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Journal

Nano Letters, 25(6)

ISSN

1530-6984

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Publication Date

2025-02-12

DOI

10.1021/acs.nanolett.4c06344

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Electrochemical removal of Se(IV) from wastewater using RuO₂-based catalysts

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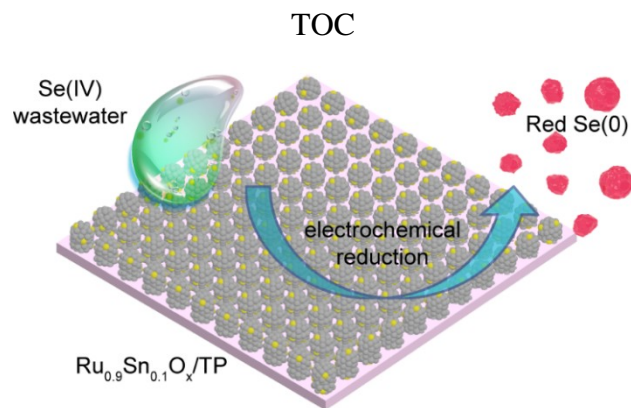
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Abstract: The removal of selenite (SeO₃²⁻) from water is challenging due to the risk of secondary pollutants. To address this, we developed RuO₂-based nanocatalysts on the titanium plate (RuO₂/TP) for direct electrochemical reduction of Se(IV) to elemental selenium [Se(0)]. Optimizing Sn doping in RuO₂ nanoparticles to induce charge redistribution enabled the Ru_{0.9}Sn_{0.1}O_x/TP catalyst to achieve ~90% Se(IV) removal across concentrations of 0.1, 1, and 10 mM at -2 mA cm⁻² over 8 hours, outperforming un-doped RuO₂/TP. Furthermore, Ru_{0.9}Sn_{0.1}O_x/TP also maintained ~90% removal efficiency in 1 mM of Se(IV) solutions containing competitive anions (0.5 M Cl⁻, 0.1 M SO₄²⁻, 0.01 M NO₃⁻, and their mixtures), demonstrating suitability for complex wastewater treatment. Importantly, the catalysts were recyclable with no observable contamination introduced into the solution.

Density functional calculations (DFT) calculations suggest that Sn doping effectively reduces the energy barrier for Se(IV) reduction to Se(0).

Key words: RuO₂/TP, Se(IV), doping, charge redistribution, energy barrier



Main text:

Selenium (Se) is an essential trace element for human health, supporting vital physiological functions such as antioxidant defense, immune system, and thyroid function^{1, 2}. As a micronutrient, selenium is involved in various biological pathways that protect against oxidation stress and support cellular functions critical to maintaining health³. However, while Se is beneficial in small amounts, it has a narrow range between beneficial and toxic levels; slight excesses can lead to severe health consequences such as hair loss, damage to the peripheral nervous system, and chronic fatigue^{4, 5, 6}. This dual role of Se underscores the delicate balance needed to maintain safe concentrations, especially in environmental sources such as drinking water, where Se contamination can pose considerable health risks. In recent years, there has been growing concern over Se contamination in various environmental settings, including freshwater bodies, drinking water supplies, agricultural runoff, and soil^{7, 8, 9}. Naturally occurring Se concentrations in water can range from 0.06-400 µg/L¹⁰. However, elevated Se levels in water bodies are often the result of anthropogenic activities, with industrial activities contributing significantly to environmental Se releases. Industries such as crude oil refinement, coal combustion, and mineral processing are estimated to account for roughly 40% of Se pollution in water systems^{11, 12, 13, 14}. The United States Environmental Protection Agency (EPA) sets stringent guidelines for Se in marine water, with a maximum allowable concentration of 300 µg/L and continuous exposure limits of 71 µg/L¹⁵.

In aquatic systems, Se predominantly exists as selenite (i.e., SeO_3^{2-}) and selenate (i.e., SeO_4^{2-}) under various pH and redox conditions^{15, 16, 17}, with Se(IV) posing greater toxicity and bioavailability risks than Se(VI). Removing Se(IV) from water sources is thus essential to minimize its adverse effects on both ecosystems and human health. Several promising removal technologies have been explored, including physicochemical methods (membrane filtration, adsorption, coagulation, and precipitation), biological transformation (microbial transformation and constructed wetland), and redox reactions (chemical and electrochemical reduction)^{11, 17, 18, 19}. Among these methods, membrane separation offers high stability and effectiveness^{20, 21}, but incurs substantial costs. Adsorption and coagulation are economically favorable but produce solid waste requiring disposal^{22, 23, 24}, increasing overall treatment costs and potentially secondary pollution. Biological treatment is cost-effective but limited by low removal efficiency^{25, 26, 27}. Redox-based techniques^{28, 29}, particularly electrochemical reduction^{16, 30, 31}, have garnered attention as a promising and cost-effective approach for Se(IV) removal.

