


 Cite this: *RSC Adv.*, 2023, 13, 8873

Interface engineering of CeO₂ nanoparticle/ Bi₂WO₆ nanosheet nanohybrids with oxygen vacancies for oxygen evolution reactions under alkaline conditions†

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Because of the interactive combination synergy effect, hetero interface engineering is used way for advancing electrocatalytic activity and durability. In this study, we demonstrate that a CeO₂/Bi₂WO₆ heterostructure is synthesized by a hydrothermal method. Electrochemical measurement results indicate that CeO₂/Bi₂WO₆ displays not only more OER catalytic active sites with an overpotential of 390 mV and a Tafel slope of 117 mV dec⁻¹ but also durability for 10 h (97.57%). Such outstanding characteristics are primarily attributed to (1) the considerable activities by CeO₂ nanoparticles uniformly distributed on Bi₂WO₆ nanosheets and (2) the plentiful Bi–O–Ce and W–O–Ce species playing the role of strong couples between CeO₂ nanoparticles and Bi₂WO₆ nanosheets and oxygen vacancy existence in CeO₂ nanoparticles, which can improve the electrochemical active surface area (ECSA) and activity, and enhance the conductivity for OERs. This CeO₂/Bi₂WO₆ consists of the heterojunction engineering that can open a modern method of thinking for high effective OER electrocatalysts.

Received 28th December 2022

Accepted 26th February 2023

DOI: 10.1039/d2ra08273j

rsc.li/rsc-advances

1. Introduction

The energy demands and increasing environmental problem lead to a lot of research efforts in studying exchangeable conversion system and energy storage.^{1–6} The oxygen evolution reaction (OER) is key to the progress of renewable energy devices such as water-splitting devices and metal–air batteries.^{7–17} At the anode, the even work of the OER depends on catalyst engineering owing to its essentially sluggish reaction kinetics and multielectron transfer paths.^{18–22} Generally, noble metal oxides such as IrO₂ and RuO₂ are well-known electrocatalysts for OERs.^{23–27} However, their high price, serious scarcity, and unsatisfied stability of electrocatalysts are greatly frustrating in that they are more widely applied to a variety of energy devices. Therefore, it is crucial to explore effective, low-cost, abundant, and robust OER catalysts on Earth.

One of the easiest members of the Aurivillius family, bismuth tungstate (Bi₂WO₆) has become an outstanding OER electrocatalyst because of its abundant, low cost, clean properties, and excellent chemical stability.^{28–31} In detail, two-

dimensional Bi₂WO₆ nanosheets have a distinctive layer form and large specific surface area. These are useful to charge transfer, electrolyte penetration as well as active site exposure, regarded as a favorable catalyst support.^{32,33} Nonetheless, by the self-aggregating motion, Bi₂WO₆ nanosheets are simply aggregated to limit and decrease the electrochemically active region, indicating that the catalytic activity of OER is low.³⁰ According to the surface structure, the adsorption actions of reaction region and charge distribution are crucial to the electrochemical catalytic action.³⁴ Therefore, the interface engineering of heterostructures has been regarded as an effective strategy for optimizing the catalyst activities.^{35–40} The close connections between different active species in engineering interfaces optimize the powerful synergistic effect, rapid charge transfer rate and activation energy, and adsorption for intermediates, overcoming the shortcomings of single ingredient materials,^{36–38} whereas the heterointerfaces usually involve structural modification such as edges and dislocations as well as atomic defects including cation and anion vacancies, forming more active sites on the surface of the catalyst.⁴¹ To accomplish this aim, it is essential to choose appropriate introduced species that form the optimal electrocatalysts. Due to its chemical properties and unique electronic structure, CeO₂ has been extensively studied as an effective supporter of the OER. The abundant oxygen vacancies of CeO₂ and flexible conversion between Ce³⁺ and Ce⁴⁺ can enable several moving oxygen atoms to access active sites as an oxygen buffer for the effective absorption of oxygen species.^{42–47} Thus, we think that the hybridization of Bi₂WO₆

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ra08273j>



and CeO_2 has to be a reasonable tactic to enhance the OER activity by the interface engineering.

In this work, we manufacture a modern sort of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ heterostructure consisting of CeO_2 nanoparticles on Bi_2WO_6 nanosheets by a hydrothermal method for OER electrocatalysts in alkaline media. The excellent electrocatalytic active site and durability come from the distinct heterostructure and combined interface synergistic effect with equally distributed CeO_2 nanoparticles fixing Bi_2WO_6 nanosheets, which disclose more activity, have charge transfer rates, and show steady heterostructures. At the heterostructure, this approach *via* bonding the shape plan and electronic transformation fulfills advancement of catalysts, which supply direction for using activity encouraging and high effectiveness and stability OER electrocatalysts.

