{H}_2\text{O} + * \rightarrow *\text{OH} + \text{H}^+ + \text{e}^-$$  

(2)

$$*\text{OH} \rightarrow *\text{O} + \text{H}^+ + \text{e}^-$$  

(3)

$$*\text{O} + \text{H}_2\text{O} \rightarrow *\text{OOH} + \text{H}^+ + \text{e}^-$$  

(4)

$$*\text{OOH} \rightarrow *\text{O}_2 + \text{H}^+ + \text{e}^-$$  

(5)
The free energy associated with these steps is defined as:

\[ \Delta G_i = \Delta G_{\text{OH}} - eu - k_B T \log_{10} pH \]  
(6)

\[ \Delta G_2 = \Delta G_0 - \Delta G_{\text{OH}} - eu - k_B T \log_{10} pH \]  
(7)

\[ \Delta G_3 = \Delta G_{\text{OOH}} - \Delta G_0 - eu - k_B T \log_{10} pH \]  
(8)

\[ \Delta G_4 = 4.92 - \Delta G_{\text{OOH}} - eu - k_B T \log_{10} pH \]  
(9)

where \( U \) is the potential of the NHE. The sum of the four \( \Delta G \) values has been set to 4.92 eV, that is, the free energy for the formation of two water molecules. This thermodynamic approach avoids the calculation of the \( \Delta G \) bond energy, which is poorly estimated at the DFT-GGA level. A pH variation will shift all the \( \Delta G \)s of the same amount without changing the orders. This is the reason why one can work theoretically in acidic pH while, experimentally, the pH is basic. A detailed explanation of how these \( \Delta G \)s are computed is given in Supporting Information (section S4.1).

The free energies of the reactions (6)-(9) allows for estimating the thermodynamics overpotential:

\[ \eta(V) = \frac{\max(\Delta G_i)}{e} - 1.23 \]  
(10)

This computational approach only calculates the thermodynamic overpotential and hence lacks kinetic information. The potential dependence of the free energy is approximated by the computational hydrogen electrode model which gives good results for coupled proton-electron transfers.\(^{51}\) The method has been successfully applied for other materials (including CoOOH compounds) to understand electrocatalytic OER activity.\(^{44-46,52}\)

### Results and discussion

CoO\(_x\)/Ta\(_5\)N\(_5\) particles were synthesized according to the literature.\(^{22,23}\) Briefly, 2 wt% (metallic base) Co-loaded Ta\(_5\)N\(_5\) was heat treated at 700 °C for 1 h under NH\(_3\) flow to generate a reproducible photocatalytic performance. The addition of \( M \) 0.05 wt% (metallic base) to CoO\(_x\)/Ta\(_5\)N\(_5\) was achieved by immersing metal ions and heating under a N\(_2\) or H\(_2\) atmosphere at 400 °C. Detailed results for physicochemical characterization are listed in Supporting Information (Figures S1-S4). The photocatalytic activities of bare Ta\(_5\)N\(_5\), CoO\(_x\)/Ta\(_5\)N\(_5\), and M/CoO\(_x\)/Ta\(_5\)N\(_5\) samples were tested for OER in the presence of 0.1 M Na\(_2\)SO\(_4\) as the sacrificial electron acceptor. Figure 1A depicts the effects of various modifications on Ta\(_5\)N\(_5\) on the photocatalytic OER. In agreement with previous reports,\(^{22,23}\) the addition of CoO, onto Ta\(_5\)N\(_5\) nanoparticles followed by heat treatment significantly improves the OER performance (44 \( \mu\)mol h\(^{-1}\)). Modification of the CoO\(_x\)/Ta\(_5\)N\(_5\) photocatalyst with trace amounts of both Rh (see also Figure S5) and Ru (0.05 wt%) further improves the performance by a factor of \( \sim 3 \), reaching a maximum rate of 133 \( \mu\)mol h\(^{-1}\). The photocatalytic OER measured on samples not containing the CoO phase (RhO\(_x\)/Ta\(_5\)N\(_5\)) showed no improvement in photocatalytic activity compared with bare Ta\(_5\)N\(_5\), as shown in Figure 1A, demonstrating that the improvement in OER efficiency is linked to synergistic effects between CoO\(_x\) and noble metals (Ru or Rh). Furthermore, the photocatalytic OER activity of Rh-CoO\(_x\)/Ta\(_5\)N\(_5\) before and after heating under \( \text{H}_2 \) did not show any significant difference, as shown in Figure S6. This result certifies that the oxidation state of active Rh and Ru species is in its oxidized form. The variation of \( M \) actually shows a very sensitive trend: a loading of 0.05 wt% shows the maximized OER efficiency, whereas further loading decreased the OER efficiency, as shown in Figure S5. At pH 10.5 (Figure 1A), the photocatalysts deactivated with time. During OER, the pH continuously decreased as the reaction consumed OH\(^-\) (or produced H\(^+\)), which would in turn affect the photocatalytic activity. Indeed, the pH value of 10.5 after several hours of reaction drastically decreased to an acidic pH (~4-5), where CoO\(_x\) was no longer stable. To verify the impact of pH, photocatalytic OER on Rh/CoO\(_x\)/Ta\(_5\)N\(_5\) was also tested at pH 12 and 14, and the results are shown in Figure S7. As expected, oxygen was monotonically generated for a long period of time because of large concentration of OH\(^-\). Accordingly, pH after the reaction remained almost unchanged (pH ~ 11-13.5).

