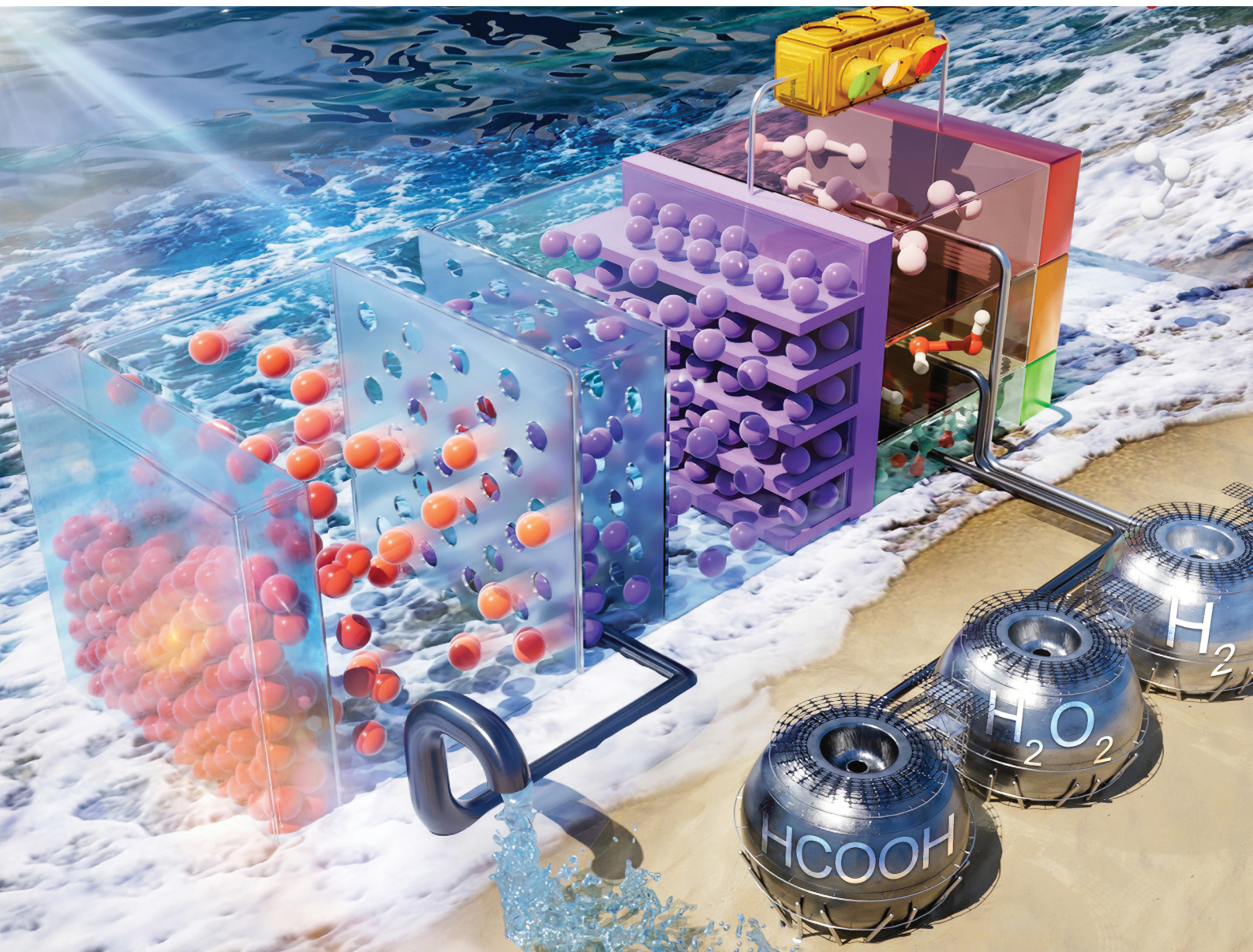


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**PAPER**

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value-added chemical production

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# A solar desalination charger for water treatment and value-added chemical production†

Seonghun Kim, <sup>a</sup> Dong Suk Han <sup>b</sup> and Hyunwoong Park <sup>\*a</sup>

This study presents a photoelectrocatalytic desalination charger for the remediation of aquatic pollutants and the production of value-added chemicals. Under 1 sun irradiation, a Co-WBVO (BiVO<sub>4</sub> doped with W and deposited with CoOOH) photoelectrode and aqueous Na<sub>x</sub>C electrode (Na on carbon felt, Na<sub>x</sub>C) pair efficiently desalinates brackish water (0.171 M NaCl) through ion-exchange membranes at an ion transport efficiency of ~100%. The desalted chloride is partially oxidized by photogenerated holes into reactive chlorine species (RCSs) at a faradaic efficiency (FE) of >90%. The *in situ* generated RCSs are actively involved in the sequential oxidation of As(III) and NH<sub>4</sub><sup>+</sup>. Meanwhile, the desalted Na<sup>+</sup> is rapidly inserted into Na<sub>x</sub>C without any accumulation. Upon coupling with the charged Na<sub>x</sub>C, the electrocatalytic production of H<sub>2</sub>O<sub>2</sub> *via* O<sub>2</sub> reduction with carbon nanotubes, H<sub>2</sub> *via* H<sub>2</sub>O reduction with NiMoS, and HCOOH *via* CO<sub>2</sub> reduction with porous Bi are achieved at FEs of >80%. The as-designed PEC hybrid of the proof-of-concept can be applied to various purposes, including desalination, seawater electrolysis, production of value-added chemicals, and energy storage.

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## Broader context

Producing carbon-neutral chemicals and securing clean water are considered the most critical issues facing humanity over the next five decades. Among the proposed technical solutions to address these challenges, photoelectrocatalytic (PEC) systems working with inexhaustible carbon-free solar energy have been proven to be environmentally benign and technically feasible. Considering the maritime transport of green chemicals (*e.g.*, H<sub>2</sub>), PEC systems must be operated near coastal areas with abundant saline water for cheap production.

This study presents a PEC desalination charger for hybrid water reuse and solar chemical production. The primary feature of the PEC system is that it simultaneously drives many valuable reactions in a single device. During the desalination of brackish water, the desalted Cl<sup>-</sup> is oxidized to reactive chlorine species (RCSs; represented by HOCl/OCl<sup>-</sup>), which effectively mediate the oxidation of aquatic contaminants in the photoanode compartment. The desalted Na<sup>+</sup> is concurrently accumulated in an aqueous Na metal electrode (Na on carbon felt, Na<sub>x</sub>C).

We designed a PEC desalination cell comprising visible light-active photoanodes (W-doped BiVO<sub>4</sub> deposited with CoOOH) with selective chloride oxidation reaction and a Na<sub>x</sub>C cathode with saline water (NaCl at 10 g L<sup>-1</sup>). The photoanodes were particularly tailored to partially oxidize the desalted chloride to RCSs while minimizing hyperoxidation into less reactive species (*e.g.*, ClO<sub>3</sub><sup>-</sup>) under simulated sunlight. These *in situ* generated RCSs effectively mediated the oxidation of mixed aquatic contaminants (As<sup>3+</sup> and NH<sub>3</sub>). Na<sub>x</sub>C was photocharged simultaneously with the desalted Na<sup>+</sup>. After termination of irradiation, the charged Na<sub>x</sub>C was used to produce H<sub>2</sub>O<sub>2</sub> *via* O<sub>2</sub> reduction reaction ( $E^\circ = 0.695$  V), H<sub>2</sub> *via* HER ( $E^\circ = 0$  V), and formic acid *via* CO<sub>2</sub>RR ( $E^\circ = -0.2$  V) with the as-designed carbon nanotubes (CNTs), NiMoS, and Bi, respectively. To the best of our knowledge, this is the first attempt to demonstrate a solar desalination charger. This approach should address an intrinsic challenge facing PEC systems whose operation is limited to the intermittent nature of sunlight with daily fluctuations and unavailability during nighttime.