2. Experiment method

2.1. Synthesis of Bi_2WO_6 nanosheets

First, 0.05 g hexadecyltrimethylammonium bromide (CTAB) (0.1 mmol) was dispersed in 80 ml deionized water under stirring for 10 minutes. Then, 0.917 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to the obtained solution for 30 minutes. Finally, 0.33 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to the solution and stirred for 30 minutes. Afterward, the as-obtained solution was transferred to a 100 ml Teflon-lined hydrothermal autoclave, which was then maintained at 120 °C for 24 hours. Finally, the precursor was washed several times with deionized water and dried at 50 °C overnight.

2.2. Synthesis of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids

First, 1 mmol $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (0.5482 g) was added into 50 ml deionized water under a stirring process for 30 minutes. Then, 0.5 mmol Bi_2WO_6 (0.3488 g) was added to this solution and ultrasonicated until complete dissolution. After sonication, 10 ml of NaBH_4 solution (0.05 M) was added to the solution. The product was washed several times with ethanol and deionized water and dried at 50 °C overnight. After drying overnight, the as-prepared sample was calcined at 420 °C for 2 hours.

2.3. Synthesis of CeO_2 nanoparticles

The synthesis of CeO_2 is similar to that of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid except for the additional treatment. To be more specific, although other experimental methods remain the same, only the second process of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid synthesis method was excluded.

3. Results and discussion

Fig. 1 describes the process of formation of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids *via* a hydrothermal reaction. The first process began with use of hydrothermal synthesis of Bi_2WO_6 nanosheets. The Br-ion CTAB bound on the Bi_2WO_6 surface can adsorb positively charged Ce^{4+} ions.^{31,48} Next, Ce^{4+} ions were easily reduced to CeO_2 nanoparticles by forming nanohybrids of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ using NaBH_4 as a reducing agent accumulated on the Bi_2WO_6 nanosheet.³¹ During the experiment, Bi-ions and W-

ions could be reduced by NaBH_4 that obtains the advantages of Bi–O–Ce, W–O–Ce bond formation by substituting Br– to Ce–O–. The $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid was annealed at 420 °C in air, and thus, stable fixed CeO_2 nanoparticles were bonded to the Bi_2WO_6 surface. The NaBH_4 reduction was selected because it is easy to perform and inexpensive for the manufacture of vacancies. In addition, it generates many defects for exposing more reactive sites and increases the conductivity.⁴⁹

3.1. Morphology and structure of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$

The morphology and microstructure of the prepared samples were analyzed by FE-SEM, as shown in Fig. S1, S2† and 2. As shown in Fig. S1a and b (ESI†), the microstructure of the CeO_2 sample was characterized by nanoparticles. The morphology of Bi_2WO_6 showed nanosheet features, as shown in Fig. S2a and b (ESI†). After addition of NaBH_4 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and calcination at 420 °C for 2 hours, $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ could not change the structure of Bi_2WO_6 nanosheets (Fig. 2), which implies that the microstructure of Bi_2WO_6 could be maintained by the addition of NaBH_4 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and calcination could keep the microstructure of Bi_2WO_6 . In addition, the surface nanoparticles cannot be found on the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid due to the low loading and uniform growth on the Bi_2WO_6 nanosheet of CeO_2 nanoparticles.^{28,29} Meanwhile, the irregular nanoparticles on the surface could be distinguished from the surface of the Bi_2WO_6 nanosheets. This suggests that the CeO_2 nanoparticles were successfully fixed and uniformly grown on the Bi_2WO_6 nanosheets. The distinctive heterostructure provided strong electron interaction and interfacial synergy between Bi_2WO_6 nanosheets and CeO_2 nanoparticles, which is important for adjusting the electronic structure and exposing several active sites to increase the electrocatalytic activity and durability of electrocatalysts.^{50,51}