Electrochemical reduction methods convert Se(IV) to elemental selenium [Se(0)], which is less toxic and easier to remove from water systems. However, practical challenges remain, especially concerning catalyst stability in complex water matrices¹⁷. Conventional catalysts, including those based on gold plates¹⁶, graphite¹⁷, and Fe-hydroxide³² have been effectively utilized in direct Se(IV) electrochemical reduction. However, some catalysts are subject to catalyst dissolution under operational conditions, leading to secondary contamination and limiting their practical applications. Additionally, the tendency of Se precipitates to block active sites on the electrode surface impedes sustained removal efficiency and often renders these catalysts suitable only for single-use applications, thus increasing overall treatment costs. Moreover, RuO₂/TiO₂ as a dimensionally stable anode (DSA) is widely recognized for its exceptional stability under harsh electrochemical conditions, demonstrated by its application in the chlor-alkali industry and as a durable OER anode in PEMWE^{33, 34, 35}. Its strong adhesion to the Ti substrate and resistance to oxidative degradation ensures long-term durability in complex electrochemical environments. Therefore, addressing these limitations requires developing effective DSA electrodes with a range of wastewater compositions. Such advancements are crucial for scalable Se(IV) removal solutions that align with environmental and economic sustainability goals.

Here, to enable catalyst recyclability and reduce the cost of Se(IV) removal, we designed RuO₂ and Sn-doped RuO₂ nanoparticles grown on titanium plates (Ru_{0.9}Sn_{0.1}O_x/TP) with enhanced adhesion for the direct electrochemical reduction of Se(IV) to elemental Se(0) in aqueous matrices. Inductively coupled plasma mass spectrometry (ICP-MS) results confirmed that Ru_{0.9}Sn_{0.1}O_x/TP achieved greater than 90% removal efficiency for Se(IV) at concentrations of 0.1, 1, and 10 mM, outperforming the pure RuO₂/TP catalyst. Additionally, micro-structural analyses indicated that Sn doping in RuO₂ promotes charge redistribution among Ru, O, and Sn atoms, effectively lowering the energy barrier for Se(IV) reduction to Se(0). More significantly, in the simulated wastewater containing competing ions (0.5 M Cl⁻, 0.1 M SO₄²⁻, 0.01 M NO₃⁻, as well as their mixtures), Ru_{0.9}Sn_{0.1}O_x/TP maintained ~90% Se(IV) removal efficiency. However, under conditions where Cl⁻ is oxidized to ClO⁻, the removal efficiency sharply decreased due to ClO⁻ re-oxidizing Se(0) to Se(IV). For wastewater with high Cl⁻ concentrations, Se(IV) removal may be optimized in an H-cell reactor using a Nafion membrane to prevent ClO⁻ crossover. Both the Nafion membrane and Ru_{0.9}Sn_{0.1}O_x/TP can be recycled, offering a cost-effective approach to Se(IV) removal and

broadening the potential applications of this method. Moreover, $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ showed ~110 hours of stability at -2 mA cm^{-2} in H-cell reactor under continuous flow of 1 mM Se(IV) with competitive anions (0.5 M Cl^- , 0.1 M SO_4^{2-} , 0.01 M NO_3^-), achieving a removal efficiency of ~30%.

Results and discussion

Inspired by the potential of substrate-supported nanoparticles, we hypothesized that directly growing nanoparticles on the substrate surface would greatly enhance adhesion compared to traditional methods, like spraying or coating nanoparticles, thereby reducing the need for frequent electrode replacement and lowering overall costs in water treatment applications. To investigate this, we synthesized $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ *via* an annealing process using RuCl_3 and SnCl_4 as precursors, with a titanium plate as the substrate (Fig. 1a). X-ray diffraction (XRD) analysis identified that the synthesized nanocatalysts as rutile-phase ruthenium oxides (RuO_2 , PDF#-40-1290)³⁶, with a dominant (110) peak (Fig. S1), which is known for its stability and catalytic activity. This crystalline orientation suggests that the catalyst layer is well-integrated with the substrate, potentially increasing durability during repeated water treatment cycles. Scanning electron microscope (SEM) confirmed that RuO_2 and $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x$ nanoparticles were uniformly distributed across the titanium surface, with visible cracks that could provide additional active sites (Fig. S2, and Figs. 1b-d), improving the catalyst's accessibility to Se(IV) ions and enhancing overall efficiency³⁶. SEM energy dispersive spectroscopy (SEM-EDS) elemental mapping indicated a uniform distribution of Ru, Sn, and O, confirming successful Sn doping within RuO_2 (Fig. 1c, and Fig. S3). Further structural insights from transmission electron microscopy (TEM) indicated that $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x$ nanoparticles have an average diameter of ~20 nm with a distinct (110) lattice orientation (Figs. 1e and 1f, and Fig. S4). TEM-EDS mapping further confirmed homogeneous Sn incorporation into RuO_2 , with no phase separation observed (Fig. 1g), ensuring the structural and electronic stability of catalysts.