## 1. Introduction

Producing carbon-neutral chemicals and securing clean water are considered the most critical issues facing humanity over the next five decades.<sup>1–5</sup> Among the proposed technical solutions to

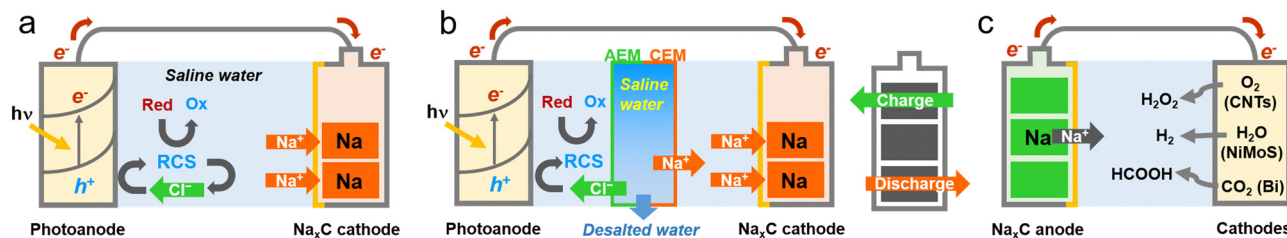
address these challenges, photoelectrocatalytic (PEC) systems working with inexhaustible, carbon-free solar energy have been proven to be environmentally benign and technically feasible.<sup>6–8</sup> For example, a PEC device with 10% efficiency can produce molecular hydrogen at ~0.7 g s<sup>-1</sup> *via* splitting clean water under the standard terrestrial 1 sun with an average daily power of ~250 W m<sup>-2</sup>.<sup>7,9–11</sup> Considering the maritime transport of H<sub>2</sub> and its liquid-phase carriers (*e.g.*, ammonia), the PEC systems must be operated near coastal areas with abundant saline water for cheap production. However, if obtaining the clean water from saline water is energy-intensive and

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**Scheme 1** Schematic illustrations of (a) solar charge with water treatment, (b) solar water treatment and charge with desalination, and (c) the discharge process with value-added chemical production. (a) A photoelectrode (bare and modified BiVO<sub>4</sub>) and an Na metal array (Na<sub>x</sub>C) electrode are directly coupled in saline water with As(III) and NH<sub>3</sub>. Upon irradiation, the photoelectrode oxidizes Cl<sup>-</sup> to reactive chlorine species (RCS) mediating the oxidation of As(III) and NH<sub>3</sub>. Simultaneously, Na<sup>+</sup> ions are inserted into the Na<sub>x</sub>C electrode. (b) Both electrodes are separated by anion- and cation-exchange membranes (AEM and CEM, respectively), and the photoelectrode is placed in non-saline water with As(III) and NH<sub>3</sub>. The middle compartment between the two membranes (desalination cell) is filled with saline water. Upon irradiation, desalination proceeds, and the desalted Cl<sup>-</sup> and Na<sup>+</sup> undergo the same reactions as those in (a). (c) The charged Na<sub>x</sub>C electrode is coupled to three different electrodes (CNTs, NiMoS, and porous Bi) to produce H<sub>2</sub>O<sub>2</sub> via O<sub>2</sub> reduction, H<sub>2</sub> via H<sub>2</sub>O reduction, and HCOOH via CO<sub>2</sub> reduction, respectively.

significantly carbon-footprinted, the technoeconomic merits of the PEC system would weaken.

Recently, PEC desalination systems have been proposed for hybrid water reuse and solar chemical production.<sup>12</sup> In contrast to the conventional PEC reactions, the PEC desalination mimics electro dialysis in terms of system construction. The primary feature of the PEC desalination process is to simultaneously drive many valuable reactions in a single device (Scheme 1). Specifically, desalted Cl<sup>-</sup> is oxidized to reactive chlorine species (RCSs, represented by HOCl/OCl<sup>-</sup>) which effectively mediate the oxidation of aquatic contaminants in the photoanode compartment.<sup>12</sup> The desalted Na<sup>+</sup> is concurrently accumulated in the cathode compartment and increases the catholyte conductivity, assisting the H<sub>2</sub> evolution reaction (HER) and CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). This proof-of-concept was further demonstrated using an expandable multi-stack PEC desalination device for the chloride oxidation reaction (ClOR), and metal composite cathodes for the HER and CO<sub>2</sub>RR.<sup>12–14</sup> During the decomposition of aqueous substrates in the photoanode compartment, either HER or CO<sub>2</sub>RR occurred at a faradaic efficiency of >90%. Concurrent desalination of saline water (salinity 5–36 g L<sup>-1</sup>) proceeded with low specific energy consumption (1.1 kW h m<sup>-3</sup>). The as-produced H<sub>2</sub> energy was estimated to further contribute to saving energy by 25–30%.<sup>13</sup>

We noted the potential use of the accumulated Na<sup>+</sup> in charging an aqueous Na metal electrode. This approach should address an intrinsic challenge facing PEC systems whose operation is limited to an intermittent nature of sunlight with daily fluctuation and unavailability during nighttime. The aqueous Na metal electrode is characterized by its theoretical specific energy (1165 mA h g<sup>-1</sup>) and high cell voltage (–2.71 V).<sup>15,16</sup> In this study, we designed a PEC desalination cell comprising visible light-active photoanodes (W-doped BiVO<sub>4</sub> deposited with CoOOH) with a selective ClOR and aqueous Na metal cathode (Na on carbon felt, Na<sub>x</sub>C) with saline water (NaCl at 10 g L<sup>-1</sup>). The photoanode was particularly tailored to partially oxidize the desalted chloride to RCSs while minimizing hyper-oxidation into less reactive species

(e.g., ClO<sub>3</sub><sup>-</sup>) under simulated sunlight. These *in situ* generated RCSs effectively mediated the oxidation of mixed aquatic contaminants (As<sup>3+</sup> and NH<sub>3</sub>). Simultaneously, the Na<sub>x</sub>C was photocharged with desalted Na<sup>+</sup>. After termination of irradiation, the charged Na<sub>x</sub>C was utilized for the production of H<sub>2</sub>O<sub>2</sub> via the O<sub>2</sub> reduction reaction (ORR) ( $E^\circ = 0.695$  V), H<sub>2</sub> via HER ( $E^\circ = 0$  V), and formic acid via the CO<sub>2</sub>RR ( $E^\circ = -0.2$  V) with the as-designed CNTs, NiMoS, and Bi, respectively. To the best of our knowledge, this is the first attempt to demonstrate a solar desalination charger.

## 2. Experimental section

### 2.1. Synthesis of materials

Bare and W-doped BiVO<sub>4</sub> (BVO and WBVO, respectively) were synthesized by electrodeposition and calcination.<sup>17,18</sup> Fluorine-doped SnO<sub>2</sub> (FTO) substrates (~50 nm-thick FTO layer coated onto soda lime glass with resistivity of 6–9 Ω sq<sup>-1</sup>, Pilkington) were cleansed with ethanol (99.9%, Duksan) under ultrasonication and dried with an N<sub>2</sub> stream. For Bi deposition, BiNO<sub>3</sub>·5H<sub>2</sub>O (75 mM, 10 mL, Junsei) was dissolved in aqueous KI solution (0.4 M, Sigma-Aldrich) adjusted at pH 1.7 using HNO<sub>3</sub> (60%, Daejung). Then, *p*-benzoquinone (0.23 M, dissolved in 99.9% ethanol, Sigma-Aldrich) was added to the Bi solution and stirred for 5 min. The as-prepared FTO substrate (working electrode) with a Pt rod (counter electrode) and saturated calomel electrode (SCE, reference electrode) was immersed in the Bi solution and held at –0.2 V vs. SCE for 15 min using a potentiostat (Ivium). The Bi-deposited electrode was rinsed with deionized water (18 MΩ cm) and dried under ambient conditions. Then, vanadyl acetylacetonate (VO(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, 0.2 M, 0.26 mL, Sigma-Aldrich) dissolved in dimethyl sulfoxide (DMSO, Sigma-Aldrich) was dropped onto the Bi-deposited electrode and annealed at 450 °C for 2 h. The sample electrodes were immersed in KOH (1 M) solutions for 30 min and rinsed with deionized water to remove residual V<sub>2</sub>O<sub>5</sub>. For the synthesis of WBVO, tungsten chloride (WCl<sub>6</sub>, Sigma-Aldrich) was added to the vanadyl acetylacetonate solution at various



concentrations (0.55–2.77 mM, corresponding to doping levels of 0.3–1.5 at%). When necessary, the as-synthesized WBVO samples were immersed in aqueous Co(II) solution ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.1 M, Sigma-Aldrich) and biased at  $-0.9$  V vs. SCE with deposition charges of 5–30 mC (denoted as Co-WBVO). Unless otherwise specified, the W doping level was 0.3 at% and the Co deposition charge was 10 mC. Prior to photoelectrolysis, the Co-WBVO electrode underwent six times potential sweeping from  $-0.4$  to  $1.5$  V vs. SCE.