To further examine the structure of CeO_2 nanoparticles on the surface of Bi_2WO_6 nanosheets, the crystal structure of CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ was investigated by FE-TEM analysis, as shown in Fig. S3, S4† and 3. As illustrated in Fig. S3a and b,† the FE-TEM images displayed CeO_2 with nanoparticle structure, implying that the CeO_2 nanoparticles were synthesized. The HRTEM image of CeO_2 indicated that the *d*-spacing of the lattice fringes is 0.271 and 0.312 nm, corresponding to the (200) and (111) planes, respectively, as shown in Fig. S3c†.⁵² Meanwhile, the FE-TEM images represented Bi_2WO_6 with a sheet-like form, and the nanosheets can be seen in Fig. S4a and b,† showing that Bi_2WO_6 nanosheets were synthesized. As shown in Fig. S4c,† the HRTEM image shows that the *d*-space of lattice fringes is 0.272 nm, corresponding to the (020) plane of

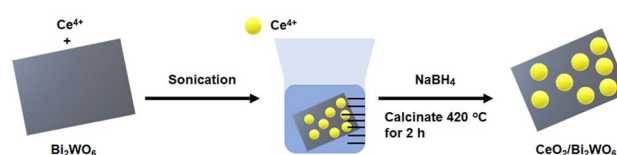


Fig. 1 Schematic illustration of synthesis process of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids.



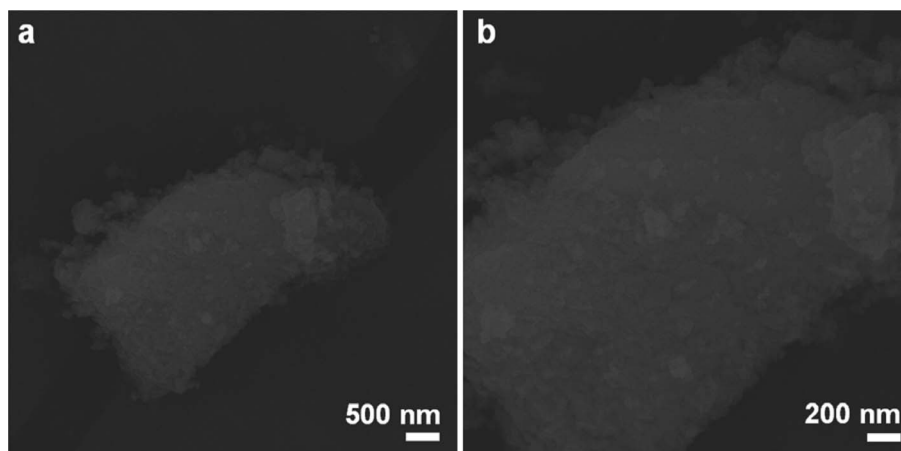


Fig. 2 FE-SEM images at (a) low magnification and (b) high magnification of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids.

Bi_2WO_6 .⁵³ The FE-TEM images of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids are displayed in Fig. 3a and b. The $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ sample was large and had nanosheet properties, and irregular CeO_2 nanoparticles were dispersed on the Bi_2WO_6 nanosheets. In addition, it could be found that some nanoparticles were spread out on the Bi_2WO_6 nanosheets, confirming that the CeO_2 nanoparticles were grown on the Bi_2WO_6 nanosheets, which is consistent with the FE-SEM results.⁵⁴ Fig. 3c shows the HRTEM image of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrid catalyst, and the lattice edges of CeO_2 nanoparticles and Bi_2WO_6 nanosheets might be surely differentiated, and the lattice edges of 0.271 nm, 0.312 nm, and 0.272 nm corresponded to the (200) and (101) planes of CeO_2 and the (020) plane of Bi_2WO_6 , respectively. Finally, to investigate the elemental composition of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids catalyst, the energy dispersive X-ray

spectrometry (EDS) was perfected in Fig. 3e. The four elements of Ce, Bi, W, and O were uniformly distributed over the whole $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrid catalyst, which suggested that the CeO_2 nanoparticles combined with the surface of Bi_2WO_6 nanosheets, confirming that the CeO_2 nanoparticle/ Bi_2WO_6 nano sheet heterostructure was successfully synthesized.

To confirm the crystal structure and phase composition of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 catalysts, we conducted X-ray diffraction (XRD), as shown in Fig. 4a. The peaks at 28.7°, 33.3°, 47.6°, 56.5°, 59.3°, and 69.5° corresponded to the (111), (200), (220), (311), (222), and (400) planes of CeO_2 , respectively. These results were consistent with the CeO_2 crystal structure (JCPDS No. 81-0792).⁵⁵ Similarly, the diffraction peaks of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ and Bi_2WO_6 matched JCPDS No. 73-2020 of Bi_2WO_6 .⁵⁶ In addition, no diffraction peaks were studied from other materials.