![Figure 1](image-url)

**Figure 1.** (A) Time courses of photocatalytic OER showing the effect of RhO\(_x\)/CoO\(_x\)/Ta\(_5\)N\(_5\) and RuO\(_x\)/CoO\(_x\)/Ta\(_5\)N\(_5\) (50 mg, 0.1 M Na\(_2\)SO\(_4\), pH 10.5 adjusted by NaOH) under visible light irradiation (420 < \( \lambda \) < 800 nm)); (B) photocatalytic reaction stability test using RhO\(_x\)/CoO\(_x\)/Ta\(_5\)N\(_5\) (50 mg, 0.1 M Na\(_2\)SO\(_4\), pH 14 adjusted by NaOH, 100 mL, under visible light irradiation (420 < \( \lambda \) < 800 nm)).

To investigate the stability of the RhO\(_x\)/CoO\(_x\) cocatalyst, the photocatalytic OER was conducted for up to 2 days at pH 14; the result is depicted in Figure 1B. The OER rate was initially slightly higher and then reached a steady-state rate after ~6 h, evolving a total of 2 mmol oxygen. The photocatalytic OER remained unchanged for the next 48 h after evacuation, indicating the excellent stability of Ta\(_5\)N\(_5\) and RhO\(_x\)/CoO\(_x\) as the photocatalyst and OER cocatalyst, respectively. After this long-term test, the action spectra were taken to calculate the QE; the results are shown in Figure 2 (and summarized in Table S1). The QE estimated between 400 and 680 nm correlates well with the estimated absorbance of the Ta\(_5\)N\(_5\) samples (which agrees with previous reports (Figure S1)).\(^{7,18}\) which is consistent with the bandgap excitation of Ta\(_5\)N\(_5\). The QE was observed >10% for wavelengths ranging between 440 and 520 nm, with a maximum value of 30% at 480 nm. The QE value at 500 nm (28%)
is much higher than the highest QE value ever reported for CoO$_2$-loaded Na$_2$CO$_3$/Ta$_2$N$_5$ and modified MgO-CoO$_2$/Ta$_2$N$_5$ for 500-600 nm wavelengths, in addition, a comparable QE value for CoO$_2$-loaded LaTiO$_2$N has been reported only at lower wavelengths (27% at 440 nm). Nevertheless, the choice of Na$_2$S$_2$O$_3$ as a strong sacrificial reagent may give rise to undesired reaction pathways (leading, e.g. to sulfate radicals), and the QE values may not reflect the true photonic efficiency, as quoted in the literature. The choice of the reagent was, however, carefully conducted to be able to carry out the reactions under alkaline conditions (pH 12-14) and an internal comparison of QE should be still valid. Separate experiments confirmed that no O$_2$ was evolved under dark in the presence of photocatalyst or under illumination in the absence of photocatalyst. In our previous work, we compared the photocatalytic OER using different electron acceptors for CoO$_2$/Ta$_2$N$_5$ samples. Figure S8 shows the comparison of photocatalytic OER on CoO$_2$/Ta$_2$N$_5$ in AgNO$_3$ (pH 8.5, La$_2$O$_3$ buffer) and Na$_2$S$_2$O$_3$ (pH 14, NaOH adjusted). The OER rate in AgNO$_3$ was higher than in Na$_2$S$_2$O$_3$, likely owing to the rapid kinetics of single electron transfer for Ag$^+$ ion reduction (thus expecting an even higher QE), compared to sluggish multiple electron transfer for S$_2$O$_5^-$ ion reduction. However, Ag$^+$ reduction leads to deposition of metallic Ag particles on Ta$_2$N$_5$ surface, and thus, strictly speaking, the process is not catalytic. More importantly, Ag cannot be used in strong alkaline solution as deposition of silver oxide occurs.

