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Perspective

Lead-Free Halide Perovskites for Photocatalysis via High-Throughput Exploration[†]

Astita Dubey, Sheryl L. Sanchez, Jonghee Yang, and Mahshid Ahmadi*

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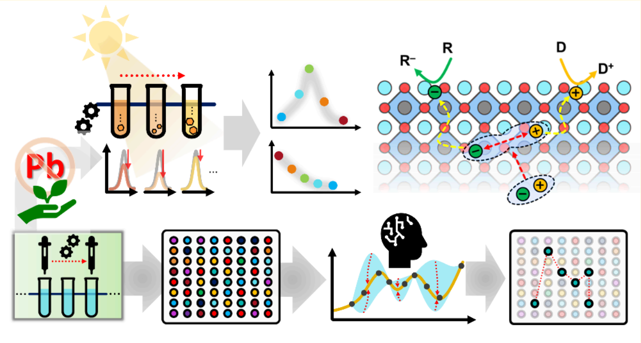
ABSTRACT: This Perspective navigates the transformative synergy between machine learning (ML) techniques and high-throughput (HT) methodologies in the realm of photocatalysis, aiming to overcome the inefficiencies and drawbacks associated with existing photocatalysts. Pb-free hybrid perovskite (HP) nanocrystals (NCs) emerge as promising candidates, offering distinctive physicochemical and optical attributes in addition to nontoxicity. The integration of HT automated methods accelerates the synthesis and characterization of novel Pb-free HP materials while also addressing challenges in obtaining large, high-quality data sets for training ML models. The proposed multidisciplinary approach, combining experimental and computational simulations, aims to unravel the complexities of photocatalytic systems, fostering the development of innovative strategies for materials development. The convergence of experimental techniques, computational simulations, and ML is poised to revolutionize photocatalysis (PC), propelling the field into an era of unprecedented discovery and innovation.



INTRODUCTION

Pb-Free HPs as Potential Candidates for PC. Photocatalysis (PC) presents a promising approach for the environmentally friendly breakdown of organic pollutants. However, challenges, such as inefficiency, limited light absorption, cost, and potential toxicity, remain unresolved. Semiconductor-based photocatalysts are at the forefront of extensive research efforts in various photocatalytic applications. These include nitrogen fixation,[1] carbon dioxide reduction,[2] methane degradation,[3] chemical synthesis,[4] and water splitting[5] for both hydrogen and oxygen evolution reactions. They are also pivotal in environmental cleanup, particularly through the photodegradation of pollutants.[6−8] A notable example of photocatalysis in aqueous environments is the degradation of organic dyes in water. These dyes, commonly used in industries like textiles, plastics, paper, and cosmetics, are not only nonbiodegradable but also pose significant risks to human health and aquatic life.

In photocatalytic degradation, a semiconductor nanocrystal (NC) absorbs light of an energy larger than the band gap of the material to generate photoexcited electrons in the conduction band and holes in the valence band. These photoexcited charge carriers either recombine or diffuse to the surface of the photocatalyst and interact with molecular oxygen and water to produce a plethora of reactive oxygen species (ROS), e.g., hydroxyl radicals (•OH), superoxide radicals (•O_2^-), singlet oxygen, and hydrogen peroxide (H_2O_2), at the active site of photocatalyst. The ROS are highly reactive and have the potential to cleave the C−C bonds as well as the aromatic rings, which results in the degradation of the molecular structure of the organic pollutant.[6−8] Therefore, the most critical phases in photocatalysis are light absorption, charge carrier generation and separation, and surface redox reactions, as shown in Figure 1a. The expected major properties required in efficient photocatalysts are having a narrow band gap (i.e., E_g = 2.5−1.4 eV), a large number of active sites on the surface, recyclability, less recombination of photoinduced charge carriers, and facile charge transport from the bulk to the surface of the catalyst (Figure 1b). Besides, nontoxicity, low cost, easy production, and chemical stability should be achieved toward their ubiquitous applications. Hence, the efficiency of photocatalysts hinges on these main primary criteria.

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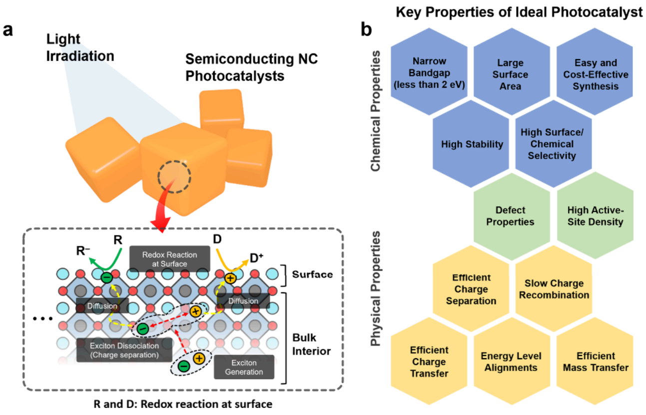

Figure 1. (a) Schematic representing the main steps involved in the photocatalytic reaction. (b) The hexagons show the expected key features in an ideal photocatalyst.