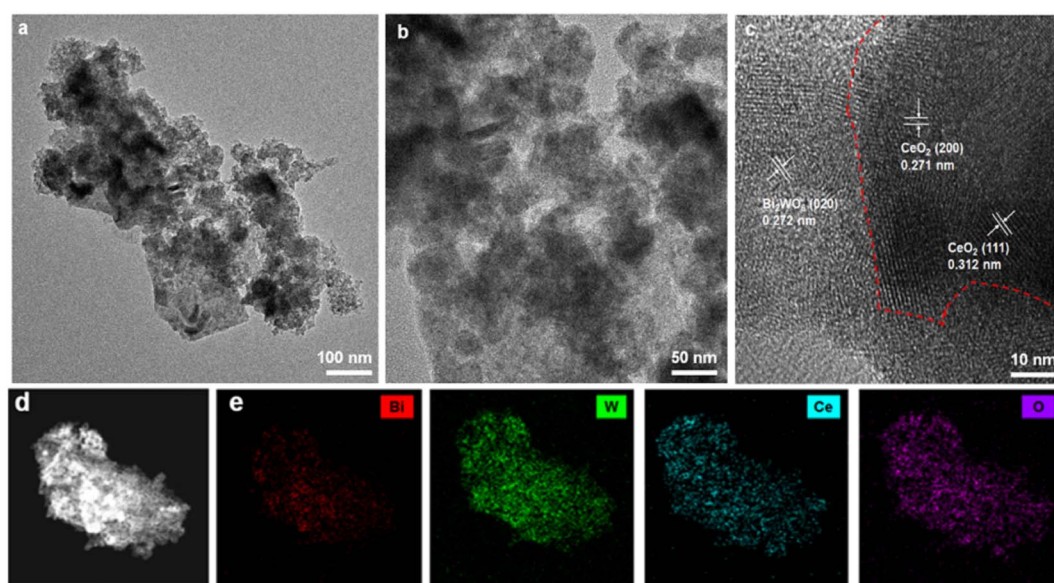


Fig. 3 FE-TEM images at (a) low magnification and (b) high magnification of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids. (c) HRTEM image of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids. (d) Dark-field FE-TEM image of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids. (e) EDS mapping images for Bi, W, Ce, and O elements distributed at $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nano hybrids.