For further characterization of the photocatalyst materials after the reaction, we selected Na$_2$S$_2$O$_3$ as an electron acceptor yielding a catalytic process which can be used in alkaline solution.

Figure 2. Quantum efficiency of RhO$_2$/CoO$_2$/Ta$_2$N$_5$ and absorption coefficient of Ta$_2$N$_5$ (50 mg, 0.1 M Na$_2$S$_2$O$_3$, pH 14 adjusted by NaOH, 100 mL, 300 W Xe lamp; the photon numbers are shown in Table S1).

To address the improvement of the OER performance occurring over CoO$_2$/Ta$_2$N$_5$, separate electrochemical measurements of the active catalyst component isolated from the semiconductor led to a quantitative understanding of their photocatalytic OER activity. Electrodes mimicking the CoO$_2$, and M-doped CoO$_2$ on Ta$_2$N$_5$ were prepared on various substrates of Co plate and Ni foam (NF). As a reference, a Ni plate was also used to evaluate the noble metal addition. Figure 3 shows the $ir$ corrected potential-current diagram and Tafel plots for CoO$_2$, and M/CoO$_2$. The addition of M (Rh and Ru) drastically lowered the OER onset potential, consistent with the claims in the literature for other noble metals (Au, Ir, etc.). As a control experiment, the electrode with M supported on an NF or Ni plate gave lower performance, exhibiting poorer OER activities of M itself and/or little synergetic effects (Figure S9 and S10). The double layer capacitance ($C_d$), which is known to reflect an electrochemical active surface area, was also evaluated using impedance spectroscopy (Figure S11) and cyclic voltamograms (Figure S12). Figures S13 summarizes the obtained $C_d$ of the electrodes. The $C_d$ of M/CoO$_2$, and NiO$_2$ were found to be slightly greater than those of bare CoO$_2$, and NiO$_2$ (1–2 times for the cobalt substrate at 1.5–1.6 V vs. RHE). The observed difference in $C_d$, i.e., electrochemical active surface area, with/without noble metal addition was, however, much smaller than the difference in the OER activity. This observation clearly excludes the possibility that the enhanced OER performance simply originates from the increase in the surface area. Figure S14 provides measured charge transfer resistances of the electrodes by impedance data fitting. Noble metal addition to CoO$_2$, particularly RhO$_2$/CoO$_2$, significantly lowered the charge transfer resistance, which is consistent with the improved OER activity. These results confirm that the photocatalytic OER was improved by the metal doping and that synergetic effects between Co and M were present. Although the noble metal addition resulted in an improved OER performance, it did not significantly alter the Tafel slope (~40 mV dec$^{-1}$). These observations suggest that a similar reaction mechanism is prevalent, but that the intrinsic catalytic activity should be improved by Rh or Ru addition (i.e., enlargement in exchange current). The potential of the cocatalyst during the photocatalysis is shifted as a consequence of hole transfer, and even if the extent of the shift is identical between CoO$_2$ and M/CoO$_2$, the doped one will benefit from photocatalytic OER kinetics.

The mechanistic insight during electrocatalytic OER was further investigated by DFT calculations. The evaluation of the thermodynamic overpotential was performed using the protocol proposed by Bajdich et al. This protocol is presented briefly in the experimental section and more precisely in Supporting Information (section S4.1). In brief, the overpotential is imposed by the larger free energy (equations (6)-(9)) of the four steps of the catalytic cycle (equations (2)-(5)). The computed geometries for each of the four steps are presented in Figure 4 for the non-doped situation.