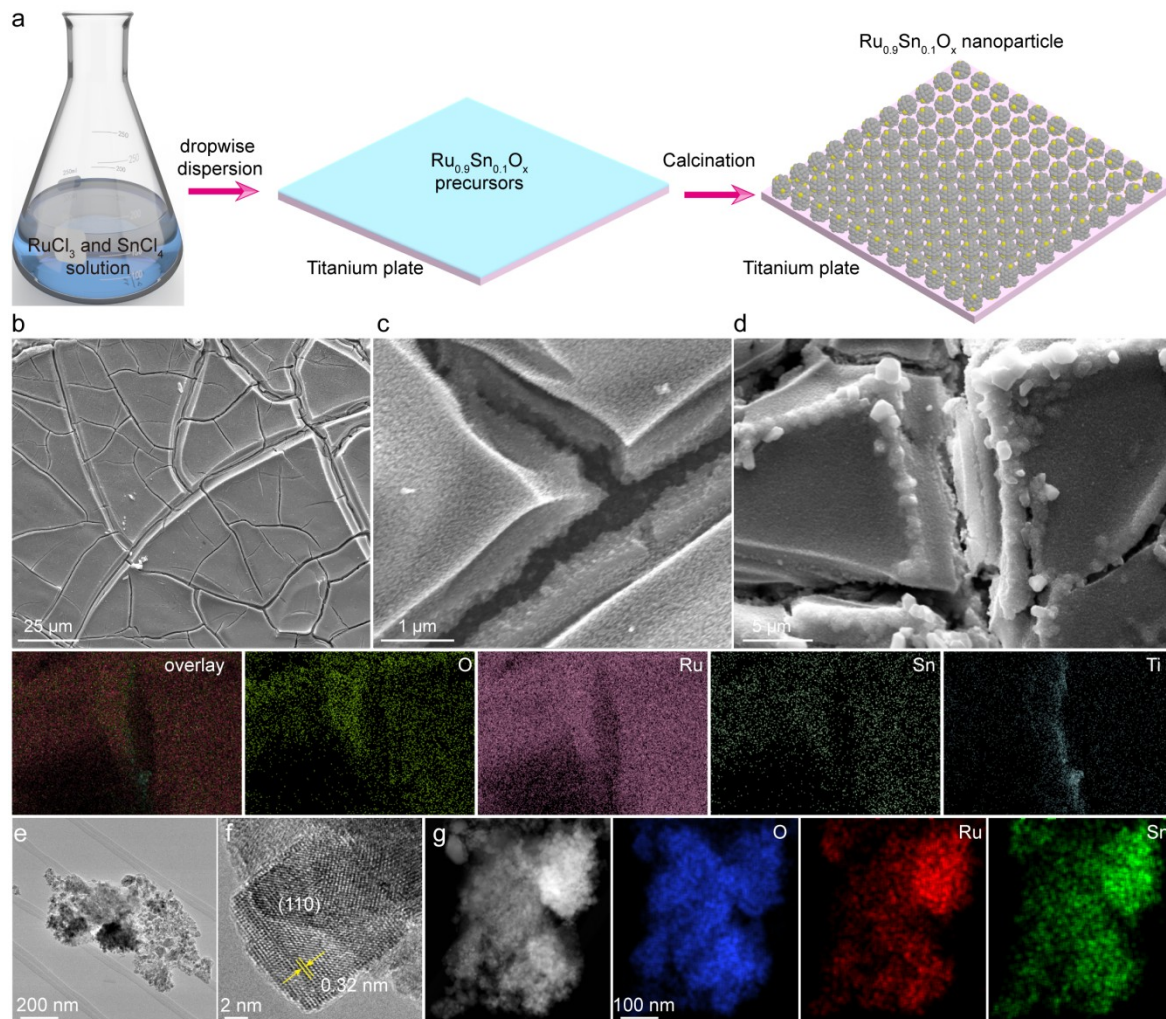


Figure 1. (a), Schematic illustration of the preparation process for RuO₂/TP and Ru_{0.9}Sn_{0.1}O_x/TP. (b, c), SEM images of Ru_{0.9}Sn_{0.1}O_x/TP. (d), SEM-EDS elemental mapping of Ru_{0.9}Sn_{0.1}O_x/TP. (e), TEM image of Ru_{0.9}Sn_{0.1}O_x/TP. (f), HR-TEM image of Ru_{0.9}Sn_{0.1}O_x/TP. (g), TEM-EDS elemental mapping of Ru_{0.9}Sn_{0.1}O_x/TP.

