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Photoelectrode materials for photo-assisted electrochemical water treatment

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Mohamed Ateia Ibrahim (environmental engineer and group leader at the US Environmental Protection Agency and adjunct assistant professor at Rice University) and Ashley Hesterberg Butzlaff (environmental engineer at the US Environmental Protection Agency) discuss material-based guidelines for optimizing photoelectrode design with a focus on utilizing advanced nanostructure fabrication techniques to enhance charge separation and transport, as well as identifying and integrating the most effective co-catalysts to improve efficiency and stability. These insights are critical for the development of practical and efficient photo-assisted electrochemical systems, essential for future water-treatment technologies.

The escalating global water crisis underscores the urgent need for transformative technologies that can sustainably purify water and remediate wastewater. An emerging solution lies in photo-assisted electrochemical (PEC) systems, which utilize light-absorbing semiconductor photoelectrodes to drive water-treatment redox reactions. However, the adoption of PEC systems hinges on addressing critical material limitations. Conventional oxide semiconductors, such as TiO_2, demonstrate inadequate solar-to-chemical conversion efficiencies that would necessitate cost-prohibitive bias voltages. Therefore, a paradigm shift is vital for coupling earth-abundant and non-toxic light absorbers with oxygen evolution co-catalysts for balanced and efficient charge transfer. Interfacial engineering is also imperative for suppressing losses at the photoelectrode surface while retaining stability. This article identifies material-based guidelines for photoelectrode design to provide practical and economic PEC systems.

M.A. discusses nanostructured photoanodes

A major area of focus has been nanostructured transition-metal-oxide photoanodes, such as titania (TiO_2), tungsten oxide (WO_3), iron oxide (Fe_2O_3), and bismuth vanadate ($BiVO_4$).[1] TiO_2 is one of the most studied photoanode materials, but rapid recombination and its wide band gap limit visible-light harvesting. Ti/TiO_2 nanotube arrays grown by anodization enhance charge separation and transport and can be doped with carbon and nitrogen to extend the absorption spectrum and boost PEC activity. Monoclinic WO_3 has suitable band-edge positions for water oxidation and a smaller band gap than TiO_2, enabling visible-light activity. However, WO_3 can suffer from poor charge-carrier separation. To address this, WO_3 nanowire arrays on conductive substrates, such as fluorine-doped tin oxide (FTO) glass, have shown much improved PEC performance. Coupling WO_3 with narrow-band-gap semiconductors, such as CdSe, could further facilitate visible-light PEC activity.

Fe_2O_3 is earth abundant and stable for water oxidation but has issues with poor charge conductivity. However, porous α-Fe_2O_3 nanotube arrays synthesized by anodization have shown higher photocurrents and excellent PEC degradation of organic pollutants.[2] Incorporating electrocatalysts such as cobalt-oxide nanoparticles onto Fe_2O_3 photoanodes can also expedite charge transfer and boost PEC efficacy. $BiVO_4$ has emerged as a promising photoanode material given its small (2.4 eV) band gap, which enables visible-light absorption up to 530 nm. $BiVO_4$/WO_3, as a heterogeneous p-n junction, has achieved high PEC activity under visible-light irradiation. Composite $BiVO_4$/TiO_2 photoanodes also display enhanced charge separation and stability.[1] Other novel metal-oxide photoanodes, such as gallium oxide and bismuth oxyhalides (such as BiOI and BiOBr), have shown potential, but improving efficiencies and stability will require further work.[3]

Supporting electrocatalysts

Deploying oxygen evolution catalysts, such as CoPi, Ni, and Ni-Fe oxides, is an effective strategy for accelerating surface charge transfer and speeding up oxidation kinetics in PEC systems. Loading photoanodes, such as Fe_2O_3 and $BiVO_4$, with these co-catalyst nanoparticles has enabled higher photocurrents and treatment efficiencies. However, electrocatalyst aggregation and detachment remains a key issue. Employing conductive scaffolds, such as nickel foam, as both the catalyst support and cathode in PEC cells has also improved performance and avoided the use of expensive catalysts, such as Pt.[4] Graphene-based nanocomposites as co-catalysts show particular promise in augmenting charge transport and

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Table 1. Nanostructured photoelectrode fabrication methods with their relative cost and feasibility

Semiconductor material	Co-catalyst material	Fabrication method	Relative cost	Feasibility
Cu_2O	IrO_x thin film	radio-frequency sputtering	$	moderate
			low material costs but vacuum processing increases the expense somewhat; scalable	
CdS	Pd quantum dots	chemical bath deposition	$	high
			a very low-cost process with commonly available materials; rapid deposition across large area	
TiO_2	Pt nanoparticles	hydrothermal treatment	$$	moderate
			moderate fabrication expense; expensive co-catalyst; process tuning is needed to improve yield	
$BiVO_4$	CoPi	photoelectrochemical electrodeposition	$$	moderate
			additional electrochemical equipment increases costs; co-catalyst stability needs improvement for practical use	
WO_3	RuO_x nanoparticles	thermal oxidation	$$	moderate
			a sustainable process with moderate cost for metal-oxide precursor; device integration needs optimization	
GaP	Rh nanorods	MBE	$$$	low
			ultra-high-vacuum MBE systems drastically increase the fabrication expense; mostly limited to research studies	
α-Fe_2O_3	NiO_x nanoclusters	ALD	$$$	low
			precise ALD processing enables excellent quality but very high operational costs; scale-up is difficult	

The listed semiconductor and co-catalyst materials are listed as only clarifying examples with each method. Abbreviations: CoPi, cobalt phosphate; MBE, molecular beam epitaxy; ALD, atomic layer deposition.

separation in PEC photoelectrodes. Metal nanoparticles coupled to graphene sheets exhibit photocatalytic and electrocatalytic functionality.