The overpotential was computed for the following scenario:

(i) The reaction happens on a Co atom on the non-doped surface.

(ii) The reaction happens on a Co atom with one dopant substituting the first neighbor Co.

(iii) The reaction happens on the dopant that substitutes one Co atom.

The computed thermodynamic overpotentials are presented in Table 1. It is clearly shown that Ru(IV) and Rh(IV) dopants make reaction energies more similar for the four steps, therefore enhancing the catalytic activity of surface Co atoms (see Figures S15–S17 for all the intermediate structures for the reaction, which happen in the presence of Ru(IV) and Rh(IV), all computed $\Delta G_s$ and bond length and charges). The rate enhancement induced by Rh(IV) and Ru(IV) is the consequence of a decrease of the reaction energy $\Delta G_s$ (corresponding to the $^*O \rightarrow ^*OOH$ step). The cause of this energy decrease is different for Rh(IV) and Ru(IV) dopings. For the Rh(IV), it is caused by a stabilization of the $^*OOH$ state, and for the Ru(IV), it is due to a destabilization of the $^*O$ state (see supporting information for more
performed on the Co atom. A large amount of dopants will inhibit the catalytic activity for a large amount of dopant (Figure S5).

Table 1. Computed overpotential (in V) for reaction occurring on Co atom (“On Co” line) or on the dopant (“On dopant” line).

<table>
<thead>
<tr>
<th></th>
<th>Non-doped</th>
<th>Rh(III)</th>
<th>Rh(IV)</th>
<th>Ru(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On Co</td>
<td>0.61</td>
<td>0.64</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td>On dop</td>
<td>--</td>
<td>0.95</td>
<td>0.67</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Figure 4. (A) Scheme of surface intermediates along the four elementary steps for oxygen evolution reaction; (B) Gibbs free energy for the four steps described in (A) for reaction happening on a Co atom using non-doped and M-CoOOH.

Figure 3. (A) Linear-sweep voltammograms (LSVs) and (B) Tafel plots over various electrodes: RhO₅/CoOₓ, RuO₅/CoOₓ, and CoOₓ. Measurements were carried out in 1.0 M NaOH electrolyte solution with O₂ bubbling at a −1 mV s⁻¹ scan rate and at 298 K. Solid line: with iR correction. Dotted line: without iR correction.

The dopants are not themselves good catalysts for the OER, as highlighted by the higher overpotential computed for these reaction paths compared with reactions performed on the Co atom. A large amount of dopants will inhibit the catalytic activity of the system because the concentration of Co on the surface will reduce and the dopants are not efficient for catalysis. This explains the experimental result, that is, a reduction of the catalytic activity for a large amount of dopant (Figure S5).

Interestingly, for Rh(III) and large decrease (resp. increase) of ΔG₁ (resp. ΔG₂) is computed. This is ascribed to a large destabilization of the surface vacancy state * itself as a consequence of the low spin state of Co(II) induced by Rh(III).
that metal addition on CoO, have an impact in the short-lived sample’s pump induced charge dynamics, the time window of which is characteristic for the hole dynamics in bare Ta$_3$N$_5$ samples as discussed below.

![Figure 5. OPTP dynamics, normalized to the long-lived plateau at 1200 ps, under 400 nm excitation for Ta$_3$N$_5$ (black diamonds), CoO/Ta$_3$N$_5$ (red squares), RuO$_2$/CoO$_2$/Ta$_3$N$_5$ (orange circles) and RhO$_2$/CoO$_2$/Ta$_3$N$_5$ (cyan stars) samples under an N$_2$ atmosphere. (A) and (B) indicate the same data but different time scale.](image)

![Figure 6. OPTP dynamics, normalized to the long-lived plateau at 1200 ps, under 400 nm excitation for Ta$_3$N$_5$ (black diamonds) and under 800 nm excitation for CoO/Ta$_3$N$_5$ (red squares), RuO$_2$/CoO$_2$/Ta$_3$N$_5$ (orange circles) and RhO$_2$/CoO$_2$/Ta$_3$N$_5$ (cyan stars) samples under an N$_2$ atmosphere. (A) and (B) indicate the same data but different time scale.](image)