For photocharging processes, an arrayed aqueous Na metal electrode (Na on carbon felt,  $\text{Na}_x\text{C}$ , 4 TO ONE Co., Ulsan, Korea) with four-unit (coin-type) cells was coupled to the photoelectrodes. Each array was composed of a top cap, NASICON ( $\text{Na}_3\text{Si}_2\text{Zr}_2\text{PO}_{12}$ , diameter of 16 mm, ion conductivity of  $\sim 2.5 \times 10^{-3}$  S  $\text{cm}^{-1}$ ), 1 M  $\text{NaCF}_3\text{SO}_3$  (Sigma-Aldrich) dissolved in tetraethylene glycol dimethyl ether (Sigma-Aldrich), sodium metal on carbon felt, a spacer, a spring, and a bottom cap. All fabrication processes were conducted in glove boxes.<sup>19</sup> For  $\text{H}_2$  production, NiMoS (mixed  $\text{Ni}_2\text{S}_3$  and  $\text{MoS}_2$ ) was electrochemically fabricated onto porous Ni substrates.<sup>13</sup> For  $\text{H}_2\text{O}_2$  production, multi-walled carbon nanotubes (CNTs) were loaded onto a commercial carbon paper (315  $\mu\text{m}$ -thick, Sigracet 39 BB).<sup>20</sup> For  $\text{CO}_2$  reduction to formic acid, a porous, dendrite-structured Bi electrode was fabricated on Cu substrates *via* galvanostatic electrodeposition (5 A  $\text{cm}^{-2}$ ) for 5 s.<sup>21</sup> Detailed synthetic procedures of the electrocatalysts were described elsewhere.<sup>13,20,21</sup>

## 2.2. Photoelectrocatalytic and electrocatalytic activity tests

Linear sweep voltammograms of the as-synthesized bare and modified BVO electrodes were obtained at a scan rate of 20  $\text{mV s}^{-1}$  under simulated sunlight (AM 1.5G, 100  $\text{mW cm}^{-2}$ , ABET Tech) in a single compartment cell containing 0.171 M NaCl (Daejung, 99%). An SCE and Pt foil were used as reference and counter electrodes, respectively. Electrochemical impedance spectra and Mott-Schottky plots were obtained in the frequency range of 0.01–100 kHz at 0 V and 1 kHz at 0.73 V vs. SCE, respectively. The incident photon-to-current efficiency (IPCE) was estimated using the following equation:

$$\text{IPCE (\%)} = 1239.8 (\text{V nm}) \times J_{\text{ph}} \times 100\% / P_{\text{light}} \times \lambda \quad (1)$$

where  $J_{\text{ph}}$ ,  $P_{\text{light}}$ , and  $\lambda$  are the photocurrent density ( $\text{mA cm}^{-2}$ ), incident light power (100  $\text{mW cm}^{-2}$ ), and wavelength (nm), respectively. The PEC activities were examined for the ClOR in a two-compartment cell divided by a proton-exchange membrane (Nafion 117, Chemours) containing 0.171 M NaCl (pH  $\sim 6.5$ ) under galvanostatic conditions ( $J_{\text{ph}} = 1$   $\text{mA cm}^{-2}$ ).

For oxidation of aquatic substrates with simultaneous charging with Na ions, the as-synthesized photoelectrodes (working electrode) were coupled to the  $\text{Na}_x\text{C}$  electrode (counter electrode) and SCE in a single compartment cell with 0.171 M NaCl containing 1 mM  $\text{NH}_3$  ( $\text{NH}_4\text{Cl}$ , Aldrich) and/or 1 mM arsenite ( $\text{As}(\text{III})$ ,  $\text{NaAsO}_2$ , Aldrich) at pH  $\sim 6.5$ . (Scheme 1a). While applying a constant  $J_{\text{ph}}$  (1  $\text{mA cm}^{-2}$ ), a photopotential ( $E_{\text{ph}}$ ) of the working electrode (vs. SCE) and a potential difference ( $E_{\text{cell}}$ )

between the photoelectrode and  $\text{Na}_x\text{C}$  electrode were simultaneously recorded using a potentiostat (Ivium) and multimeter (Keysight, 34461A), respectively. For simultaneous ternary reactions (desalination of saline water, oxidation of ammonia and/or  $\text{As}(\text{III})$ , and charging with Na ions), a cell comprising a photoanode compartment with 0.171 M NaCl (20 mL) containing 1 mM  $\text{As}(\text{III})$  and/or  $\text{NH}_3$ , desalination compartment with saline water (0.171 M NaCl, 5 mL), and cathode compartment with 5 mM NaCl (20 mL) was designed with an anion exchange membrane (AEM, AMI-7001S, Membranes International) and a cation exchange membrane (CEM, CMI-7000S, Membranes International) (Scheme 1b). The desalination compartment was circulated at a flow rate of 10  $\text{mL min}^{-1}$  using a peristaltic pump (Ismatec, Reglo ICC). While applying a constant  $J_{\text{ph}}$  of 1  $\text{mA cm}^{-2}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  in the electrolyte and saline water were quantified to examine the inter-compartment ion transport.

After the PEC processes, the charged  $\text{Na}_x\text{C}$  electrode was wired to (i) a CNT electrode in 0.1 M  $\text{K}_2\text{SO}_4$  purged with  $\text{O}_2$  (pH 6.5) for hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) production *via*  $\text{O}_2$  reduction, (ii) a NiMoS electrode in 0.1 M KOH purged with  $\text{N}_2$  (pH  $\sim 13$ ) for  $\text{H}_2$  evolution *via*  $\text{H}_2\text{O}$  reduction, or (iii) a Bi electrode in 0.1 M  $\text{KHCO}_3$  purged with  $\text{CO}_2$  (pH 6.8) for formate ( $\text{HCOO}^-$ ) production *via*  $\text{CO}_2$  reduction (Scheme 1c). Prior to bulk electrolysis, linear sweep voltammograms (vs. SCE) of each electrocatalyst (working electrode) were obtained with the charged  $\text{Na}_x\text{C}$  (counter electrode) in a single compartment cell. While applying  $J$  of  $-1$  and  $-3$   $\text{mA cm}^{-2}$  to the working electrodes, the potentials of the working electrodes (vs. SCE) and  $E_{\text{cell}}$  (potentials difference between the working and counter electrode) were simultaneously recorded using the potentiostat and multimeter, respectively. In addition, the CNTs and charged  $\text{Na}_x\text{C}$  were galvanically coupled *via* direct wiring or through an LED bulb ( $\lambda = 566$  nm, size of  $3\phi$ , forward voltage of 1.8–2.2 V, max current of 20 mA, DFRobot Co.).

During the PEC desalination and discharging processes, aliquots were intermittently sampled and analyzed. The anions ( $\text{Cl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ ) and cations ( $\text{Na}^+$  and  $\text{NH}_4^+$ ) were analyzed using ion chromatographs (Thermo Scientific, DIONEX ICS-1100) equipped with a conductivity detector, IonPac As-11HC (4  $\times$  250 mm) column for anions, and IonPac CS-12A (4  $\times$  250 mm) column for cations, respectively.<sup>22</sup> RCSs ( $\text{HClO}$ / $\text{ClO}^-$ ) were quantified using the *N,N*-diethyl-*p*-phenylenediamine (DPD) reagent (Hach method).<sup>22</sup>  $\text{As}(\text{V})$  and  $\text{H}_2\text{O}_2$  were quantified using the molybdenum blue method<sup>23</sup> and DMP method,<sup>23,24</sup> respectively. Formate was quantified using high-performance liquid chromatography (Waters 2695 Separation Module) equipped with a dual absorbance detector (Waters 2487, 210 nm) and a column (BIO-RAD, Aminex HPLC-87H, 300 mm  $\times$  7.8 mm).<sup>21,25</sup>  $\text{H}_2$  was quantified using a gas chromatograph (GC, Agilent 7820) equipped with a thermal conductivity detector (TCD) and carboxen 1000 column. Detailed analytical methods for the as-mentioned chemicals were described in the cited references.

The Faradic efficiency (FE), specific energy consumption (SEC, for 50% desalination), and ion transport efficiency (ITE) were estimated by the following equations:



$$FE (\%) = (\text{Amount of product} \times 2F) \times 100\% / (J \times A \times t) \quad (2)$$

$$SEC (\text{kW h m}^{-3}) = E_{\text{cell}} \times J \times A \times t / (\text{saline water volume}) \quad (3)$$

$$ITE (\%) = (\text{Amount of transported monovalent ion}) / (J \times A \times t) \quad (4)$$

where  $F$ ,  $E_{\text{cell}}$ ,  $J$ ,  $A$ , and  $t$  are the Faraday constant ( $96485 \text{ C mol}^{-1}$ ), operating cell voltage (V), operating current density ( $\text{mA cm}^{-2}$ ), electrode area ( $\text{cm}^2$ ), and time (s), respectively. In eqn (2), the product refers to chemicals produced with 2 electron-transfers (*i.e.*,  $\text{HClO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ , and  $\text{HCOOH}$ ). To reflect pH differences, when necessary, “V vs. SCE” was converted to “ $V_{\text{RHE}}$ ” by the following:  $V_{\text{RHE}} = V \text{ vs. SCE} + 0.241 + 0.059 \times \text{pH}$ .

