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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.6b00508 • Publication Date (Web): 23 May 2016

Downloaded from <http://pubs.acs.org> on May 29, 2016

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

Ela Nurlaela,[†] Hai Wang,^{‡,§} Tatsuya Shinagawa,[†] Sean Flanagan,[†] Samy Ould-Chikh,[†] Muhammad Qureshi,[†] Zoltán Mics,[‡] Philippe Sautet,^{||} Tangui Le Bahers,^{||} Enrique Cánovas,[‡] Mischa Bonn,[‡] and Kazuhiro Takanabe^{*,†}

[†]Division of Physical Sciences and Engineering, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), 4700 KAUST, Thuwal, 23955-6900, Saudi Arabia.

[‡]Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

[§]Graduate School of Material Science in Mainz, University of Mainz, Staudingerweg 9, 55128 Mainz, Germany.

^{||}Université de Lyon, Université Claude Bernard Lyon 1, ENS Lyon, Centre Nationale de Recherche Scientifique, 46 allée d'Italie, 69007 Lyon Cedex 07, France.

ABSTRACT: Understanding photophysical and electrocatalytic processes during photocatalysis in a powder suspension system 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 Ta₃N₅ 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 Na₂S₂O₈ 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 $\mu_e \sim 0.1\text{--}3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), which are not perturbed by the addition of CoO_x-related phases. Furthermore, we find that Ta₃N₅ 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 Ta₃N₅ 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.^{1–6} The main challenge lies in identifying materials suitable for efficient photocatalysis, i.e., with an optical response in the visible light region, and energy levels compatible with chemical reduction and/or oxidation. These properties converge in Ta₃N₅,^{1–18} 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.^{1–21} For efficient photocatalysis with the powder semiconductor, a solid-electrolyte interface is effectively utilized for charge separation, therein directly inducing surface chemical redox reactions. One strategy to improve the photocatalytic activity of Ta₃N₅ is to decorate the surface with an oxygen evolution reaction (OER) electrocatalyst, being an essential component to achieve high efficiency.^{21–24} 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 Ta₃N₅ surface; when appropriate, heat treatment is applied to construct an intimate CoO_x-Ta₃N₅ interface.²² 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)-catalyst interface, exploiting the differences in Fermi levels between them.^{25–29}

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.³⁰⁻³² Recently, the combination of CoO_x and a noble metal ($M\text{-CoO}_x$), such as an Au-CoO_x electrode, has drastically improved its performance, compared with that of its mono-metallic counterpart.³⁰ Because of its electro-negativity, Au may serve as an electron sink, facilitating the oxidation of Co^{II} and Co^{III} to Co^{IV} and increasing the availability of the active sites for OER.³⁰ In situ Raman spectroscopy during the electrochemical OER supports this scenario; it has been demonstrated that the population of Co^{IV} states is promoted in the presence of Au, which explains the higher current density on the Au-CoO_x sample.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}).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 $M\text{-CoO}_x$ in OER efficiency.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 $\text{CoO}_x/\text{BaTaO}_2\text{N}$ system, the addition of RhO_x has been found to significantly improve the photocurrent and lower the onset potential.³⁴ It was speculated that there is a synergetic 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 $\text{Ba-TaO}_2\text{N}$.³⁴ 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_2O_3 and TiO_2 photoanodes, revealed an increase in photogenerated holes' lifetime when adding a cocatalyst.³⁵⁻³⁷

In this work, we present a comprehensive study regarding the nature of enhanced photocatalytic OER on Ru and Rh co-loaded $\text{CoO}_x/\text{Ta}_3\text{N}_5$ 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 $\mu_e \sim 0.1\text{-}3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which are not perturbed by adding CoO_x -related phases. Furthermore, we find that Ta_3N_5 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_3N_5 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_3N_5) 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_3N_5 particles were prepared from commercially available crystalline Ta_2O_5 ($\geq 99.99\%$ metal basis, <5 microns, Sigma-Aldrich) by applying direct NH_3 nitridation under high temperature, as reported elsewhere.^{7,22-24} In a typical experiment, a total