Figure 6. In Figure 6, we compare carrier dynamics inferred by TRTS for bare Ta$_3$N$_5$ at 400 nm excitation and CoO/Ta$_3$N$_5$, RhO$_2$/CoO$_2$/Ta$_3$N$_5$ and RuO$_2$/CoO$_2$/Ta$_3$N$_5$ at 800 nm excitation. The data are also normalized at 1200 ps. In contrast to the 400 nm excitation beyond Ta$_3$N$_5$ bandgap, a 800 nm excitation is able to photoexcite only the CoO phases. As expected, no response was observed at 800 nm for the bare Ta$_3$N$_5$ sample. Consequently, the fact that the long-lived (ns timescale) photoconductivity dynamics are identical in all of the systems (Figure 6A) demonstrates that electron transfer from the nano-scaled CoO phase to the bulk-like Ta$_3$N$_5$ phase is efficient in the (M)/CoO/Ta$_3$N$_5$ samples. This electron transfer also suggests that the presence of a type II-like band alignment between CoO, and Ta$_3$N$_5$ phases. To further support this scenario, TRTS measurements were conducted on the samples consisting on CoO, and M/CoO$_2$ supported on SiO$_2$, which were prepared with exactly the same treatment as Ta$_3$N$_5$ samples. No TRTS real conductivity signal was resolved for all the SiO$_2$ supported samples, consistent with lack of electron transfer on the type I-like band alignment between CoO$_2$ and SiO$_2$. Furthermore, the identical long-lived components present for all samples, including bare Ta$_3$N$_5$, can be unambiguously assigned to electrons populating the Ta$_3$N$_5$ conduction band. These electrons do not experience enhanced recombination after the addition of CoO$_2$-related phases, e.g., CoO$_2$ or M/CoO$_2$ addition to Ta$_3$N$_5$ does not promote surface acceptors in the latter (at least to the extent that can affect carrier dynamics within the ~1 ns time window). As evident from Figure 6B, the dynamics within the first 10 ps are different between the two excitation cases; this strongly suggests that the short-lived component resolved in pure Ta$_3$N$_5$ samples under 400 nm excitation is a signature of ultrafast trapping of the holes in defects of the Ta$_3$N$_5$ phase. Such short carrier lifetime was reported at 8 ps for Ta$_3$N$_5$ by the time resolved spectroscopies.$^{18}$ In addition, the dynamics of Ta$_3$N$_5$ in Figure 6 reveal that the weights of the long-lived electrons and the short-lived holes are roughly equal, indicating that electron and hole mobilities in the Ta$_3$N$_5$ phase are rather similar. This observation agrees well with similar effective masses for electrons and holes theoretically estimated for Ta$_3$N$_5$.$^{17,28}$ The ultrafast quenching of holes at the Ta$_3$N$_5$ phase is consistent with its poor OER performance (provided that trapped holes are not energetically suitable to promote OER after trapping). From THz characterization, we cannot conclude whether the hole traps are present in the surface or in the bulk phase. The improvement of OER performance for the CoO/Ta$_3$N$_5$ sample compared with the bare Ta$_3$N$_5$ sample, although not directly revealed by the TRTS measurements, could correlate with a kinetic competition between hole trapping at the Ta$_3$N$_5$ and CoO$_2$ phases; the scavenging of holes toward the CoO$_2$ phases will be favored for samples containing noble metals if the relative band offset between Ta$_3$N$_5$ and CoO$_2$ is appropriately shifted after metal addition (a consequence of enhanced donor-acceptor free Gibbs energy gap; in good agreement with the following DFT results).

![Figure 7. THz photoconductivity measured at the photoexcitation wavelength of 400 nm (photoexcitation fluence 100 μJ cm$^{-2}$) for a pump-probe delay time of 200 ps. The closed symbols represent the real part and the open symbols show the imaginary part of the photoconductivity. The lines represent the fit of the spectra using the Drude-Smith model.](image)
This model is a phenomenological model commonly used for transport in disordered systems. Here, \( \sigma_{\text{DC}} \) is the extrapolated DC conductivity, \( \tau \) is the scattering time and \( c \) characterizes the measure of back-scattering of carriers in the sample. For all samples, we find \( c \) parameters between \(-0.9\) and \(-1\), which is indicative of electrons being confined at a length scale comparable to the size of a single \( \text{Ta}_5\text{N}_3 \) nanocrystal. From the data in Figure 7, we infer mobilities of electrons in the \( \text{Ta}_5\text{N}_3 \) phase of \( \mu \sim 0.1-3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \).