X-ray photoelectron spectra (XPS) were conducted to characterize RuO₂/TP and Ru_{0.9}Sn_{0.1}O_x/TP, focusing on composition and chemical states. This characterization aims to clarify the influence of Sn doping on the electronic structure and bonding environment of RuO₂. As shown in Fig. 2a, the Ru 3d spectra were deconvoluted into two doublets. The lower-energy peaks at ~280.7 eV (Ru 3d_{5/2}) and ~284.9 eV (Ru 3d_{3/2}) correspond to Ru⁴⁺³⁷, while the peaks at ~282.3 eV and ~286.9 eV represent satellite peaks. In comparison to RuO₂, the corresponding peaks in Ru_{0.9}Sn_{0.1}O_x/TP shifted to higher binding energy, suggesting charge redistribution among Ru, Sn, and O, potentially influencing catalytic performance by enhancing electronic interactions. For Sn 3d, the peaks at ~485.7 eV (Sn 3d_{5/2}) indicate that Sn exists partially in the +2 valence state³⁸, while the peak at ~494.6 eV (Sn 3d_{3/2}) with a

peak-to-peak separation of 8.9 eV reflects some Sn in the +4 valence state³⁹ (Fig. 2b). This mixed-valence state distribution suggests that Sn in $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ contributes to charge redistribution, which may improve catalytic efficiency by facilitating redox flexibility in Se(IV) reduction reactions. Ti 2p peaks at ~462.2 eV (Ti 2p_{3/2}) and ~464.4 eV (Ti 2p_{1/2}) confirm the +4 state valence state⁴⁰, corresponding to TiO₂ formation on the titanium plate surface. In $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$, these peaks shifted to slightly higher binding energies, likely due to electronic interactions from Sn incorporation. This shift suggests that Sn influences the surface chemistry, stabilizing the oxide layer on titanium and possibly contributing to improved stability (Fig. 2c). For O1s, the peak at ~529.3 eV is attributed to M–O bond, and the peak at 530.6 eV to the lattice oxygen⁴¹ (Fig. 2d). The O1s peak in $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ exhibited a negative shift relative to RuO₂/TP, further indicating a charge redistribution that increases electron density around oxygen. This analysis of Ru 3d, Sn 3d, and Ti 2p states supports that charge redistribution occurs among these elements via bridging oxygen atoms.

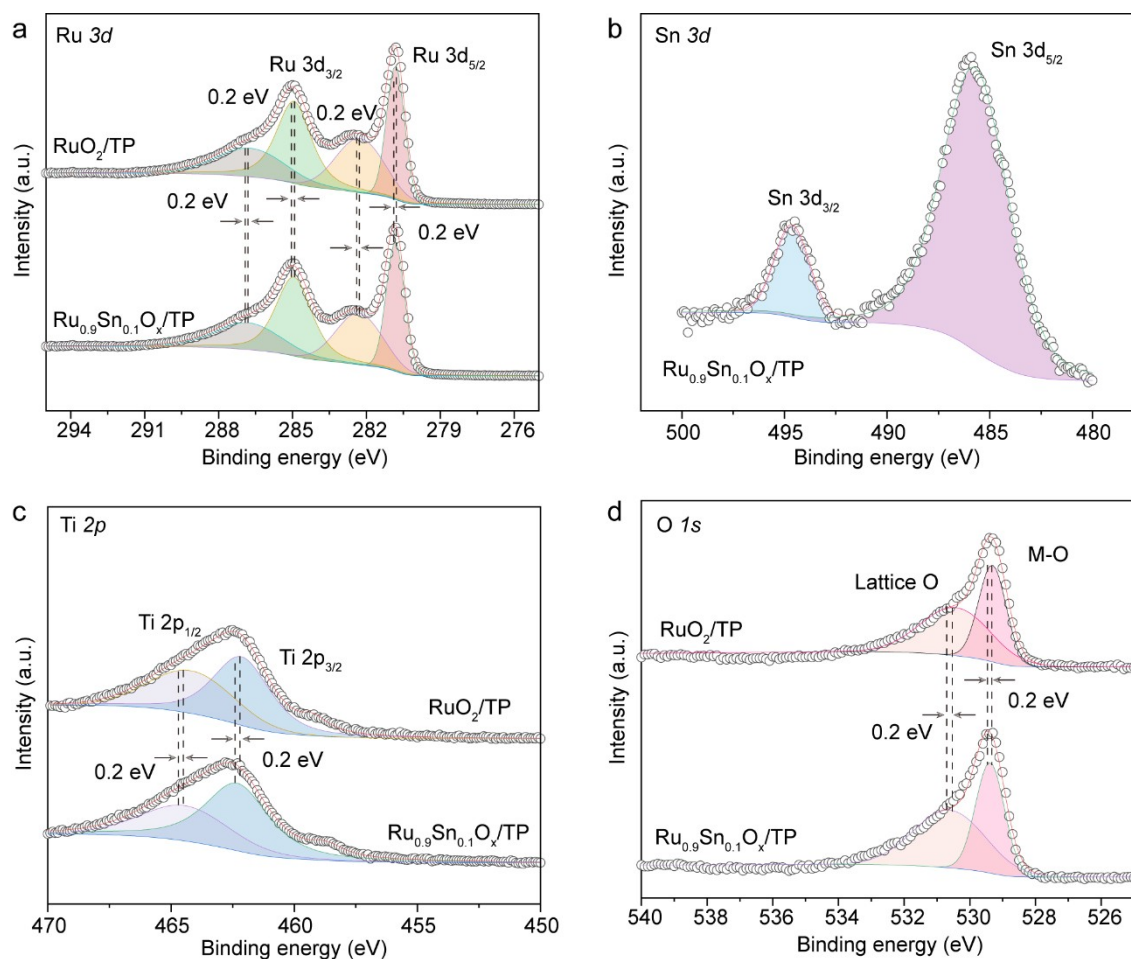


Figure 2. Comparison of (a) Ru 3d, (b) Sn 3d, (c) Ti 2p, and (d) O 1s XPS spectra of RuO₂/TP vs. Ru_{0.9}Sn_{0.1}O_x/TP.