### 2.3. Surface characterization

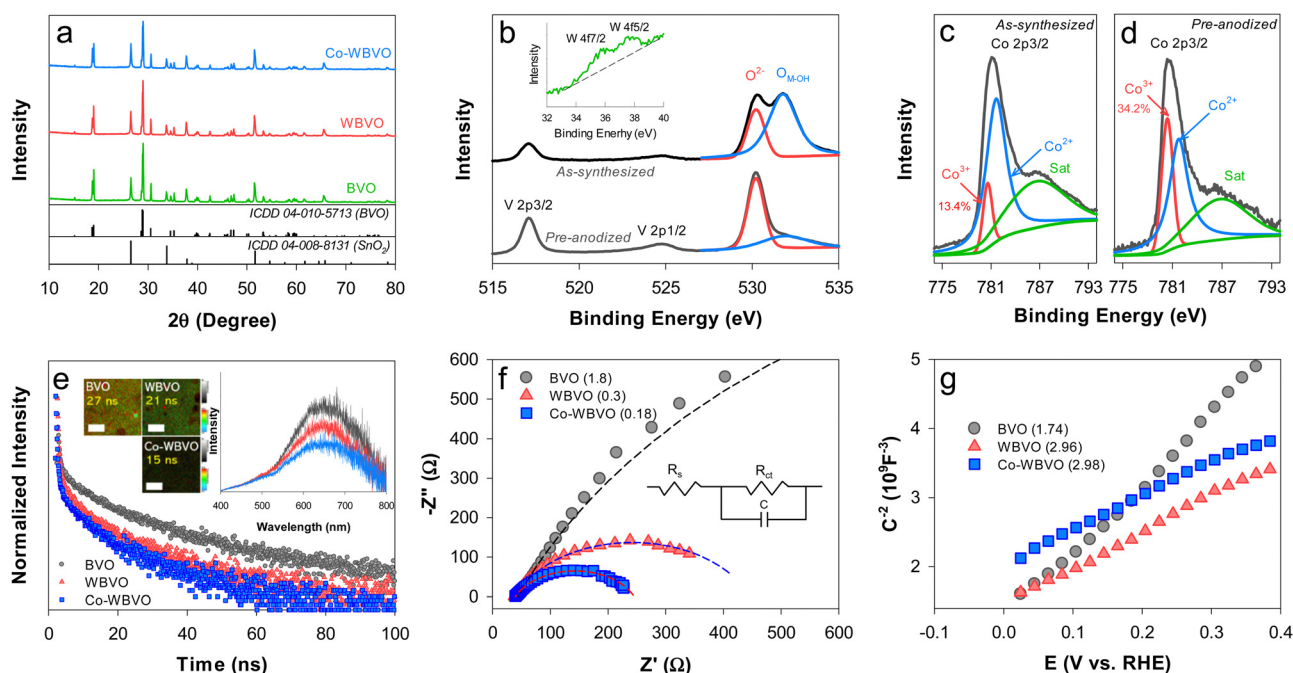
The top and cross-sectional morphologies of the as-synthesized bare and modified BVO samples were examined using a field emission scanning electron microscope (FE-SEM, Hitachi SU8200; accelerating voltage of 5 kV; emission current of 9.8  $\mu\text{A}$ ; working distance 10.8 mm). X-ray diffraction (XRD, PANalytical EMPUREAN) with Cu-K $\alpha$  radiation (40 kV and 30 mA) and X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo Fisher Scientific) with Al-K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) were employed to examine the crystallite structures of the samples and binding states of the component elements, respectively. A UV-visible absorption spectrometer (Shimadzu, UV-2450) was

used to examine the transmittance of the samples. The time-resolved photoluminescence (TRPL) study was carried out using a confocal microscope (MicroTime-200, Picoquant, Germany). The lifetime measurements were performed at the Korea Basic Science Institute (KBSI), Daegu Center, Korea. A single-mode pulsed diode laser (375 nm with 30 ps pulse width and average power of  $\sim 10 \mu\text{W}$  operating in 2 MHz repetition rate) was used as an excitation source. The steady-state PL spectrum was obtained by dividing and guiding emission photons through an optical fiber to the external spectrometer (F-7000, Hitachi). A detailed analytical procedure of TRPL was described elsewhere.<sup>26</sup>

## 3. Results and discussion

### 3.1. Photoelectrocatalytic activity of the as-synthesized electrodes

The as-synthesized BVO sample exhibited the typical monoclinic crystal structure (ICDD# 04-010-5713) (Fig. 1a). W-doping did not influence the crystallinity of BVO. Neither W- nor Co-oriented XRD peaks (*e.g.*,  $\text{WO}_3$  and  $\text{Co}_2\text{O}_3$ , respectively) were observed with WBVO and Co-WBVO, because of trace amounts of doped W and deposited Co. The bare and modified BVO samples showed the morphologies grown *via* interparticle connection, with an overall film thickness of  $\sim 1.8 \mu\text{m}$  (Fig. S1, ESI<sup>†</sup>). Compared to the bare BVO, the morphology of WBVO was more distinct with small particles, while Co-WBVO had a



**Fig. 1** (a) XRD patterns of the FTO substrate, BVO, WBVO, and Co-WBVO. XPS spectra of (b) the V 2p and O 1s bands (inset: W 4f bands) and (c) and (d) the Co 2p<sub>3/2</sub> bands for Co-WBVO (as-synthesized and pre-anodized). The numbers in (c) and (d) refer to the areal fractions of the deconvoluted Co<sup>3+</sup> peaks with respect to the Co peaks. (e)–(g) Optical and electrochemical characterization of BVO, WBVO, and Co-WBVO: (e) TRPL spectra. The inset shows 2D emission lifetime images and PL spectra. The white bars represent 20  $\mu\text{m}$ , and the numbers are average emission decay lifetimes ( $\tau$ ). (f) EIS spectra in 0.171 M NaCl. The numbers in parentheses refer to the charge transfer resistance ( $R_{\text{ct}}$ ) values (k $\Omega$ ) estimated by fitting the spectra to the Randles circuit model. (g) Mott–Schottky plots in 0.171 M NaCl. The numbers in parentheses refer to donor density ( $N_{\text{D}}$ ,  $\times 10^{22} \text{ cm}^{-3}$ ).

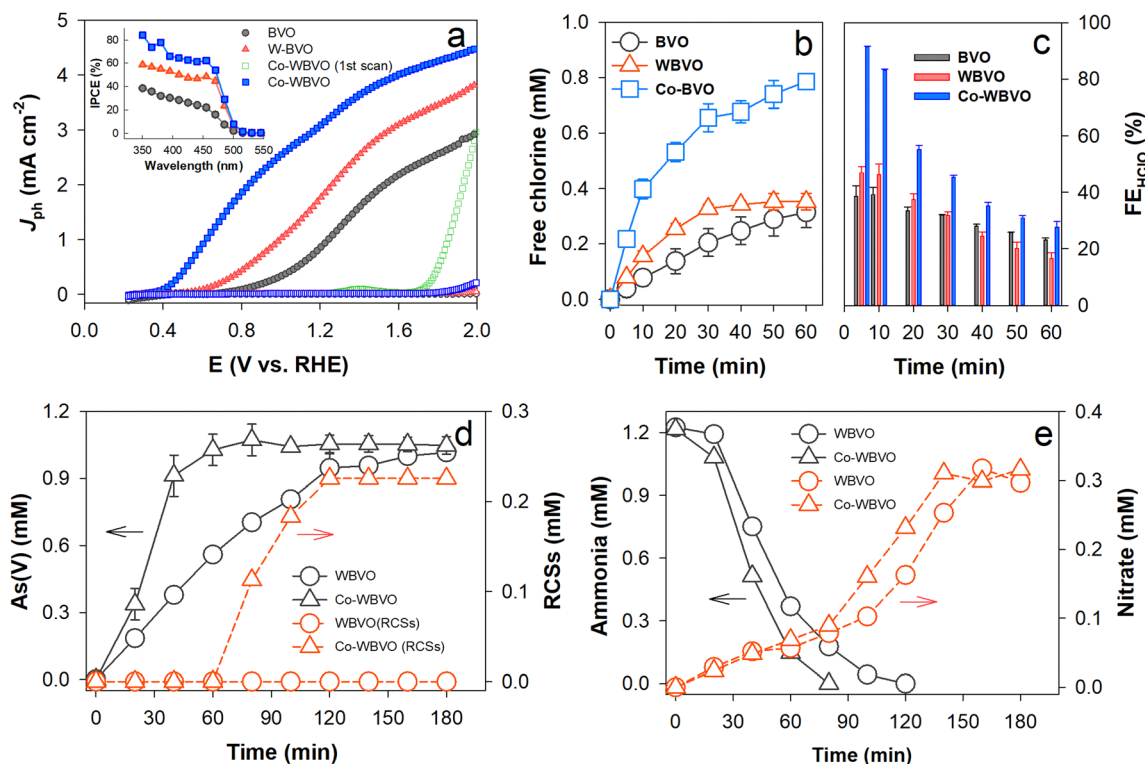


rougher surface and less agglomeration. Meanwhile, XPS analysis with Co-WBVO obviously revealed the presence of W and Co. The atomic level of W was estimated to be 0.25% with respect to Bi (Fig. 1b). However, the W doping did not induce spectral difference of the Bi 4f and V 2p bands (Fig. S2, ESI†). Notably, the oxidation states of the deposited Co were mixed with  $\text{Co}^{2+}$  (781.6 eV) and  $\text{Co}^{3+}$  (780.5 eV) at a  $\text{Co}^{3+}$  fraction of 13.4% (Fig. 1c). After pre-anodization, the fraction of  $\text{Co}^{3+}$  increased to  $\sim 34\%$  (Fig. 1d). A concurrent decrease in the metal-OH intensity of the O 1s band was also observed. This change should indicate that the as-deposited Co species was primarily  $\text{Co}(\text{OH})_2$ <sup>27,28</sup> and oxidized to  $\text{CoOOH}$  upon repetitive anodic scans.<sup>29</sup> Co deposition onto WBVO did not induce a significant change in the film thickness. This further indicates that the thin Co layer did not interfere with light absorption.<sup>30</sup>