If Rh or Ru is incorporated into the \( \text{CoO}_x \) structure, there should be an influence on the electronic structure. Density of states (DOS) of these systems estimated by DFT calculation are shown in Figure 8, which analyzes the variations of electronic structures at band edges. It is shown that the valence band positions are positively shifted by doping. The top of the valence band has a contribution from the dopant but, in all cases, these states above the reference energy of \( \text{CoOOH} \) have a larger contribution from the bulk \( \text{CoOOH} \) material (>95%) than the dopant (<5%). These increases in the energy of the valence band edge upon doping improve the thermodynamic of the charge transfer and consequently its kinetics. Such small increase of valence band edge energy sufficiently accounts for an improvement of charge transfer efficiency. For the \( \text{Rh(IV)} \) and \( \text{Ru(IV)} \) doping, states localized on the dopant and oxygen atoms linked to the dopant clearly appear within the bandgap. These intermediate dopant states are responsible for the variation of the valence and conduction band edge energies. These results support the TRTS experiments, where a kinetic competition between hole transfer toward the \( \text{CoO}_x \) phase and trapping at the \( \text{Ta}_5\text{N}_3 \) phase is suggested.

**Conclusions**

We have shown a simple and effective method for improving the photocatalytic OER rate of \( \text{CoO}_x/\text{Ta}_5\text{N}_3 \) by adding a trace amount of Ru or Rh. By using electrochemistry and TRTS, we have provided experimental evidence where the possible causes of enhanced photocatalytic OER are two-fold: improved electrolysis and charge transfer. TRTS measurements demonstrate that \( \text{Ta}_5\text{N}_3 \) phases alone suffer ultrafast hole trapping; the \( \text{CoO}_x \) decoration must induce a kinetic competition between hole transfer toward the \( \text{CoO}_x \) phase and trapping at the \( \text{Ta}_5\text{N}_3 \) phase (which could be linked with OER improvement); reducing the work functions of \( \text{CoO}_x \) phases after noble metal addition (as revealed by DFT) will necessarily increase the free Gibbs energy for hole transfer toward the \( \text{CoO}_x \) phases, and then the kinetic competition between hole trapping at \( \text{Ta}_5\text{N}_3 \) and transfer from the \( \text{Ta}_5\text{N}_3 \) phase toward \( M-\text{CoO}_x \) should be favored for the latter (and, accordingly, the OER efficiency). In addition, \( C_0 \) sites neighboring dopant ions present a lower overpotential and therefore are more active for electrolytic OER, evident by electrochemical measurements and DFT. This study demonstrates the clear advancement of powder-photocatalyst characterization in combination with first-principle modeling for designing highly efficient solar energy conversion devices.

**ASSOCIATED CONTENT**

**Supporting Information.** Detailed experimental, physical and chemical characterizations are presented in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 8.** Calculated DOS of the computed of the pure \( \text{CoOOH} \) surface and the doped \( \text{CoOOH} \) surfaces. The energy reference is the vacuum level. Black curves are the total DOS and red curves are the projected DOS on the dopant. Filled and empty areas correspond to occupied and unoccupied states, respectively. Inset: Isosurface of the square of the moduli of selected states. Red, blue, white and green atoms are oxygen, cobalt, hydrogen and dopant, respectively.

To interrogate the nature of electron transport in bare and decorated \( \text{Ta}_5\text{N}_3 \) phases, we measured the complex ac photoconductivity spectra of the samples in the THz frequency range. Figure 7 shows the obtained photoconductivity response (normalized by the photon density). In Figure 7, the real part of the photoconductivity increases with the frequency and the imaginary part of the conductivity is negative. This is the characteristic signature of the transport of localized carriers, which can be modeled by using the Drude-Smith model,

\[
\sigma(\omega) = \frac{\sigma_{\text{DC}}}{1 - i\omega\tau} \left( 1 + \frac{c}{1 - i\omega\tau} \right).
\]