Electrochemical performance

To evaluate the electrochemical performance of RuO_2/TP and $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ electrodes for Se(IV) removal, we conducted a series of tests at various current densities (-0.2 mA cm^{-2} and -2 mA cm^{-2}) and potentials (-0.6 V vs. SCE) in $0.1 \text{ M KH}_2\text{PO}_4$ solution containing different concentrations of Na_2SeO_3 (0.1 mM , 1 mM , and 10 mM). Linear sweep voltammetry (LSV) curves were shown in Supplementary Fig. 5. These tests aimed to assess the efficiency of Se(IV) reduction and the impact of current density and Se(IV) concentration on the removal process (Figs. 3a-3c). The size of the RuO_2/TP used for the Se(IV) reduction in the H-cell reactor was $2 \times 2 \text{ cm}^2$. ICP analysis showed that RuO_2/TP achieved a Se(IV) removal efficiency of $\sim 65\%$ at -0.2 mA cm^{-2} for $0.1 \text{ mM Na}_2\text{SeO}_3$ (Fig. 3a). However, when tested at -2 mA cm^{-2} or -0.6 V (vs. SCE), the reduction mechanism shifted to a 6-electron process, as indicated by red precipitation observed at the bottom of the H-cell reactor (Fig. S6). Under -2 mA cm^{-2} , RuO_2/TP reached $\sim 91\%$ for 0.1 mM Se(IV) removal efficiency within 8 hours, suggesting that increased current density enhances Se reduction (Fig. 3a). Conversely, lower current densities (-0.2 mA cm^{-2} and -0.6 V (vs. SCE)) resulted in lower removal efficiencies (Fig. 3a), likely due to Se accumulation on the electrode surface, blocking further Se(IV) reduction. For higher Se(IV) concentrations (1 mM and 10 mM), RuO_2/TP removal efficiency dropped significantly at lower currents due to rapid gray Se precipitation (Figs. 3b and 3c). However, at -2 mA cm^{-2} , removal efficiency was maintained at $\sim 83\%$ for 1 mM and 75% for 10 mM Se(IV) , indicating high current density mitigates Se precipitation. To remove the accumulated Se, the RuO_2/TP electrode was used as the anode at 50 mA/cm^2 for 30 minutes for oxygen evolution reaction (OER), restoring electrode activity for reuse.