In light of the aforementioned prerequisites, to date, several types of semiconductors NCs photocatalysts have been rationally constructed, including chalcogenides, oxides (MoC, Ga_2O_3, MoS_2, Bi_2WO_6, ZnS/CuS, SeO_2, WO_3, Nb_2O_5, ZnS, Fe_2O_3, Ag_2CO_3, AgX, and CeO_2),[9−11] carbon nitride (g-C_3N_4), reduced graphene oxide (rGO), quantum dots,[12,13] and Pb-based halide perovskite (HPs),[14] like $CsPbX_3$, $MAPbX_3$, and $FAPbX_3$ (X = Cl, Br, I). In particular , some photocatalysts like TiO_2, ZnO, Fe_2O_3, $MnFe_2O_4$, WO_3, Bi_2WO_6, and $BiVO_4$, which have been extensively investigated, exhibit notable photocatalytic efficiency against various organic pollutants, like rhodamine B, methyl orange, and methylene blue.[11,15−18]

Nonetheless, the primary drawback associated with the current photocatalysts lies in their wide band gap, deep trap states, rapid recombination of charge carriers, surface reconstruction, and nonreproducibility.[19,20] Furthermore, the synthesis conditions for these oxide-based photocatalysts are exceptionally harsh and time-consuming, necessitating high temperatures and pressures.[21−28] Hence, the synthesis process is energy-intensive and cost-ineffective. Consequently, due to these aforementioned limitations, the practical commercialization of these existing photocatalysts is unfeasible owing to their inefficient catalytic performances.

Pb-based halide perovskites (HPs) have demonstrated significant advancements in the past decade in photovoltaics, with an escalation in power conversion efficiency from 3.8% to 26.1%.[29] Such triumph is primarily attributed to the excellent photoactive behaviors of the HPs, which also have promising functionalities as photocatalysts. Furthermore, HPs can be miniaturized into the form of nanocrystals (NCs) via solution processing, which enables on-demand tailoring of surface facets and dimensionalities with a substantial surface-to-volume ratio.[30] These features can provide a substantial number of photocatalytic active sites on the surface and thereby can benefit from the photocatalytic actions. Notwithstanding, HPs grapple with the presence of toxic Pb and exhibit long-term instability, posing substantial challenges to their integration into everyday life.

Ensuring prolonged stability is imperative for the practical utilization of halide perovskites in real-world photocatalytic systems, necessitating effective mitigation strategies. Surface-related issues further complicate their application in photocatalysis. The surfaces of halide perovskite materials have a propensity to trap charge carriers and undergo surface recombination, detrimentally affecting the overall efficiency of photocatalytic processes.[14,31,32] Effectively passivating these surfaces to minimize such effects has emerged as a formidable challenge. Halide perovskites exhibit distinct behavior in photocatalytic applications compared to photovoltaics and light-emitting applications. In photocatalysis, the focus is on utilizing photogenerated charge carriers for chemical reactions, differing from the emphasis on charge extraction in photovoltaics.[14,33,34] Photocatalytic reactions involve redox chemistry, with variations in redox properties and mechanisms compared with photovoltaic charge transfer processes. The surface of the halide perovskites plays a crucial role in photocatalysis, influencing the catalytic activity through surface states, defects, and passivation layers. Creating active catalytic sites on the material's surface is a key aspect, involving modifications, doping, or cocatalyst incorporation, distinct from charge transport considerations in photovoltaics.[35] Notably, the presence of toxic elements, particularly lead, in many halide perovskites raises environmental and health concerns during photocatalytic processes.

Thus, there is a critical quest for novel Pb-free HPs for photocatalytic applications such as dye degradation and environmental remediation. Such exploration cannot compromise factors such as toxicity (Pb-based materials), cost (metal-based catalysts), or complexity in synthesis (metal-oxide or oxide-perovskite). Pb-free HP NCs are promising alternatives due to their distinctive physicochemical and optical attributes. The research advancements of Pb-free HPs are due to their tunable optical band gap ranging from 3.1 (400 nm) to 1.4 eV (885 nm),[36−40] large absorption coefficient with a reduced recombination of photoinduced charge carriers, defect tolerance, long diffusion length of the charge carrier, and nontoxicity compared to their Pb-based counterparts. Moreover, these materials demonstrate impressive electrical properties, such as efficient charge transport. They are cost-effective and easily producible through solution-processing routes and ecofriendly mechanochemical activation methods. In the domain of Pb-free HPs, there exists a considerable potential for the creation of multifunctional materials through a systematic approach to compositional design, leveraging solution alloying or doping methodologies. Thus, a comprehensive elucidation of the inherent structure−property relationships for the diverse Pb-free HP materials is necessary.