Evaluation conditions and scale-up

Photoelectrode PEC performance for model compounds drops significantly in complex water matrices containing diverse organics, inorganics, and solids. Natural organic matter can readily adsorb onto photoelectrode surfaces, interfering with light absorption and pollutant oxidation. It is vital to assess photoelectrode PEC activity by using real wastewaters or secondary effluents to reveal fouling issues and matrix effects. Furthermore, PEC testing over extended operational time and cycles is critical prior to scale-up, whereas most studies examine short-term stability over only hours to hundreds of hours. Photocorrosion mechanisms must be deciphered to guide strategies for improving photoelectrode lifetimes. For example, $BiVO_4$ remains inadequate because it is susceptible to corrosion. Exploring surface coatings, such as Al_2O_3 and TiO_2, has shown some promise in passivating photoanodes such as $BiVO_4$.[5]

Flexible, scalable manufacturing techniques will be imperative for translating promising lab-based photoelectrodes into practical water-treatment applications. Conventional methods of fabricating semiconductor devices are often not economically viable at large scales. Roll-to-roll processing, inkjet printing, and spray deposition are interesting alternatives for continuous, high-throughput photoelectrode production. Present fabrication methods for nanostructured photoelectrodes and their relative feasibilities are presented in Table 1. Effective photoelectrode modules should maximize efficiency by optimizing flow-cell-reactor designs to minimize spacing. Computational fluid dynamics (CFD) modeling can guide optimized electrode configuration and hydrodynamics. Advanced controls of adjustable flow and current and online monitoring to track PEC performance are also critical.

Practical takeaways

In summary, recent advances in nanostructured metal-oxide photoelectrodes and hybrid co-catalyst systems show tremendous promise to enhance visible-light PEC activity. However, intensive research and development is still needed to drive the adoption of PEC technology. Research efforts should focus on synthesis scale-up, integrated treatment schemes, reactor engineering, and rigorous long-term evaluation under application-relevant conditions. Deploying material informatics with knowledge of defect tolerance, light management, and catalyst integration will be decisive in

elevating PEC systems as a transformative water-treatment technology. Multicomponent systems integrating dissimilar materials via gradient doping or heterogeneous junctions provide new directions for synergistically melding complementary properties. The machine-learning-guided discovery of computational materials can accelerate the identification of optimal PEC photoelectrodes.

Tandem systems that couple PEC technology with other treatment units, such as anaerobic digestion, provide a promising integrated approach. The PEC process can degrade bio-recalcitrant organics and disinfect pathogens, enabling the removal of constituents that inhibit biological treatment. A subsequent biological step can degrade intermediates and residuals cost effectively. Exploring portable or floating PEC-bioreactor systems could provide sustainable water-reuse and -treatment capabilities in rural areas or developing communities.

A.B. responds: Expanding the focus from material design to reactor performance and treatment applications

The above discussion provides a succinct and thorough overview of recent advances in photoactive electrode materials. Most importantly, the present shortcomings of photoelectrode materials are addressed from a realistic yet optimistic perspective. Here, I expand Dr. Ateia's main points by focusing on reactor scale-up and future applications.

Nanostructured materials can be derived from diverse substrates to provide increasingly versatile structures with increased photoelectrode stability, light absorption, active sites, and charge transfer and separation.[6] Moreover, nanostructures provide ideal platforms for well-defined catalyst integration and unique heterojunctions. Similarly, interfacial engineering can provide increased photocurrents through enhanced charge transfer and separation, such as that achieved with TiO_2/PbS-CdS quantum-dot heterostructured photoelectrodes.[7] However, with expanding and diverse synthesis options, nanostructured photoelectrode synthesis must maintain simplicity and uniform quality with scale-up. These aspects become increasingly important with multi-step synthesis and the addition of catalysts and/or interfacial layers.

Innovative photoelectrode materials are subject to extensive physical, chemical, and (photo)electrochemical characterization, but photoelectrode performance is often evaluated in idealized or synthetic environments.[8,9] Inaccurate performance metrics, determined in unrealistic settings, hinder and misguide reactor scale-up. Overly optimistic operational parameters and/or material efficiencies at bench scale will ultimately produce disappointing results at pilot and full scale. In contrast, performance assessed under conditions that approach application settings (1) accelerates optimized reactor design, (2) identifies practical operational parameters (e.g., voltage, energy density, and energy consumption), and (3) quantifies the effect of variable conditions (e.g., influent water quality, treatment volumes, and solar irradiance).

With meticulous material design, PEC systems can serve as a valuable pre- or post-treatment step that can be easily added to existing treatment plants. This PEC application would encourage photoelectrode design to prioritize the selective formation of the desired intermediate and terminal products. For example, PEC systems can produce more readily biodegradable products to serve as a pre-treatment step for biological systems.[10] Photoelectrode by-products should be identified and quantified, as commonly done for traditional electrodes (i.e., disinfection by-products with boron-doped diamond electrodes), so that PEC applications can be identified and the impacts on long-term material performance and stability can be determined. Ultimately, improvements in material design cannot be fully utilized or recognized without increased interdisciplinary efforts for scalable systems.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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