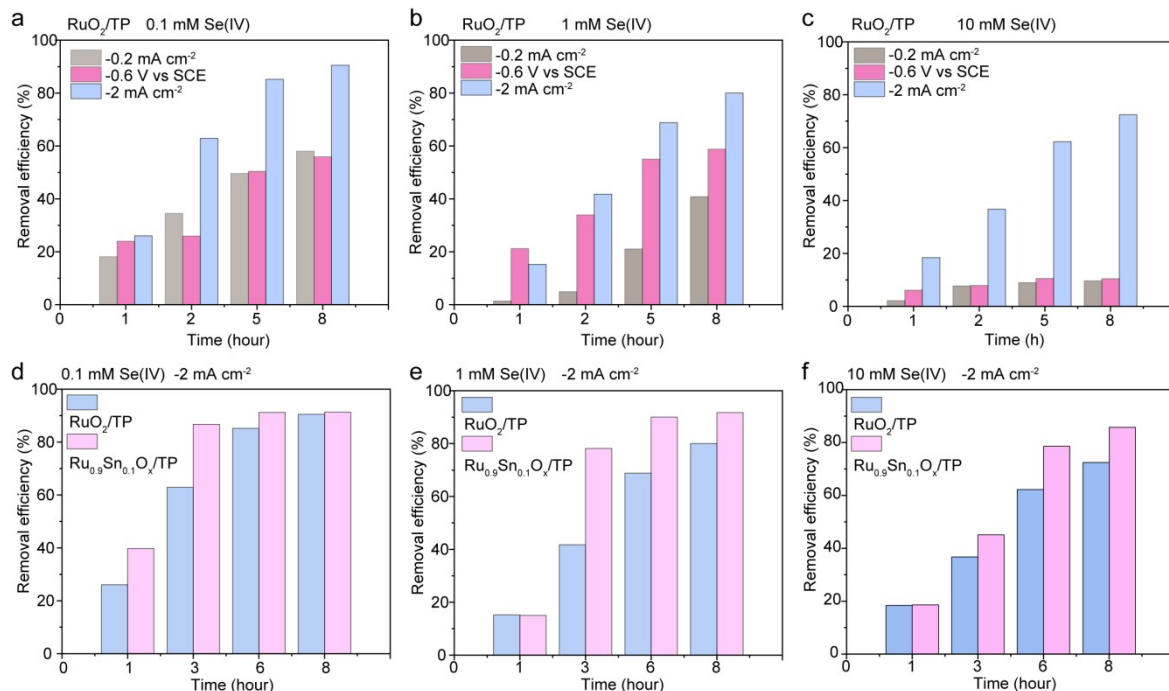


Figure 3. Electrochemical reduction of 0.1 mM (a), 1 mM (b), 10 mM (c) Se(IV) using RuO₂/TP under -0.2 mA cm⁻², -2 mA cm⁻², and -0.6 V (vs. SHE) conditions in an H-cell reactor. Comparative electrochemical reduction of 0.1 mM (d), 1 mM (e), 10 mM (f) Se(IV) using RuO₂/TP vs. Ru_{0.9}Sn_{0.1}O_x/TP under -2 mA cm⁻² in an H-cell reactor.

In comparison, Ru_{0.9}Sn_{0.1}O_x/TP demonstrated ~90% removal efficiency for Se(IV) across concentrations from 0.1 mM to 10 mM at -2 mA cm⁻² (Figs. 3d-3f), surpassing RuO₂/TP and suggesting enhanced capability for Se(IV) reduction. In simulated wastewater containing 1 mM Se(IV) along with competitive anions (0.5 M Cl⁻, 0.1 M SO₄²⁻, 0.01 M NO₃⁻), Ru_{0.9}Sn_{0.1}O_x/TP maintained ~90% removal efficiency (Fig. 4a), even when all anions were combined (Fig. 4b). These experiments, conducted in an H-cell reactor with a Nafion membrane, indicate that competitive anions generally did not affect Ru_{0.9}Sn_{0.1}O_x/TP's performance in Se(IV) reduction. Similarly, when experiments were conducted in a one-chamber reactor, it was found that SO₄²⁻ and NO₃⁻ had minimal impact on Se(IV) reduction efficiency (remained at ~90%). However, the presence of Cl⁻ led to a drastic drop in efficiency to ~8%, likely due to Cl⁻ oxidation to ClO⁻ ³⁶, which reoxidizes Se(0) to Se(IV) (Fig. 4c), thereby counteracting the Se(IV) reduction process. These findings suggest that for wastewater containing Cl⁻, an H-cell reactor with a membrane is therefore preferred to prevent ClO⁻ crossover, whereas a single-chamber reactor may suffice for solutions with SO₄²⁻ and NO₃⁻, reducing costs. In all tests, Ru_{0.9}Sn_{0.1}O_x/TP showed high durability, with reactivation

achieved by using the electrode as the anode at 50 mA cm^{-2} for 30 minutes, enabling its reuse in Se(IV) reduction. Moreover, $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ showed ~ 110 hours of stability at -2 mA cm^{-2} in H-cell reactor under a continuous flow of 0.39 mL/min of 1 mM Se(IV) with competitive anions (0.5 M Cl^- , 0.1 M SO_4^{2-} , 0.01 M NO_3^-), achieving a removal efficiency of $\sim 30\%$ (Fig. 4d, and Fig. S7). RuO_2/TP -based electrodes also hold promise for dual use as both cathode and anode in future two-electrode systems, given their efficacy in OER. Post-reaction characterizations revealed that $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ was stable for removal of Se(IV) (Figs. S7-S11). The surface appeared to undergo restructuring during the reduction and re-oxidation steps, which aimed to oxidize the Se(0) precipitating on the surface of the catalysts. These reduction and oxidation cycles lead to the catalyst's reconstruction.