TRPL was used to examine the charge transfer dynamics of the bare and modified BVO films (Fig. 1e). Upon excitation at  $\lambda = 375$  nm, the PL spectra showed broad emission bands in the  $\lambda$  range of 400–800 nm, with the maximum at  $\lambda \sim 650$  nm (*ca.* 1.9 eV) (Fig. 1e inset). These emission bands were attributed to the radiative recombination of photogenerated electron and hole pairs *via* intermediate trap states within the bandgap.<sup>31,32</sup> However, the maximum emission intensity was lowered by W-doping and Co-deposition, indicating inhibited charge recombination. The normalized TRPL emission intensity with bare BVO exponentially decayed with an average

lifetime ( $\tau$ ) of 27 ns. WBVO exhibited the same decay profile yet with a relatively small  $\tau$  value (21 ns). Co-deposition further decreased the  $\tau$  value to 15 ns. The 2D-emission lifetime images showed that the brightness was not uniform throughout the detected regions with BVO and WBVO (Fig. 1e inset). However, Co-WBVO was entirely dark due to the fast, uniform charge transfer kinetics. EIS analysis was also performed to gain insight into the interfacial charge transfer resistance ( $R_{\text{ct}}$ ) (Fig. 1f). The Nyquist plots showed a large semicircle with  $R_{\text{ct}}$  of  $\sim 1.8$  k $\Omega$  for BVO, whereas WBVO and Co-WBVO exhibited significantly reduced semicircles with  $R_{\text{ct}}$  values of  $\sim 0.3$  and 0.18 k $\Omega$ , respectively. The predominant effect of  $\text{W}(\text{vi})$ -doping on the reduction of  $R_{\text{ct}}$  was attributed to an increase in donor density ( $N_{\text{D}} \sim 3 \times 10^{22}$  cm<sup>-3</sup>), enhancing the electrical conductivity of BVO ( $N_{\text{D}} \sim 1.7 \times 10^{22}$  cm<sup>-3</sup>) (Fig. 1g). Co-deposition also contributed to reduction in  $R_{\text{ct}}$  but marginally, which was attributed to a similar  $N_{\text{D}}$  value to that of WBVO.

The linear sweep voltammograms with bare and modified BVO photoanodes were obtained in aqueous NaCl solutions (0.171 M, pH  $\sim 6.5$ ) (Fig. 2a). The bare BVO showed an onset potential ( $E_{\text{on}}$ ) of  $\sim 0.8$  V<sub>RHE</sub> with  $J_{\text{ph}} \sim 1.45$  mA cm<sup>-2</sup> for CLOR ( $J_{\text{ph,CLOR}}$ , estimated at  $E^{\circ}(\text{Cl}_2/\text{Cl}^-) = 1.36$  V<sub>RHE</sub>). This  $J_{\text{ph,CLOR}}$  value is quite comparable to those in the literature (Table S1, ESI†). W-doping significantly influenced the voltammograms, leading to the lowest  $E_{\text{on}}$  ( $\sim 0.6$  V<sub>RHE</sub>) and the highest  $J_{\text{ph,CLOR}}$  (2.4 mA cm<sup>-2</sup>) at doping levels of 0.3–0.6 at% (Fig. S3, ESI†).



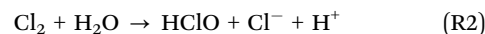
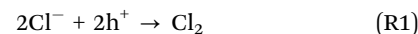
**Fig. 2** PEC activities of the bare and modified BVO samples in 0.171 M NaCl. (a) Linear sweep voltammograms. The inset shows IPCE profiles at  $E = 1.36$  V<sub>RHE</sub>. (b) and (c) RSC (represented by HClO) production and  $\text{FE}_{\text{RCSs}}$ . (d) Oxidation of As(III) (1 mM) to As(V) and production of RCSs with Co-WBVO. (e) Oxidation of  $\text{NH}_3$  (1 mM) and concurrent production of nitrate ( $\text{NO}_3^-$ ). The bulk PEC reactions (b)–(e) were performed in a two-compartment cell at  $E = 0.73$  V<sub>SCE</sub> (corresponding to  $E = 1.36$  V<sub>RHE</sub>; note that the solution pH changed with time, and hence, the SCE scale was used).



Although the primary role of the W dopant is to enhance charge separation (see Fig. 1e), its heavy doping induces a structural change from the monoclinic scheelite to tetragonal scheelite.<sup>33,34</sup> This should decrease the PEC activity at W-doping levels over 0.6 at%. Notably, the Co-WBVO showed different voltammograms with repetitive potential sweeps. In the first sweep,  $E_{\text{on}}$  ( $\sim 1.7 V_{\text{RHE}}$ ) was  $\sim 0.9 V$  more positive than those without Co deposition (*i.e.*, BVO and WBVO) and  $J_{\text{ph,ClOR}}$  increased dramatically at  $E > E_{\text{on}}$ . From the second to the fifth sweep,  $E_{\text{on}}$  gradually shifted to low potential and reached to  $0.4 V_{\text{RHE}}$  with  $J_{\text{ph,ClOR}}$  of  $3.55 \text{ mA cm}^{-2}$  (Fig. S4, ESI<sup>†</sup>). These changes in the voltammogram were attributed to gradual oxidation of the as-deposited  $\text{Co(OH)}_2$  to  $\text{CoOOH}$  during the oxidative potential sweeps (see Fig. 1c and d).<sup>30</sup> This Co oxidation shifted the flatband potential of WBVO from 0 to  $-0.1 V_{\text{RHE}}$  (see Fig. 1g), enhancing band-bending and charge separation.<sup>28,35</sup> It was also found that the optimal charge amount for Co deposition was 10 mC (Fig. S5, ESI<sup>†</sup>). A further deposition at 30 mC degenerated Co-WBVO. In agreement with the voltammogram profiles, the IPCE values of Co-WBVO were greater than those of BVO and WBVO (Fig. 2a inset). However, the onset wavelengths for  $J_{\text{ph}}$  generation and IPCE were the

same at  $\lambda \sim 505 \text{ nm}$  for bare and modified BVOs, owing to their similar bandgaps of 2.45 eV (Fig. S6, ESI<sup>†</sup>). This indicates that the employed surface modification enhanced the charge transfer efficiency,<sup>36</sup> not affecting the intrinsic electronic structure of BVO.

The ClOR was further examined at  $E = 1.36 V_{\text{RHE}}$  in a two-compartment cell divided by a proton-exchange membrane (Fig. 2b). With bare BVO, a stable  $J_{\text{ph,ClOR}}$  of  $\sim 1.5 \text{ mA cm}^{-2}$  flowed over 60 min (Fig. S7, ESI<sup>†</sup>) and RCSs (represented by  $\text{HClO}$ ) were produced *via* ClOR with photogenerated holes ( $\text{h}^+$ ) (reactions (R1) and (R2)).