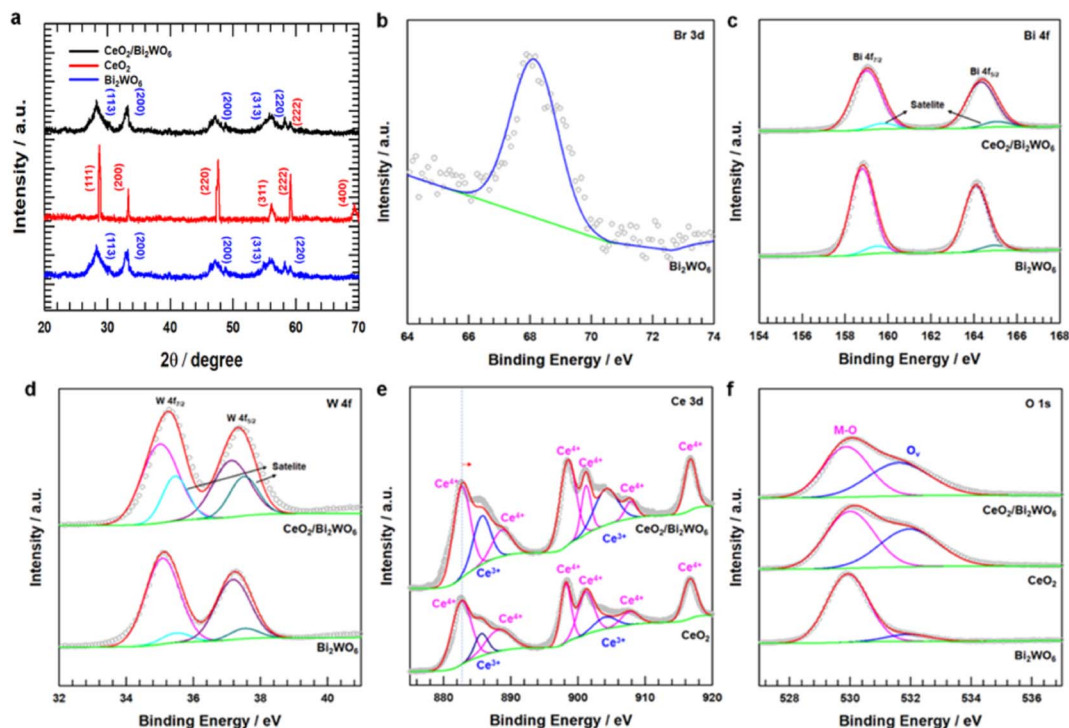


Fig. 4 (a) XRD pattern of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. (b) XPS Br 3d deconvolution spectrum of Bi_2WO_6 . (c) XPS Bi 4f deconvolution spectrum of Bi_2WO_6 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. (d) XPS W 4f deconvolution spectrum of Bi_2WO_6 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. (e) XPS Ce 3d deconvolution spectrum of CeO_2 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. (f) XPS O 1s deconvolution spectrum of CeO_2 , Bi_2WO_6 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$.

This might be the surface of the Bi_2WO_6 nanosheets of the CeO_2 nanoparticles due to low loading and even growth.^{29–31}

To identify the chemical valence states and surface elemental contents, the X-ray photoelectron (XPS) spectra recorded for CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ are shown in Fig. S5† and 4b–f. As shown in Fig. S5,† the XPS survey spectrum indicated the existence of Ce, Bi, W, and O elements, in accordance with the above-mentioned XRD result (Fig. 4a). Fig. 4b–f displays the high-resolution spectra of Br 3d, Bi 4f, W 4f, Ce 3d and O 1s, respectively. In the case of pure Bi_2WO_6 , the binding energies of the Br 3d peak were determined to be 68.6 eV, as shown in Fig. 4b, confirming that the Br ions of CTAB were bound to the surface Bi and W atoms of Bi_2WO_6 .⁵³ As shown in

Fig. 4c, Bi_2WO_6 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ could be divided into two Bi 4f peaks. The properties of $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ were two peaks at 164.3 and 159.2 eV that matched Bi^{3+} ions of Bi_2WO_6 .⁵⁷ The shoulder peaks $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$, corresponding to 165.6 and 160.6 eV, appeared at a higher binding energy. The peaks of Bi, represented at a higher energy, meant that the Bi atoms had higher electrical positivity in binding with the surface Br atoms.^{53,57} Similarly, for the high-resolution XPS W 4f spectrum (Fig. 4d), $4f_{7/2}$ and $4f_{5/2}$ electron orbits of W^{6+} corresponded to two feature peaks at 35.2 eV and 37.3 eV, respectively. In addition, the orbits of $\text{W } 4f_{7/2}$ and $\text{W } 4f_{5/2}$ belonged to the satellite peaks at 35.6 eV and 37.6 eV, respectively. Compared to Bi_2WO_6 , the binding energy of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ was moved slightly to the

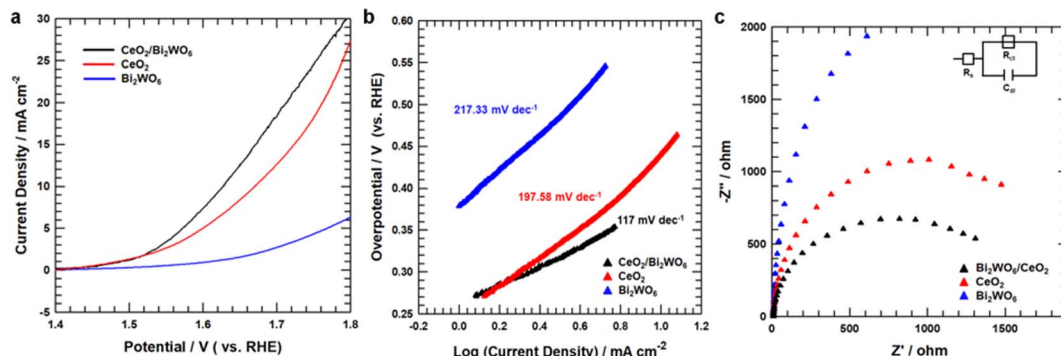


Fig. 5 (a) OER LSV curves for CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ in a N_2 -saturated 1.0 M KOH electrolyte. (b) Tafel plots for CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. (c) Nyquist plots for CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ recorded at 1.65 V.