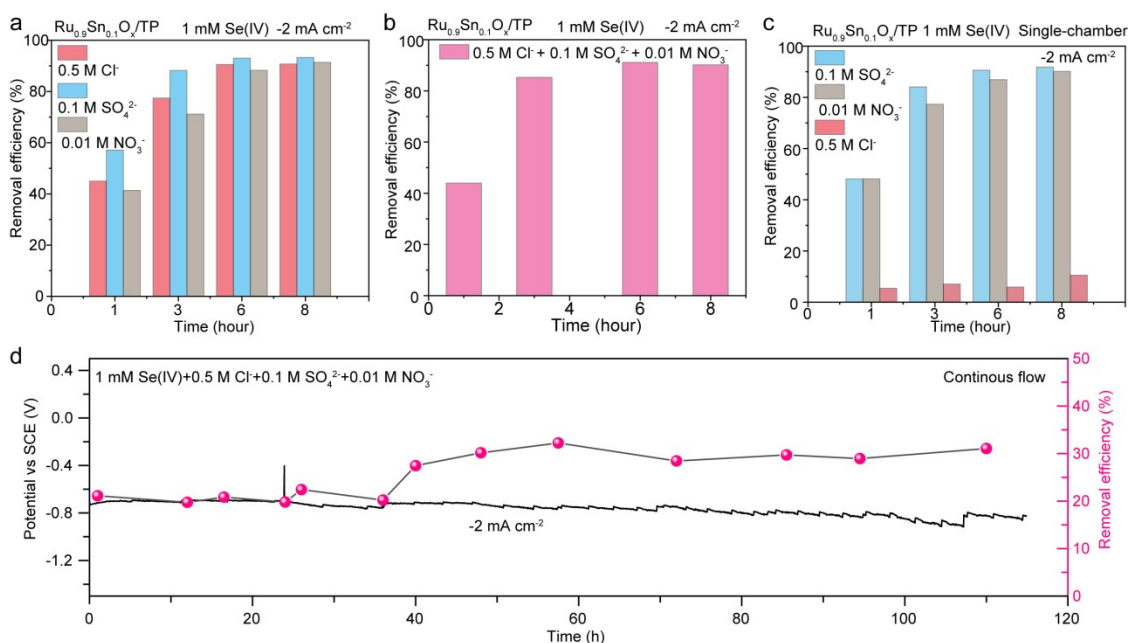
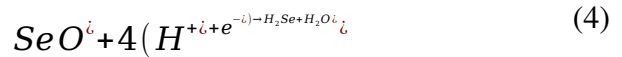
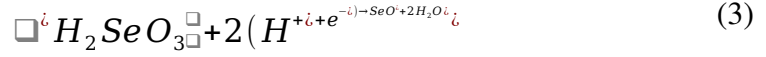
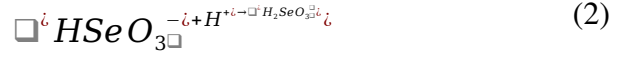
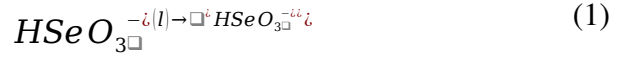


Figure 4. (a), Comparative electrochemical reduction of 1 mM of Se(IV) with competing ions (0.5 M Cl^- vs. 0.1 M SO_4^{2-} vs. 0.01 M NO_3^-) using $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ under -2 mA cm^{-2} in H-cell reactor. (b), Electrochemical reduction of 1 mM of Se(IV) with a combination of competing ions ($0.5 \text{ M Cl}^- + 0.1 \text{ M SO}_4^{2-} + 0.01 \text{ M NO}_3^-$) using $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ under -2 mA cm^{-2} in H-cell reactor. (c), Comparative electrochemical reduction of 1 mM of Se(IV) with competing ions (0.5 M Cl^- vs. 0.1 M SO_4^{2-} vs. 0.01 M NO_3^-) using $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ under -2 mA cm^{-2} in one-chamber reactor. (d), Stability of $\text{Ru}_{0.9}\text{Sn}_{0.1}\text{O}_x/\text{TP}$ under -2 mA cm^{-2} for removal of 1 mM of Se(IV) in a continuous flow, with competing ions (0.5 M Cl^- vs. 0.1 M SO_4^{2-} vs. 0.01 M NO_3^-) in an H-cell reactor.

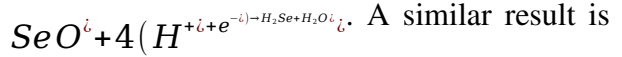
DFT calculations

At the experimental $\text{pH} = 5.5$, we expect the predominant aqueous selenium oxyanion

species to be HSeO_3^- . Based on this, we propose the following potential reactions for selenium reduction:



In the proposed pathway, the adsorbed *HSeO_3^- is first protonated to form H_2SeO_3 (Reaction 1). Subsequently, the system undergoes electron and proton transfer to reduce Se and produce H_2O (Reactions 2 and 3). An alternative pathway suggests that SeO is initially reduced to Se and then to H_2Se . However, a comparison of reaction enthalpies indicates that further reduction of Se to $\text{Se}(-2)$ is not energetically favorable. The energy diagrams at the equilibrium potential ($U = 0$ V) versus RHE and at the applied potential ($U = 0.505$ V) are presented in Fig. 5. At $U = 0$ V, the energy diagram for RuO_2 reveals that the rate-determining step in the overall Se reduction reactions is:



A similar result is observed in the energy diagram for $\text{Ru}_{0.875}\text{Sn}_{0.125}\text{O}_2$ at $U = 0$ V. When the applied potential is adjusted to $U = 0.505$ V (Fig. S11), all of the reaction steps for $\text{Ru}_{0.875}\text{Sn}_{0.125}\text{O}_2$ become exothermic. We note that this potential is close to the experimentally observed potential at which the experiments show appreciable Se reduction. In contrast, there remains a thermodynamic energy barrier in Reaction 1 for RuO_2 . This observation explains why $\text{Ru}_{0.875}\text{Sn}_{0.125}\text{O}_2$ exhibits superior reduction performance compared to RuO_2 , which is consistent with the experimental results.