The FE for RCS production ( $\text{FE}_{\text{RCSs}}$ ) with bare BVO was  $\sim 40\%$  in the initial stage (Fig. 2c). W-doping significantly increased  $J_{\text{ph,ClOR}}$  ( $\sim 2.4 \text{ mA cm}^{-2}$ ) but marginally  $\text{FE}_{\text{ClOR}}$  ( $\sim 48\%$ ). This indicates that the primary effect of W-doping was to enhance charge separation, with marginal contribution to charge injection (*i.e.*, catalytic reaction).<sup>36</sup> With Co-WBVO, the RCS production was 4-5-fold enhanced with an  $\text{FE}_{\text{RCSs}}$  of  $> 90\%$

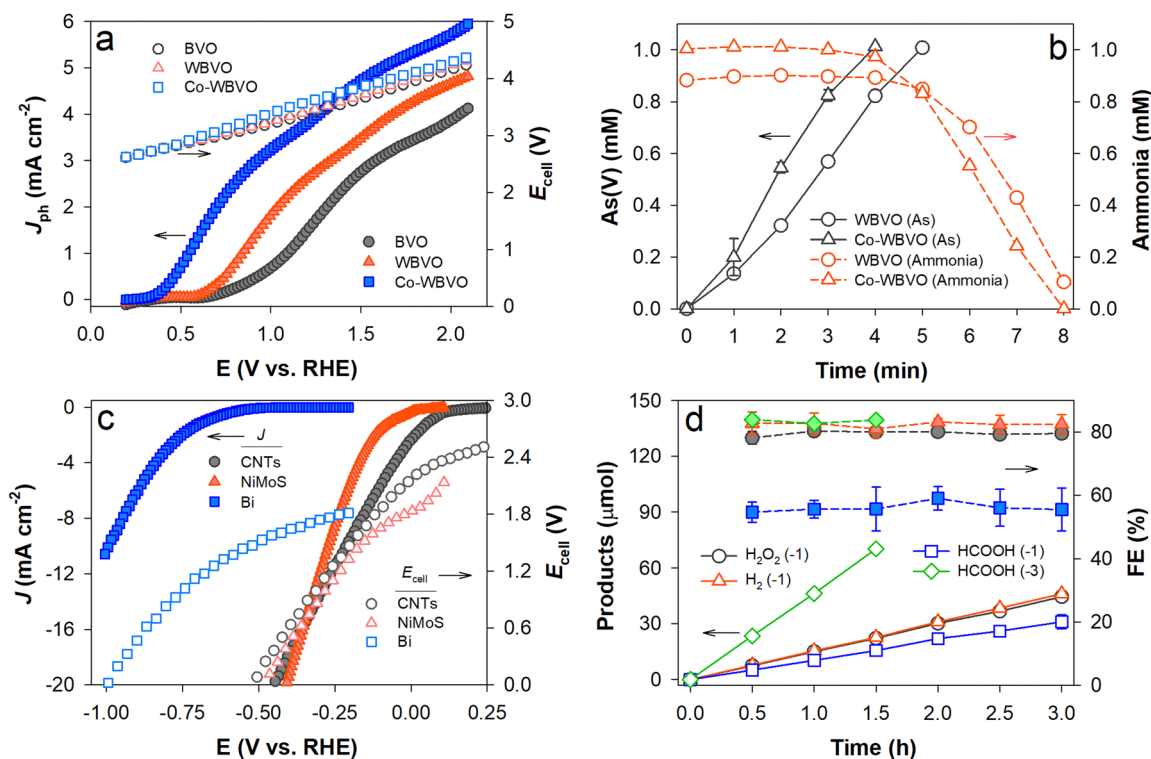
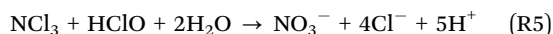
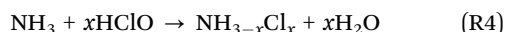


Fig. 3 (a) and (b) PEC charge and (c) and (d) electrocatalytic discharge reactions. In the photocharge stage, the photoanodes were coupled to the  $\text{Na}_x\text{C}$  electrode in a 0.171 M  $\text{NaCl}$  solution with mixed  $\text{As(III)}$  and  $\text{NH}_3$ . Scheme 1a shows the experimental setup. In the discharging stage, the charged  $\text{Na}_x\text{C}$  electrode was disconnected from the photoanodes. It was then connected to each of three different electrocatalysts (CNTs for  $\text{O}_2$  reduction in 0.1 M  $\text{K}_2\text{SO}_4$  purged with  $\text{O}_2$  at pH 6.5;  $\text{NiMoS}$  for  $\text{H}_2$  evolution in 0.1 M  $\text{KOH}$  purged with  $\text{N}_2$  at pH 13;  $\text{Bi}$  for  $\text{CO}_2$  reduction in 0.1 M  $\text{KHCO}_3$  purged with  $\text{CO}_2$  at pH 6.8). Scheme 1c shows the experimental setup. (a) Linear sweep voltammograms of the photoelectrodes and concurrent changes in the cell voltages ( $E_{\text{cell}}$ ) of the photoelectrode– $\text{Na}_x\text{C}$  pairs. (b) Simultaneous oxidation of  $\text{As(III)}$  (1 mM) and  $\text{NH}_3$  (1 mM) at  $J = 1 \text{ mA cm}^{-2}$  during the photocharge stage. (c) Linear sweep voltammograms of the electrocatalysts and concurrent changes in the  $E_{\text{cell}}$  values of the electrocatalyst and charged  $\text{Na}_x\text{C}$  pairs. (d) Production and FEs of  $\text{H}_2\text{O}_2$  *via*  $\text{O}_2$  reduction with CNTs,  $\text{H}_2$  *via* water reduction with  $\text{NiMoS}$ , and  $\text{HCOOH}$  *via*  $\text{CO}_2$  reduction with  $\text{Bi}$  during the discharge stage. The numbers in parentheses are the applied  $J$  values (unit:  $\text{mA cm}^{-2}$ ).



( $J_{\text{ph,ClOR}} \sim 3.55 \text{ mA cm}^{-2}$ ). Notably, the production of RCSs leveled off in the later stage of PEC reaction for all three photoelectrodes. Considering that diffusion of HClO to the counter electrode compartment was inhibited because of the membrane, the as-observed leveling off phenomenon should be attributed to the oxidation of HClO to chlorate ( $\text{ClO}_3^-$ ) (Fig. S8, ESI<sup>†</sup>). Nevertheless, the FE values for chlorate formation with Co-WBVO ( $\sim 10\%$ ) were significantly lower than those with BVO ( $\sim 30\%$ ) and WBVO ( $\sim 20\%$ ), indicating that the deposited CoOOH catalyzed the selective oxidation of  $\text{Cl}^-$  to HClO.

The as-produced RCSs were active for *in situ* oxidation of As(III) to As(V) (reaction (R3)). With WBVO at  $E = 1.36 V_{\text{RHE}}$  in NaCl solution, As(V) was produced with an apparent rate constant ( $k_{\text{app}}$ ) of  $0.45 \text{ min}^{-1}$  (Fig. 2d). With Co-WBVO, the As(V) production was significantly enhanced with  $k_{\text{app}}$  of  $0.78 \text{ min}^{-1}$ . RCSs were produced right after the complete oxidation of As(III) ( $\sim 60 \text{ min}$ ), confirming that the RCSs were the primary reactive species.<sup>37</sup> No further increase in the amount of RCSs in  $\sim 120 \text{ min}$  was attributed to concurrent oxidation of HClO to  $\text{ClO}_3^-$ . The decomposition of ammonia was also examined (Fig. 2e). Similar to the case of As(III) oxidation, Co-WBVO exhibited a faster decomposition kinetics than WBVO. For both photoelectrodes, the ammonia decomposition accompanied the gradual production of nitrate. Even after a complete decomposition of ammonia, the nitrate production continued because of the sequential oxidation of *N*-chloroamine intermediates (e.g.,  $\text{NH}_{3-x}\text{Cl}_x$ ) by HClO (reactions (R4) and (R5)).<sup>38</sup> Compared to As(III), the slower oxidation of ammonia was attributed to the eight-electron transfer reaction, requiring four HClO molecules per 1 ammonia molecule.



### 3.2. PEC charging and electrocatalytic discharging reactions

To drive PEC ClOR and charging with sodium ions, WBVO and Co-WBVO photoelectrodes were coupled to arrayed  $\text{Na}_x\text{C}$  electrodes (four units) in aqueous NaCl solutions containing both As(III) and  $\text{NH}_3$ . Fig. 3a shows the linear sweep voltammograms with the photoelectrodes and simultaneous changes in the cell voltages ( $E_{\text{cell}}$ s) of the photoelectrode and  $\text{Na}_x\text{C}$  array electrode pairs. The overall voltammogram profiles were similar to conventional ones with the Pt counter electrode (see Fig. 2a). However,  $J_{\text{ph}}$  with  $\text{Na}_x\text{C}$  was greater than that with Pt. Increasing a number of  $\text{Na}_x\text{C}$  enhanced the  $J_{\text{ph}}$  values (Fig. S9a, ESI<sup>†</sup>). It appears that the  $\text{Na}^+$  insertion (charging) kinetics with  $\text{Na}_x\text{C}$  was comparable to the  $\text{H}^+$  reduction with Pt and partially influenced the behavior of the photoelectrodes.<sup>39</sup> With increasing potential bias,  $E_{\text{cell}}$  increased linearly because of the PEC charging of  $\text{Na}_x\text{C}$ , yet less significantly with more unit  $\text{Na}_x\text{C}$  electrodes (Fig. S9b, ESI<sup>†</sup>). When  $J_{\text{ph}}$  of  $1 \text{ mA cm}^{-2}$  was applied to WBVO and Co-WBVO, photopotentials ( $E_{\text{ph}}$ ) of  $\sim 0.7 V_{\text{SCE}}$  and  $\sim 0.5 V_{\text{SCE}}$  ( $1.06$  and  $0.86 V_{\text{RHE}}$ , respectively) were maintained over 8 h, with  $E_{\text{cell}}$ s of  $\sim 4.0$  and  $\sim 3.7 \text{ V}$ , respectively

(Fig. S10, ESI<sup>†</sup>). During the PEC ClOR with Co-WBVO and simultaneous charging of  $\text{Na}_x\text{C}$  arrays, As(III) was continuously oxidized to As(V) for 4 h (Fig. 3b). Soon after completion of the As(III) oxidation, the ammonia decomposition was initiated and completed in  $\sim 4 \text{ h}$  (hence a total  $\sim 8 \text{ h}$  for completion of both As(III) oxidation and ammonia decomposition). A similar behavior was observed for WBVO yet with retarded kinetics. Compared to WBVO, the faster decomposition rates with Co-WBVO should be attributed to greater  $\text{FE}_{\text{RCSs}}$  values (i.e., greater amounts of RCSs; see Fig. 2b).