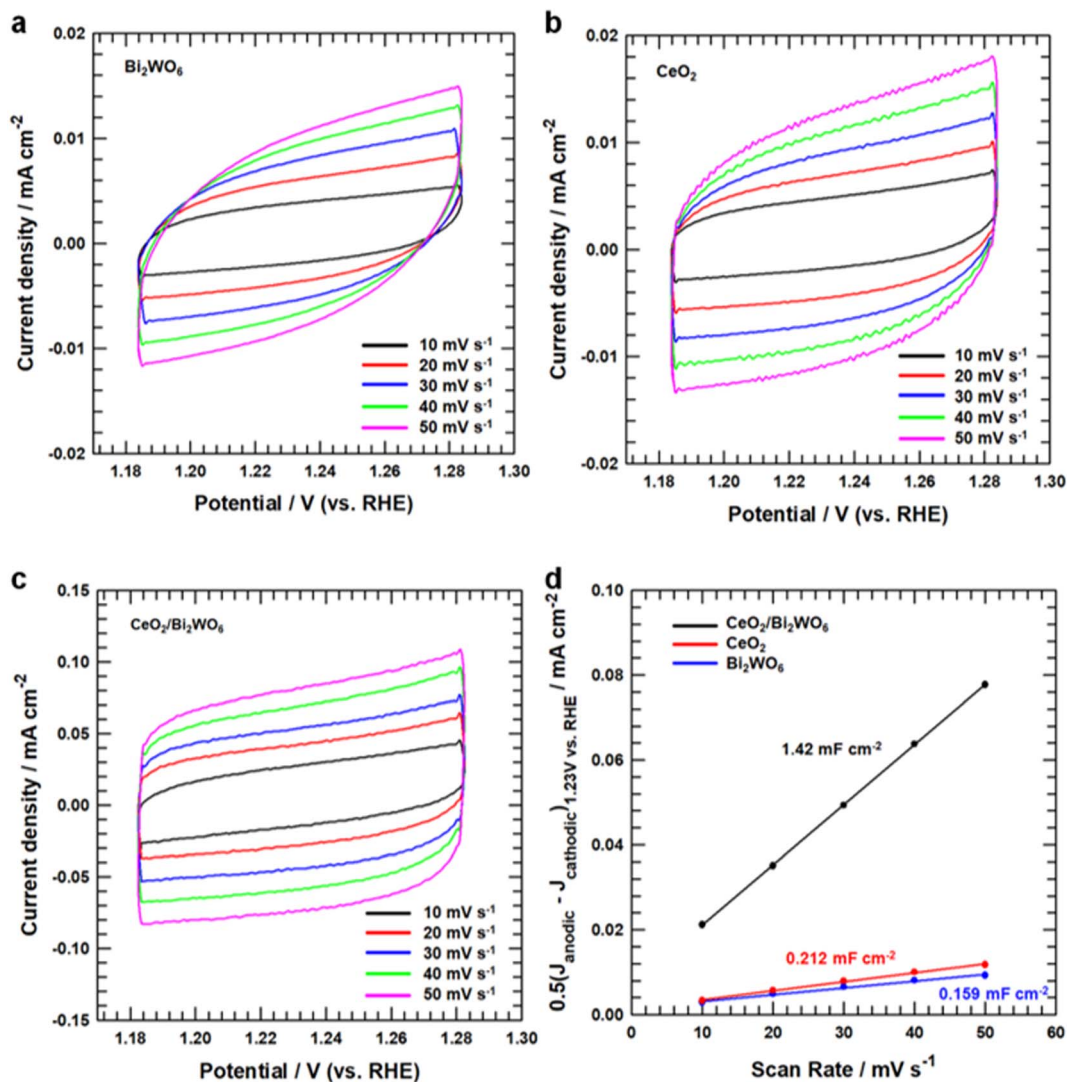


Fig. 6 CV curves (a) CeO_2 , (b) Bi_2WO_6 , and (c) $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ in a non-faradaic current region (1.18–1.28 V vs. RHE) at different scan rates of 10, 20, 30, 40, and 50 mV s^{-1} . (d) Linear fitting of the capacitive currents versus CV scan rates of CeO_2 , Bi_2WO_6 , and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$.

negative parts, confirming that the electropositive W appearing on the Bi_2WO_6 nanosheets was increasingly higher.^{28,53} The high-resolution XPS Ce 3d spectrum for $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ was composed with the peaks compared to CeO_2 (Fig. 4e). The Ce 3d spectrum of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ and CeO_2 samples could be separated into eight peaks, two peaks were assigned to Ce^{3+} at 885.7 and 904.2 eV, and six peaks were assigned to Ce^{4+} at 882.7, 888.7, 898.5, 901.2, 907.9, and 916.7 eV for $\text{CeO}_2/\text{Bi}_2\text{WO}_6$.⁵⁸ According to the Ce 3d spectrum analysis, Ce^{3+} and Ce^{4+} were present in CeO_2 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$. For the Ce 3d spectrum, it might be observed that CeO_2 and $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ were plentiful in Ce^{3+} species, which showed the formation of oxygen vacancies in these two samples.⁵⁸ Besides, the binding energy of the Ce 3d spectrum in $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ had a clear positive change compared to CeO_2 . The suitable electron structure of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ could help to enhance the catalyst's OER performance by inducing charge redistribution at the interface.^{59,60} Fig. 4f shows the two peaks for the O 1s spectrum. The O 1s peak at