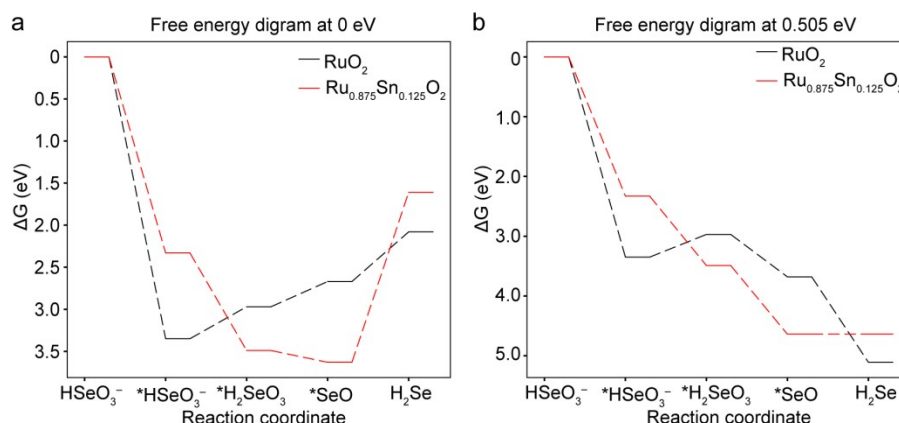


Figure 5. Calculated potential energy diagram at (a) 0 eV and (b) 0.505 eV, such as open circuit voltage (0 V), and onset potential versus RHE, which is displayed in black and red bars, respectively.

Conclusion

In this study, we developed RuO₂-based nanocatalysts grown on titanium plates (RuO₂/TP) to enable efficient electrochemical reduction of selenite Se(IV) in wastewater. The optimized Ru_{0.9}Sn_{0.1}O_x/TP electrode demonstrated high removal efficiencies of over 90% for Se(IV) concentrations of 0.1, 1, and 10 mM. Notably, Ru_{0.9}Sn_{0.1}O_x/TP maintained similar performance even in the presence of competitive ions (Cl⁻, SO₄²⁻, and NO₃⁻), underscoring its suitability for treating complex wastewater matrices. Testing in H-cell and one-chamber reactors showed that SO₄²⁻ and NO₃⁻ did not impact Se(IV) reduction efficiency on Ru_{0.9}Sn_{0.1}O_x/TP; however, the oxidation of Cl⁻ ions to ClO⁻ ions led to a significant decrease in removal efficiency. Benefiting from strong adhesion to the titanium substrate, these RuO₂/TP-based electrodes exhibited stable recyclability for Se(IV) reduction. Microstructural analyses further indicated that Sn doping promotes charge redistribution, which minimizes gray Se deposition on the electrode surface, thus enhancing removal efficiency compared to un-doped RuO₂/TP electrodes.

Supporting Information

The Supporting Information is available free of charge at

The experimental procedure, along with pre-reaction and post-reaction XRD patterns, SEM images, EDS mapping of RuO₂/TP, LSV curves, post-reaction XPS analysis of Ru_{0.9}Sn_{0.1}O_x/TP, and post-reaction SEM images of Ru_{0.9}Sn_{0.1}O_x/TP, are provided in the

Supporting Information.

Acknowledgments:

This material is based upon work supported by the National Alliance for Water Innovation (NAWI), funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Industrial Efficiency and Decarbonization Office, under Funding Opportunity Announcement DE-FOA-0001905 and Subcontract number 7630709. Work at Lawrence Berkeley Laboratory was supported by the National Alliance for Water Innovation (NAWI), funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, Advanced Manufacturing Office under Funding Opportunity Announcement DE-FOA-0001905 under Award Number DE-AC02-05CH11231, and funded in part through contract No. 4600014330 with the California State Department of Water Resources to Lawrence Berkeley National Laboratory. Theoretical calculations were performed using computational resources sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory. Auburn University acknowledges the National Alliance for Water Innovation (NAWI), funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Industrial Efficiency and Decarbonization Office, under Funding Opportunity Announcement DE-FOA-0001905 under Grant Number G00015396. S.Z. acknowledges support from Auburn University's faculty startup. This work utilized the Shared Equipment Authority (SEA) at Rice University.

Author contributions: H.W. and S.H. conceived the idea and designed experiments. H.W. supervised the project. S.H. prepared the samples, performed the experiments, and analyzed the data. S.H. and Y.F. did the SEM, SEM-EDS, and XRD characterizations. Y.F., C.Q., and C.S. did the XPS. T.W., Z.Y., and Z.X. helped with the TEM characterization. D.W. and J.C. did the DFT calculations, and A.J. supervised and guided the calculation study. S.Z. provided some valuable suggestions. S.H. and H.W. wrote the manuscript. D.W., S.Z. A.J., S.H., and H.W. revised the manuscript with inputs from all authors.

Competing interests: There is no competing interest.

Data and materials availability: All data needed to evaluate the conclusions in the paper are presented in the paper or the Supplementary Information.

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