After the PEC processes, the charged  $\text{Na}_x\text{C}$  electrode with  $8 \text{ mA h}$  ( $= 1 \text{ mA cm}^{-2} \times 1 \text{ cm}^2 \times 8 \text{ h}$ ) was coupled to CNTs,<sup>20</sup>

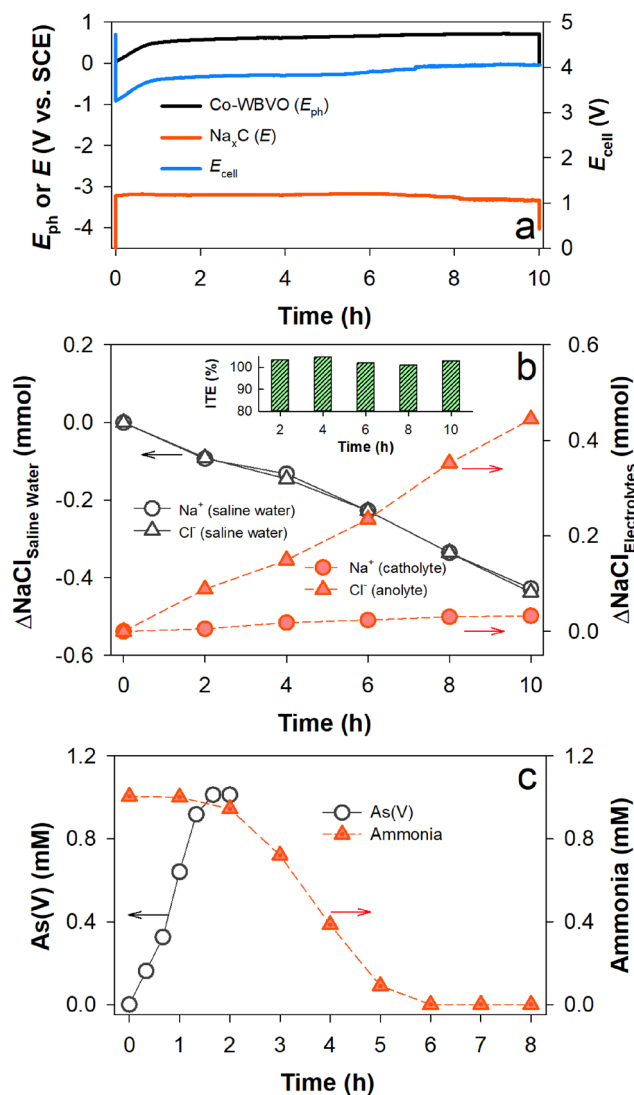
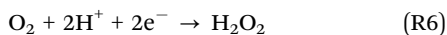


Fig. 4 Solar charge process with desalination of saline water (0.171 M NaCl) and oxidation of mixed As(III) and  $\text{NH}_3$  (each 1 mM). A Co-WBVO photoelectrode (with the SCE) and an  $\text{Na}_x\text{C}$  electrode were immersed in 0.171 M NaCl solutions. Scheme 1b shows the experimental setup. (a) Changes in the  $E_{\text{ph}}$  of Co-WBVO and the  $E_{\text{cell}}$  of the Co-WBVO- $\text{Na}_x\text{C}$  pair at  $J_{\text{ph}}$  of  $1 \text{ mA cm}^{-2}$ . (b) Changes in the amounts of  $\text{Na}^+$  and  $\text{Cl}^-$  in saline water,  $\text{Na}^+$  in the catholyte, and  $\text{Cl}^-$  in the anolyte. The inset shows the ITEs. (c) Changes in As(V) and  $\text{NH}_3$  concentrations. For the WBVO- $\text{Na}_x\text{C}$  pair, see Fig. S13 (ESI<sup>†</sup>).





NiMoS,<sup>13,40</sup> and porous Bi electrodes<sup>21,41</sup> specifically designed for the production of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>, and HCOOH (representing formic acid and formate) *via* reductions of O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>, respectively, under various conditions (reactions (R6)–(R8)).



The voltammogram with the as-synthesized CNT electrode showed  $E_{\text{on}}$  of 0.2 V<sub>RHE</sub>, corresponding to the open-circuit  $E_{\text{cell}}$  of 2.5 V for the CNTs and Na<sub>x</sub>C pair (Fig. 3c). Cathodic  $J_{\text{CNTs}}$  increased linearly with increasing negative  $E_{\text{CNTs}}$ , whereas  $E_{\text{cell}}$  decreased because of the discharging process with Na<sub>x</sub>C. Upon a constant  $J_{\text{CNTs}}$  of  $-1 \text{ mA cm}^{-2}$ ,  $E_{\text{CNTs}}$  of 0.035 V<sub>RHE</sub> and  $E_{\text{cell}}$  of  $\sim 2.25 \text{ V}$  were maintained over 3 h (Fig. S11, ESI<sup>†</sup>). Simultaneously, H<sub>2</sub>O<sub>2</sub> was linearly produced with time with an FE of  $> 80\%$  (Fig. 3d). The obtained FE values were quite similar to those in the literature,<sup>20</sup> indicating that the PEC charging and post-discharging process successfully worked.

The voltammograms with the NiMoS and Bi electrodes showed that the HER and CO<sub>2</sub>RR need  $\sim 0.2$  and  $\sim 0.7$  V-greater  $E_{\text{on}}$  values, respectively, than that for the H<sub>2</sub>O<sub>2</sub> production reaction. These led to decreases in the open-circuit  $E_{\text{cell}}$  values to 1.85 and 1.48 V, respectively. At a constant  $J$  of  $-1 \text{ mA cm}^{-2}$ , H<sub>2</sub> and HCOOH were produced linearly over 3 h, while constant potentials ( $E_{\text{NiMoS}} = -0.085 \text{ V}_{\text{RHE}}$ ;  $E_{\text{Bi}} = -0.7 \text{ V}_{\text{RHE}}$ ) and  $E_{\text{cell}}$  values (1.8 V and 1.27 V, respectively) were maintained (Fig. S11a, ESI<sup>†</sup>). The FE of H<sub>2</sub> production was  $\sim 80\%$ , which was quite similar to that in the literature.<sup>13</sup> In contrast, the FE of HCOOH production was as low as  $\sim 60\%$ . Our previous study showed that the optimal potential with the Bi electrode for CO<sub>2</sub>RR was found to be approximately  $-0.85 \text{ V}_{\text{RHE}}$ , whereas FE decreased to  $\sim 55\%$  at  $E_{\text{Bi}}$  of  $-0.7 \text{ V}_{\text{RHE}}$ .<sup>21</sup> Hence, when  $J_{\text{Bi}}$  increased to  $-3 \text{ mA cm}^{-2}$ , a stable  $E_{\text{Bi}}$  of  $-0.8 \text{ V}_{\text{RHE}}$  was obtained and the FE of HCOOH production enhanced to  $> 80\%$ . The productions of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> were also

enhanced at  $J$  of  $-3 \text{ mA cm}^{-2}$  with FEs of  $> 80\%$  (Fig. S12, ESI<sup>†</sup>). However, the Na<sub>x</sub>C electrode was rapidly discharged at  $J$  of  $-3 \text{ mA cm}^{-2}$  and  $E_{\text{cell}}$ s dropped in  $\sim 1 \text{ h}$  (Fig. S11b, ESI<sup>†</sup>).