530.2 eV was attributed to the oxygen atom bonded to the metal, and the center position at 532.1 eV was ascribed to the oxygen atom in the surrounding area of oxygen vacancies.⁶¹ However, according to the feature peak, the peak area at 532.1 eV varied greatly, which displayed that the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids had much more oxygen vacancies. Interestingly, as shown in Table S1,[†] the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids (46.8%) is higher than that of CeO_2 nanoparticles (44.6%) and Bi_2WO_6 nanosheets (9.7%). These results indicated that the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids had enough oxygen vacancies. As a result, the CeO_2 nanoparticles abundant in evenly grown oxygen vacancies on Bi_2WO_6 nanosheets were successfully synthesized.

3.2. Oxygen electrochemical performance of electrocatalysts

To study the OER catalytic active sites of all samples, we studied the electrochemical characteristics of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 for OERs in alkaline solutions (pH = 14) using a rotating disk electrode (RDE) (see Detail Methods in the ESI[†]).

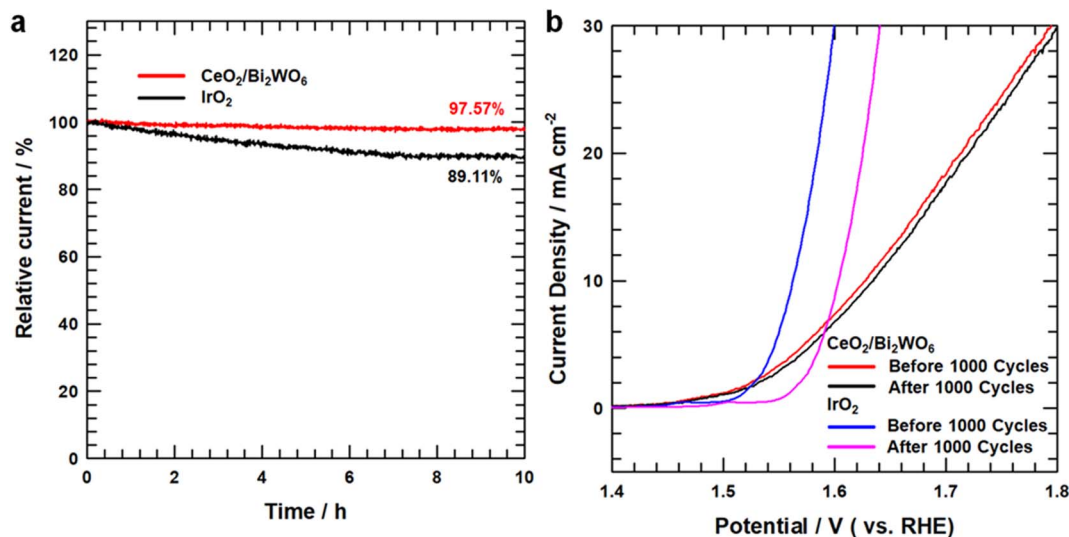


Fig. 7 (a) OER chronoamperometry test of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ and IrO_2 . (b) OER LSV curves for before and after 1000 cycles $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ and IrO_2 .

As shown in Fig. 5a, the linear sweep voltammetry (LSV) curves showed that $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ indicated a smaller overpotential of 390 mV, slightly larger than that of CeO_2 (440 mV) and Bi_2WO_6 . Besides, to evidence the outstanding OER kinetics of the samples, their Tafel slope were calculated by LSV. As shown in Fig. 5b, $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ showed a lower Tafel slope (117 mV dec^{-1}) than that of CeO_2 ($197.58 \text{ mV dec}^{-1}$) and Bi_2WO_6 ($217.33 \text{ mV dec}^{-1}$), and thus $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ had the fastest kinetic process.^{62,63} Compared with previous studies, the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ heterostructure was one of the most efficient Bi_2WO_6 -based catalysts (Table S2†). The smallest Tafel slope of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ suggested the most favorable OER kinetics, indicating that $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ possessed an outstanding OER catalytic kinetics. To investigate the OER kinetics of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 , electrochemical impedance spectroscopy (EIS) was conducted, as shown in Fig. 5c. The $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids had the lowest charge resistance (R_{ct}) than other samples at the interface between the electrolyte and the catalyst. Since R_{ct} represented the rate of charge transfer in OERs,⁶⁴ the smallest R_{ct} value of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid showed the high-speed electron transportation ability of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrid during the OER process due to the CeO_2 nanoparticles plentiful in oxygen vacancies evenly grown on Bi_2WO_6 nanosheets.²⁸