HPs exhibit expansive compositional spaces and can be crafted with extensive structural variability and dimensionality ranging from 0D to 3D, including quasi-2D HPs. Figure 2 presents a succinct collection of prospective Pb-free HPs for photocatalysis, spanning from 3D to 0D structures, predicated on their light absorption attributes.[36,37,39] 3D HPs emerge as prominently investigated materials owing to their light absorption coefficients, proficient solution processing capabilities at low temperatures, and extensive exciton diffusion lengths. Nevertheless, the challenges associated with stability and the recombination of charge carriers necessitate resolution before their effective deployment in practical photocatalytic applications. The tolerance factor (t) in 3D HPs is between 0.8 and 1, but when $t < 0.8$ or $t > 1$ it adapts to a low-dimensional structure, like 2D HPs. The general formula for 2D HPs is $(RNH_3)_2A_{n-1}B_nX_{3n+1}$, where n is the number of stacked corners shared octahedral layers [$n = 1$, 2D; $n = \infty$, 3D; and $1 < n < \infty$, quasi-2D],[36,37,39] as shown in Figure 2. In the class of 2D HPs, a key aspect of their classification revolves around crystallographic orientation, specifically along the (100),

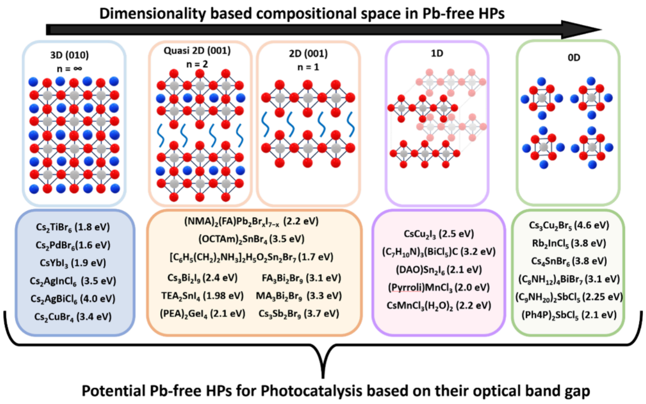

Figure 2. Variety of lead-free perovskites from 3D to 0D (left to right) based on their dimensionalities, with several examples.

(110), and (111) directions. Among these, the (100) orientation encompasses diverse structural types, such as Ruddlesden−Popper (RP) phases, Dion−Jacobson (DJ) phases, and those featuring alternating cations in the interlayer space (ACI types).[41,42] The representation of 2D HPs can be flat or corrugated structures composed of organic and inorganic layers arranged in a stacked lattice.[43] Corrugated 2D HPs introduce structural modification by incorporating undulating or folded features within the 2D layers. This corrugation can be achieved through various means, such as interplay of chemical properties, spacer cations, steric effects, and supramolecular (intermolecular) interactions.[44] The distinction lies in the added dimensionality and structural complexity introduced by the corrugations, offering additional avenues for tailoring the optical properties of these materials. The examples of "flat" 2D HPs are $(FPEA)_2PbI_4$, where FPEA = 4-fluorophenethylammonium, and $(PyrEA)PbI_4$, where PyrEA = pyridiniumethylammonium lead iodide. In contrast, $(NO_2PEA)_2PbI_4$ is found to be the rarer corrugated "(110)" 2D type perovskite.[45]

In explicating the dimensionality-based functionality of halide perovskites, critical distinctions emerge in the tunability of bandgaps, enhanced photoluminescence, quantum confinement effects, carrier mobility, stability, anisotropy, and size-dependent properties. Quasi-2D and 2D HPs exhibit optical characteristics like small Stokes shifts, narrow full width at half-maximum (fwhm), and nanosecond-range lifetimes. Conversely, corrugated 2D and 1D HPs typically manifest broad-band emissions with substantial Stokes shifts, associated with self-trapped excitons (STEs), while narrow-band emission arises from free excitons. The HPs, with a broadband emission, are characterized by a photoluminescence (PL) peak with a fwhm greater than 60 nm. The flexible and soft nature of HPs results in strong exciton−phonon interactions, leading to the entrapment of excitons within self-created potential barriers. In the cases of sufficiently strong exciton−phonon interactions, exciton movement is halted at a lattice site, resulting in self-trapping and the formation of STEs. Photoluminescence from STEs typically exhibits broad-band emission with a large Stokes shift. The luminescent characteristics are closely tied to structural dimensions, such as 3D, 2D, 1D, and 0D. Low-dimensional HPs are recognized for their broad-band emissions from STEs. Various types of broad-band emissions and the underlying mechanisms depend on the effects of structure orientations and chemical compositions in variable 2D HPs.