### 3.3. PEC desalination-coupled charging of Na<sub>x</sub>C

For coupling PEC charging and desalination processes, a membrane device composed of a photoelectrode compartment with As(III) and NH<sub>3</sub>, desalination compartment with saline water, and cathode compartment with Na<sub>x</sub>C was designed (Scheme 1b). With Co-WBVO at a constant  $J_{\text{ph}}$  of  $1 \text{ mA cm}^{-2}$ ,  $E_{\text{ph}}$  rapidly increased to  $\sim 0.53 \text{ V}_{\text{SCE}}$  in 1 h and was stabilized at  $\sim 0.6 \text{ V}_{\text{SCE}}$  over 10 h (Fig. 4a). This behavior was quite similar to that without the desalination process (Fig. S10, ESI<sup>†</sup>). The device  $E_{\text{cell}}$  followed the same trend as that of  $E_{\text{ph}}$ , reaching  $\sim 4.1 \text{ V}$  in 10 h. During the PEC charging process, the amount of chloride in the saline water decreased linearly with time and the amount of chloride in the anolyte simultaneously increased (Fig. 4b). The total  $\Delta\text{Cl}^-$  in the saline water and anolyte in 10 h were the same as  $\sim 0.45 \text{ mmol}$ , indicating a unidirectional Cl<sup>-</sup> transport from the saline water to the anolyte. Accordingly, the ITE for Cl<sup>-</sup> was maintained to be  $\sim 100\%$  over 10 h (Fig. 4b inset). The SEC for 50% desalination was estimated to be  $7.7 \text{ kW h m}^{-3}$ , which was higher than a previous study by 1.48 times.<sup>13</sup> Meanwhile, the oxidation of As(III) (1 mM) to As(V) was completed in 2 h; subsequently, the ammonia decomposition proceeded for the following 4 h (Fig. 4c). Similar behaviors were also found in the case without the desalination compartment (see Fig. 3b).

It should be noted that the amount of Na<sup>+</sup> in the catholyte insignificantly changed, although the amount of Na<sup>+</sup> in the desalination compartment continuously decreased (ITE of  $\sim 100\%$  for Na<sup>+</sup>). The different behavior of Na<sup>+</sup> from Cl<sup>-</sup> was attributed to the insertion of Na<sup>+</sup> into the Na<sub>x</sub>C electrode fast enough to keep the amount of Na<sup>+</sup> unchanged over 10 h. Based on the photocharges of 10 mA h, the amount of inserted Na<sup>+</sup> was estimated to be  $\sim 0.37 \text{ mmol}$ . Considering that the actual amount of inserted Na<sup>+</sup> for 10 h was  $\sim 0.35 \text{ mmol}$ , the charge

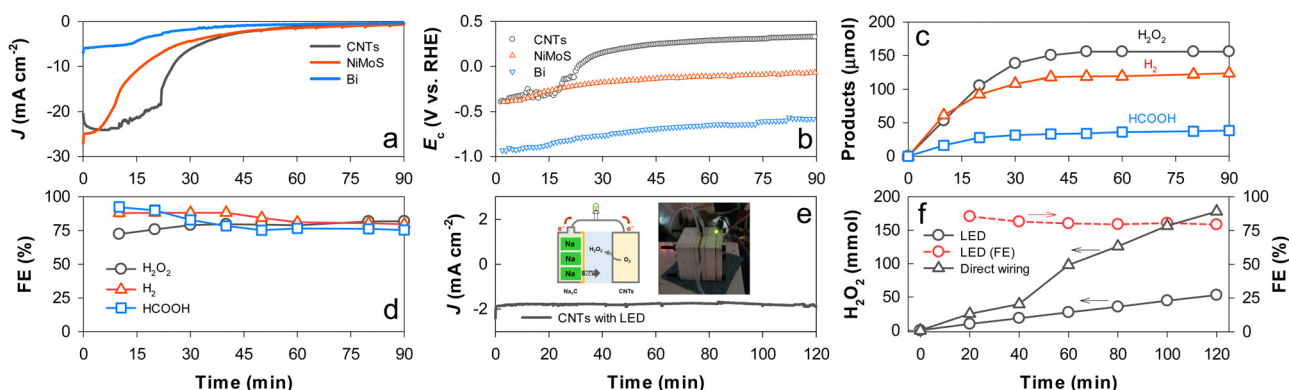


Fig. 5 (a)–(d) Electrocatalytic production of H<sub>2</sub>O<sub>2</sub> with CNTs, H<sub>2</sub> with NiMoS, and HCOOH with Bi coupled to a PEC charged Na<sub>x</sub>C electrode at an applied  $E_{\text{cell}}$  of 0 V (see Scheme 1c): (a) changes in the discharge  $J$  values of the electrocatalysts; (b) changes in the potentials ( $E_c$ ) of the electrocatalysts; (c) production of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>, and HCOOH; and (d) FEs for chemical production. (e) and (f) Electrocatalytic production of H<sub>2</sub>O<sub>2</sub> with CNTs coupled to the charged Na<sub>x</sub>C electrode *via* an LED bulb: (e) changes in the discharge  $J$  value of CNTs and (f) H<sub>2</sub>O<sub>2</sub> production and FE values with time. For comparison, H<sub>2</sub>O<sub>2</sub> production without the LED bulb is shown.



storage efficiency was estimated to be  $\sim 95\%$ . All the observed behaviors with Co-WBVO were the same as those with WBVO (Fig. S13, ESI<sup>†</sup>), except for the faster oxidation kinetics of As(III) and ammonia due to higher  $FE_{RCSs}$  with Co-WBVO.

The as-photocharged  $Na_xC$  electrode was directly wired to a CNT electrode in a single compartment cell containing  $K_2SO_4$  (pH 6.5) purged with  $O_2$ , and  $E_{cell}$  of 0 V was applied to the  $Na_xC$  and CNT electrode pair.  $J_{CNTs}$  of  $-24\text{ mA cm}^{-2}$  flowed in the initial stage and abruptly decreased in 20 min (Fig. 5a), while the initial  $E_{CNTs}$  ( $-0.4\text{ V}_{RHE}$ ) increased to  $\sim 0.3\text{ V}_{RHE}$  in the later stage (Fig. 5b). During the discharging period,  $H_2O_2$  production reached a plateau of  $\sim 155\text{ }\mu\text{mol}$  in 1 h with FE of  $\sim 80\%$  (Fig. 5c and d). When the photocharged  $Na_xC$  was coupled to the NiMoS electrode for  $H_2$  production,  $J_{NiMoS}$  decayed more rapidly than  $J_{CNTs}$  at FE of  $\sim 90\%$  for  $H_2$  production, while  $E_{NiMoS}$  gradually decreased. With the Bi electrode, the initial value of  $J_{Bi}$  ( $\sim 5\text{ mA cm}^{-2}$ ) and the amount of HCOOH were much lower than those with the other electrodes despite the same two-electron transfer process. This behavior with Bi was attributed to a large potential required for the  $CO_2RR$ . Nevertheless, the FE of HCOOH production was  $\sim 80\%$ . Finally, the  $Na_xC$  and CNT electrodes were wired through an LED bulb at  $E_{cell}$  of 0 V. A stable discharging  $J_{CNTs}$  of  $-2\text{ mA cm}^{-2}$  was obtained over 2 h with the generation of LED light (Fig. 5e).  $H_2O_2$  was produced linearly with time at an FE of  $>80\%$  (Fig. 5f).

## 4. Conclusions

We demonstrated a desalination-coupled PEC hybrid system capable of remediating aquatic pollutants *via* redox reactions of desalted  $Cl^-$  and charging an aqueous sodium metal battery with photogenerated electrons and desalted  $Na^+$ . Significant efforts have been made to synthesize high efficiency BVO-based photoelectrodes *via* W-doping and Co-deposition. The optimized Co-WBVO oxidized chlorides into RCSs at an FE  $> 90\%$ , with minimized production of non-reactive chlorine species. These *in situ* generated but storable RCSs effectively oxidized As(III) to As(V) and sequentially  $NH_4^+$  to nitrate in mixed As(III) and  $NH_4^+$  solution. During the anodic reaction with chloride,  $Na^+$  was successfully inserted into a wired  $Na_xC$  electrode. The photocharged  $Na_xC$  was further demonstrated to drive electrocatalytic conversions of  $O_2$  to  $H_2O_2$  with CNTs,  $H_2O$  to  $H_2$  with NiMoS, and  $CO_2$  to HCOOH with Bi, at FEs of  $>80\%$ . This PEC charging–discharging reaction with  $Na^+$  and  $Cl^-$  was successfully coupled to a desalination process with brackish water in a three-compartment cell with ion-exchange membranes. While desalination proceeded at an SEC of  $7.7\text{ kW h m}^{-3}$ ,  $Na^+$  and  $Cl^-$  were unidirectionally transported to the  $Na_xC$  electrode compartment and photoelectrode compartment, respectively, at an ITE of  $\sim 100\%$ . Despite a proof-of-concept, the as-designed PEC hybrid can be applied for various purposes, including desalination, seawater electrolysis, production of value-added chemicals, and energy storage.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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