To establish why $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ had better OER activity than that of other samples, we measured double-layer capacitance (C_{dl}) to judge their electrochemically active surface area (ECSA). The ECSA of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 was revealed by a cyclic voltammetry (CV) method.^{65–67} Fig. 6a–c display the CV curves at different scan rates ($10\text{--}50 \text{ mV s}^{-1}$) for $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 alkaline solutions, respectively. As the scan speed increased, the current densities of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 increased accordingly, indicating that the active sites and charge transport capability of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$, CeO_2 , and Bi_2WO_6 increased significantly. In addition, it displayed that $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ showed the highest capacitive current

compared with CeO_2 and Bi_2WO_6 . The C_{dl} and ECSA can be calculated as “ $0.5(J_{\text{anodic}} - J_{\text{cathodic}})_{1.23 \text{ V vs. RHE}} (\text{mA cm}^{-2}) / \text{scan rate} (\text{mV s}^{-1})$ ”, as shown in Fig. 6d, and the C_{dl} of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ (1.42 mF cm^{-2}) is remarkably higher than that of CeO_2 (0.212 mF cm^{-2}) and Bi_2WO_6 (0.159 mF cm^{-2}). As a result, the significant activities of C_{dl} and ECSA increased, which might be due to the high oxygen vacancy concentration of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ heterostructure, and CeO_2 nanoparticles equally grown on Bi_2WO_6 , which essentially improved the electrocatalytic activity.

The electrocatalytic stability of the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ nanohybrids and IrO_2 was tested by chronoamperometry measurements, as shown in Fig. 7a, and the current density of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ indicated the unseen modification with respect to the initial value at a retention rate of up to 97.57% after 10 hours of the OER process and showed outstanding stability in an aqueous alkaline medium. In IrO_2 , the current retention rate is below 89.11%. Besides, the durability of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ was performed by the LSV curves before and after 1000 cycles of the CV curves. As shown in Fig. 7b, the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ electrocatalyst showed a negligible decrease in current density, suggesting the good durability of $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ in alkaline solutions, while IrO_2 shows a significant decrease after 1000 cycles. Because of the synergistic effect of highly stable heterojunctions, the Bi_2WO_6 nanosheets not only guarantee rich active sites, but also ensure a variety of paths for the fast and efficient movement of electrolytes and gases. Meanwhile, the reasonably fixed CeO_2 nanoparticles increase the electrocatalytic activity and enhance the electrical contact with the electrolyte.^{68,69} The above-mentioned electrochemical results confirmed the presence of more active sites, and more efficient and faster electron transport capability in $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ than those in samples of CeO_2 and Bi_2WO_6 , confirming that the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ heterostructure catalyst had fine catalytic activity and maintained the excellent stability in an alkaline environment. Therefore, the $\text{CeO}_2/\text{Bi}_2\text{WO}_6$ heterostructure catalyst is a reasonable strategy to



optimize the OER active sites and durability of Bi₂WO₆-based catalysts.

4. Conclusion

In summary, we have developed a simple strategy to synthesize CeO₂/Bi₂WO₆ nanohybrids with more OER active sites and high durability under alkaline conditions. The characterization and electrochemical measurement results indicated that the CeO₂/Bi₂WO₆ heterostructure electrocatalyst displayed not only more OER catalytic active sites with a smaller overpotential of 390 mV and a lower Tafel slope of 117 mV dec⁻¹ but also durability for 12 h. The distinct heterointerface generates hard bonded electronic effects and the interfacial synergistic effect, making the CeO₂ nanoparticles uniformly anchored onto Bi₂WO₆ for the atoms to expose more active sites, which provided CeO₂/Bi₂WO₆ with electrocatalytic active sites for OERs. Meanwhile, the hard coupled and interfacial synergistic effect really endows the heterojunction structure with good stability for practical application. This CeO₂/Bi₂WO₆ heterostructure catalyst has been developed *via* shape design.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Chung-Ang University Research Scholarship Grants in 2023 and also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2020R1A2C2010445).

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