of $0.5 \text{ g Ta}_2\text{O}_5$ 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_3N_5 was conducted using the wet-impregnation method.^{22,23} A known amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%) and $0.1 \text{ g Ta}_3\text{N}_5$ were suspended in $5 \text{ mL H}_2\text{O}$ 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 tubular furnace was conducted under NH_3 flow. A noble metal cocatalyst (Rh or Ru) was subsequently deposited onto the Co-impregnated Ta_3N_5 (hereafter, $\text{CoO}_x/\text{Ta}_3\text{N}_5$) 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 $\text{Na}_3\text{RhCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and were of analytical grade (Aldrich, 99.99% trace metal basis). For TRTS measurements, SiO_2 supported M/CoO_x samples were prepared in an identical procedure. Nonporous spherical SiO_2 (COSMO 30, JGC Catalysts and Chemicals Ltd.) was selected because of similar surface area as Ta_3N_5 ($10 \text{ m}^2 \text{ g}^{-1}$).

The diffuse reflectance spectra, surface oxidation state, and morphology of $\text{CoO}_x/\text{Ta}_3\text{N}_5$ and $M\text{-CoO}_x/\text{Ta}_3\text{N}_5$ 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.^{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 ($350 < \lambda < 800 \text{ nm}$). A cut-off filter (HOYA L 42) was used with the aforementioned light source ($420 < \lambda < 800 \text{ nm}$). 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 $0.1 \text{ M Na}_2\text{S}_2\text{O}_8$ 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 $\text{Na}_2\text{S}_2\text{O}_8$ was dissolved in $100 \text{ mL H}_2\text{O}$ 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(NO₃)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 contained 0.5 mM of Rh (hexachlororhodate, 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/HgSO₄ (sat. K₂SO₄) 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 potentiostat 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/Ta₃N₅ 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 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.³⁸

Our optical pump-THz probe (OTPP) 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 N₂ purged box to avoid any possible photo-oxidation.

Theoretical method

All theoretical calculations were performed using the Vienna Ab initio Software Package (VASP)^{39–41}, 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.^{43–46} 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}

The convergence criterion for the SCF cycles was fixed at 10^{−6} eV per unit cell. The E_{cut} value, defining the basis set size, was fixed at 400 eV. The k-points sampling was done with a 3×3×1 Monkhorst-Pack grid for slab calculations and 12×12×12 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.

All slabs were 2×2 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.*⁴⁴ 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.

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.⁴⁴ 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.

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).

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:

The free energy associated with these steps is defined as:

$$\Delta G_1 = \Delta G_{\text{OH}} - eU - k_B T \log_{10} pH \quad (6)$$

$$\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OH}} - eU - k_B T \log_{10} pH \quad (7)$$

$$\Delta G_3 = \Delta G_{\text{OOH}} - \Delta G_{\text{O}} - eU - k_B T \log_{10} pH \quad (8)$$

$$\Delta G_4 = 4.92 - \Delta G_{\text{OOH}} - eU - k_B T \log_{10} pH \quad (9)$$

where U is the potential of the NHE. The sum of the four ΔG 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 O_2 bond energy, which is poorly estimated at the DFT-GGA level. A pH variation will shift all the ΔG 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 ΔG 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:

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

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

$\text{CoO}_x/\text{Ta}_3\text{N}_5$ particles were synthesized according to the literature.^{22,23} Briefly, 2 wt% (metallic base) Co-loaded Ta_3N_5 was heat treated at 700 °C for 1 h under NH_3 flow to generate a reproducible photocatalytic performance. The addition of 0.05 wt% (metallic base) to $\text{CoO}_x/\text{Ta}_3\text{N}_5$ 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_3N_5 , $\text{CoO}_x/\text{Ta}_3\text{N}_5$, and $M/\text{CoO}_x/\text{Ta}_3\text{N}_5$ samples were tested for OER in the presence of 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ as the sacrificial electron acceptor. Figure 1A depicts the effects of various modifications on Ta_3N_5 on the photocatalytic OER. In agreement with previous reports,^{22,23} the addition of CoO_x onto Ta_3N_5 nanoparticles followed by heat treatment significantly improves the OER performance ($44 \mu\text{mol h}^{-1}$). Modification of the $\text{CoO}_x/\text{Ta}_3\text{N}_5$ photocatalyst with trace amounts of both Rh (see also Figure S5) and Ru (0.05 wt%) further improves the performance by a factor of ~ 3 , reaching a maximum rate of $133 \mu\text{mol h}^{-1}$. The photocatalytic OER measured on samples not containing the CoO_x phase ($\text{RhO}_x/\text{Ta}_3\text{N}_5$) showed no improvement in photocatalytic activity compared with bare Ta_3N_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- $\text{CoO}_x/\text{Ta}_3\text{N}_5$ before and after heating under 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 $\text{Rh}/\text{CoO}_x/\text{Ta}_3\text{N}_5$ 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. (A) Time courses of photocatalytic OER showing the effect of $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ and $\text{RuO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (50 mg, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, pH 10.5 adjusted by NaOH) under visible light irradiation ($420 < \lambda < 800 \text{ nm}$); (B) photocatalytic reaction stability test using $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (50 mg, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, pH 14 adjusted by NaOH, 100 mL, under visible light irradiation ($420 < \lambda < 800 \text{ nm}$)).

To investigate the stability of the $\text{RhO}_x/\text{CoO}_x$ 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 $\sim 6 \text{ h}$, 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_3N_5 and $\text{RhO}_x/\text{CoO}_x$ 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_3N_5 samples (which agrees with previous reports (Figure S1)),^{7–18} which is consistent with the bandgap excitation of Ta_3N_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_x -loaded $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ and modified $\text{MgO-CoO}_x/\text{Ta}_3\text{N}_5$ for 500–600 nm wavelengths.^{19,22} In addition, a comparable QE value for CoO_x -loaded LaTiO_2N has been reported only at lower wavelengths (27% at 440 nm).²⁵ Nevertheless, the choice of $\text{Na}_2\text{S}_2\text{O}_8$ 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.⁵³ 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,²³ we compared the photocatalytic OER using different electron acceptors for $\text{CoO}_x/\text{Ta}_3\text{N}_5$ samples. Figure S8 shows the comparison of photocatalytic OER on $\text{CoO}_x/\text{Ta}_3\text{N}_5$ in AgNO_3 (pH 8.5, La_2O_3 buffer) and $\text{Na}_2\text{S}_2\text{O}_8$ (pH 14, NaOH adjusted). The OER rate in AgNO_3 was higher than in $\text{Na}_2\text{S}_2\text{O}_8$, 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 $\text{S}_2\text{O}_8^{2-}$ ion reduction. However, Ag^+ reduction leads to deposition of metallic Ag particles on Ta_3N_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 $\text{Na}_2\text{S}_2\text{O}_8$ as an electron acceptor yielding a catalytic process which can be used in alkaline solution.

Figure 2. Quantum efficiency of $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ and absorption coefficient of Ta_3N_5 ²¹ (50 mg, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, 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 the $M\text{-CoO}_x/\text{Ta}_3\text{N}_5$, separate electrochemical measurements of the active catalyst component isolated from the semiconductor led to a quantitative understanding of their electrocatalytic OER activity. Electrodes mimicking the CoO_x and M -doped CoO_x on Ta_3N_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_x and M/CoO_x . 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.).^{30–33} 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_{dl}), which is known to reflect an electrochemical active surface area, was also evaluated using impedance spectroscopy (Figure S11) and cyclic voltammograms (Figure S12). Figures S13 summarizes the obtained C_{dl} of the electrodes. The C_{dl} of M/CoO_x and M/NiO_x were found to be slightly greater than those of bare CoO_x and NiO_x (1–2 times for the cobalt substrate at 1.5–1.6 V vs. RHE). The observed difference in C_{dl} , 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_x , particularly $\text{RhO}_x/\text{CoO}_x$, significantly lowered the charge transfer resistance, which is consistent with the improved OER activity. These results confirm that the electrocatalytic OER was improved by the metal doping and that synergistic 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 ($\sim 40 \text{ mV dec}^{-1}$). 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_x and M/CoO_x , 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.*⁴² 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:

- The reaction happens on a Co atom on the non-doped surface.
- The reaction happens on a Co atom with one dopant substituting the first neighbor Co.
- 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 ΔG_i , 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 ΔG_3 (corresponding to the $^*\text{O} \rightarrow ^*\text{OOH}$ 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 $^*\text{OOH}$ state, and for the Ru(IV), it is due to a destabilization of the $^*\text{O}$ state (see supporting information for more

discussion). Interestingly, for Rh(III) and large decrease (resp. increase) of ΔG_1 (resp. ΔG_4) 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).

Figure 3. (A) Linear-sweep voltammograms (LSVs) and (B) Tafel plots over various electrodes: RhO_x/CoO_x, RuO_x/CoO_x, CoO_x. 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).

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

	Non-doped	Rh(III)	Rh(IV)	Ru(IV)
On Co	0.61	0.64	0.40	0.42
On dopant	--	0.95	0.67	1.16

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.

To gain further insight into the improved OER performance of the nanocomposites after noble metal addition, we characterized carrier dynamics for the samples by using TRTS.³⁸ The photoconductivity dynamics were found to be linear, with the pump fluence up to $200 \mu\text{J cm}^{-2}$ and a 400 nm excitation. In Figure 5, we compare carrier dynamics inferred by TRTS for bare Ta₃N₅, CoO_x/Ta₃N₅, RhO_x/CoO_x/Ta₃N₅ and RuO_x/CoO_x/Ta₃N₅ at 400 nm excitation (greater than the Ta₃N₅ bandgap). We find that, while the long-lived ns dynamics overlap for all sample recipes (see Figure 5A), the ultrafast real photoconductivity for short pump-probe delays becomes negative upon decoration of Ta₃N₅ with CoO_x and M -CoO_x phases (see Figure 5B). Provided that the overall TRTS response reflects a combination of electron (e) and hole (h) dynamics in the samples ($\text{Re}(\sigma) = N_e \times \mu_e + N_h \times \mu_h$; where N and σ represent number of carriers and mobility), and that the CoO_x and M /CoO_x decoration is expected to affect primarily hole dynamics, we can tentatively assign the identical long-lived components to electrons populating the Ta₃N₅ conduction band. On the other hand, regarding the short-lived dynamics, as THz stimulated emission was ruled out experimentally, the observation of a pump-induced negative conductivity must be linked with carrier heating in the metallic phases of the samples.⁵⁴⁻⁵⁶ Unfortunately, this inhibits the unambiguous quantification of hole transfer processes from Ta₃N₅ to the CoO_x phases. In any case, as evident from Figure 5B (see also Figure S18), the strength of the pump-induced negative real conductivity associated with the CoO_x phase is clearly enhanced after M decoration. This demonstrates

that metal addition on CoO_x 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_3N_5 samples as discussed below.

Figure 5. OPTP dynamics, normalized to the long-lived plateau at 1200 ps, under 400 nm excitation for Ta_3N_5 (black diamonds), $\text{CoO}_x/\text{Ta}_3\text{N}_5$ (red squares), $\text{RuO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (orange circles) and $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (cyan stars) samples under an N_2 atmosphere. (A) and (B) indicate the same data but different time scale.

Figure 6. OPTP dynamics, normalized to the long-lived plateau at 1200 ps, under 400 nm excitation for Ta_3N_5 (black diamonds) and under 800 nm excitation for $\text{CoO}_x/\text{Ta}_3\text{N}_5$ (red squares), $\text{RuO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (orange circles) and $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ (cyan stars) samples under an N_2 atmosphere. (A) and (B) indicate the same data but different time scale.

In Figure 6, we compare carrier dynamics inferred by TRTS for bare Ta_3N_5 at 400 nm excitation and $\text{CoO}_x/\text{Ta}_3\text{N}_5$, $\text{RhO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ and $\text{RuO}_x/\text{CoO}_x/\text{Ta}_3\text{N}_5$ at 800 nm excitation. The data are also normalized at 1200 ps. In contrast to the 400 nm excitation beyond Ta_3N_5 bandgap, a 800 nm excitation is able to photoexcite only the CoO_x phases. As expected, no response was observed at 800 nm for the bare Ta_3N_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_x phase to the bulk-like Ta_3N_5 phase is efficient in the $(M)/\text{CoO}_x/\text{Ta}_3\text{N}_5$ samples. This electron transfer also suggests that the presence of a type II-like band alignment between CoO_x

and Ta_3N_5 phases. To further support this scenario, TRTS measurements were conducted on the samples consisting on CoO_x and M/CoO_x supported on SiO_2 , which were prepared with exactly the same treatment as Ta_3N_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_x and SiO_2 . Furthermore, the identical long-lived components present for all samples, including bare Ta_3N_5 , can be unambiguously assigned to electrons populating the Ta_3N_5 conduction band. These electrons do not experience enhanced recombination after the addition of CoO_x -related phases, e.g., CoO_x or M/CoO_x addition to Ta_3N_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_3N_5 samples under 400 nm excitation is a signature of ultrafast trapping of the holes in defects of the Ta_3N_5 phase. Such short carrier lifetime was reported at 8 ps for Ta_3N_5 by the time resolved spectroscopies.¹⁸ In addition, the dynamics of Ta_3N_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_3N_5 phase are rather similar. This observation agrees well with similar effective masses for electrons and holes theoretically estimated for Ta_3N_5 .^{57,58} The ultrafast quenching of holes at the Ta_3N_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 $\text{CoO}_x/\text{Ta}_3\text{N}_5$ sample compared with the bare Ta_3N_5 sample, although not directly revealed by the TRTS measurements, could correlate with a kinetic competition between hole trapping at the Ta_3N_5 and CoO_x phases; the scavenging of holes toward the CoO_x phases will be favored for samples containing noble metals if the relative band offset between Ta_3N_5 and CoO_x 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 $100 \mu\text{J cm}^{-2}$) 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.

Figure 8. Calculated DOS of the computed of the pure CoOOH surface and the doped 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 Ta_3N_5 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,

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

This model is a phenomenological model commonly used for transport in disordered systems.³⁸ Here, σ_{DC} is the extrapolated DC conductivity, τ 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 Ta_3N_5 nanocrystal. From the data in Figure 7, we infer mobilities of electrons in the Ta_3N_5 phase of $\mu \sim 0.1\text{--}3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

If Rh or Ru is incorporated into the 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 CoOOH have a larger contribution from the bulk 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.^{59–61} For the Rh(IV) and 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 CoO_x phase and trapping at the Ta_3N_5 phase is suggested.

Conclusions

We have shown a simple and effective method for improving the photocatalytic OER rate of $\text{CoO}_x/\text{Ta}_3\text{N}_5$ 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 electrocatalysis and charge transfer. TRTS measurements demonstrate that Ta_3N_5 phases alone suffer ultrafast hole trapping; the CoO_x decoration must induce a kinetic competition between hole transfer toward the CoO_x phase and trapping at the Ta_3N_5 phase (which could be linked with OER improvement); reducing the work functions of CoO_x phases after noble metal addition (as revealed by DFT) will necessarily increase the free Gibbs energy for hole transfer toward the CoO_x phases, and then the kinetic competition between hole trapping at Ta_3N_5 and transfer from the Ta_3N_5 phase toward $M\text{-CoO}_x$ should be favored for the latter (and, accordingly, the OER efficiency). In addition, Co sites neighboring dopant ions present a lower overpotential and therefore are more active for electrocatalytic 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>.

AUTHOR INFORMATION

Corresponding Author

* Kazuhiro Takanabe,

E-mail: kazuhiro.takanabe@kaust.edu.sa

ACKNOWLEDGMENT

The research reported in this work was supported by the King Abdullah University of Science and Technology. The authors also acknowledge the PSN and IDRIS computation centers for providing calculation resources.

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