Also, surface defects of photocatalysts play a pivotal role by influencing the electronic structure, surface reactivity, and charge carrier dynamics of the photocatalyst. In particular, the ionic lattice binding nature of HPs renders diverse types of surface defects, opening up a wide range of surface chemical reaction scenarios. Cationic/anionic vacancies or dopants as defects create localized states within the band structure, altering the catalyst's ability to generate charge carriers. Additionally, defects can serve as active sites at the surface for photoredox reactions, thereby facilitating the conversion of target species. The strategic harnessing of such defects in photocatalysis is crucial for tailoring the optoelectronic properties of HPs and optimizing their catalytic performance.

Other HP structures including $A_2M^{4+}X_6$, $A_2M_3^{3+}X_9$, and $A_3M^+M^{3+}X_6$ are also being reported for Pb-free perovskites. Nontoxic exchange cations like Sn^{2+}, Ge^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, and Cu^{2+} can substitute Pb^{2+} in the perovskite moiety.[36,39] However, the substitution of Ca^{2+} and Sr^{2+} ions widens the band gap and the effective mass of charge carriers. Besides, their hydroscopic nature is undesired. Sn^{2+}- and Ge^{2+}-based HPs are being studied; for example, $CsSnI_3$, $MASnI_3$, and $FASnI_3$ exhibit direct optical bandgaps in the range of 1.3−1.4 eV.[46] Ge-based HPs like $CsGeI_3$, $MAGeI_3$, and $FAGeI_3$, also exhibit direct bandgaps of 1.6, 1.9, and 2.2 eV, respectively.[47] Nevertheless, these materials face stability issues, as they quickly transform to tetravalent (Sn^{4+},and Ge^{4+} respectively) oxidation states when exposed to air, which leads to phase transformation and even decomposition, making them inefficient candidates for photocatalysis. In contrast, the Mn^{2+} and Cu^{2+} substituting Pb in the perovskite structure do not possess instability issues and maintain desirable optical properties required for photocatalysis.[48,49]

Apart of these, $A_3B_2X_9$-type Pb-free HPs exhibit bandgaps ranging between 1.9 and 2.9 eV.[50] In particular, the inorganic low-dimensional HPs with the formula $Cs_3M_2X_9$ (where M = Bi, Sb and X = Br, I) have been developed to improve stability with a narrow band gap. For example, $Cs_3Bi_2X_9$ (X = Br, I) has a narrow band gap from 2.2 to 1.7 eV and robustness under ambient conditions.[36,51] These attributes collectively designate it as a promising material for application in photocatalytic assessments aimed at mitigating pollutants.

The double HPs with a formula of $A_2B^+B^{3+}X_6$ (A = Cs^+, MA^+; B^+ = Ag^+, Na^+, In^+; B^{3+} = In^{3+}, Bi^{3+}, Sb^{3+}) showcase exceptional optoelectronic properties.[41] $Cs_2AgBiBr_6$ has an indirect band gap of 1.95 eV with strong nonradiative recombination, which is undesirable for photocatalytic applications.[52] A complete substitution of Cs^+ with heterocyclic ion azetidinium (Az^+) forms a direct band gap of 3.2 eV in the 1D $[(CH_2)_3NH_2]_2AgBiBr_6$ material,[53] whereas $Cs_2AgInCl_6$ has a narrower direct band gap of 1.1 eV[54] with low trap density, making it more suitable for photocatalysis.

The lanthanide-based double HPs like $Cs_2NaTbCl_6$ exhibit strong green emission due to *f*−*f* transitions. However, there are several drawbacks associated with the utilization of lanthanide-based HPs in photocatalytic processes.[55] One significant challenge is the limited availability of lanthanides, which are rare earth elements. This scarcity can lead to increased production costs. Additionally, the extraction and processing of lanthanides can have environmental impacts, raising concerns about sustainability and ecofriendliness. Another drawback is the potential toxicity of certain lanthanide ions, which may pose health risks, especially in the case of accidental release into the environment or human exposure

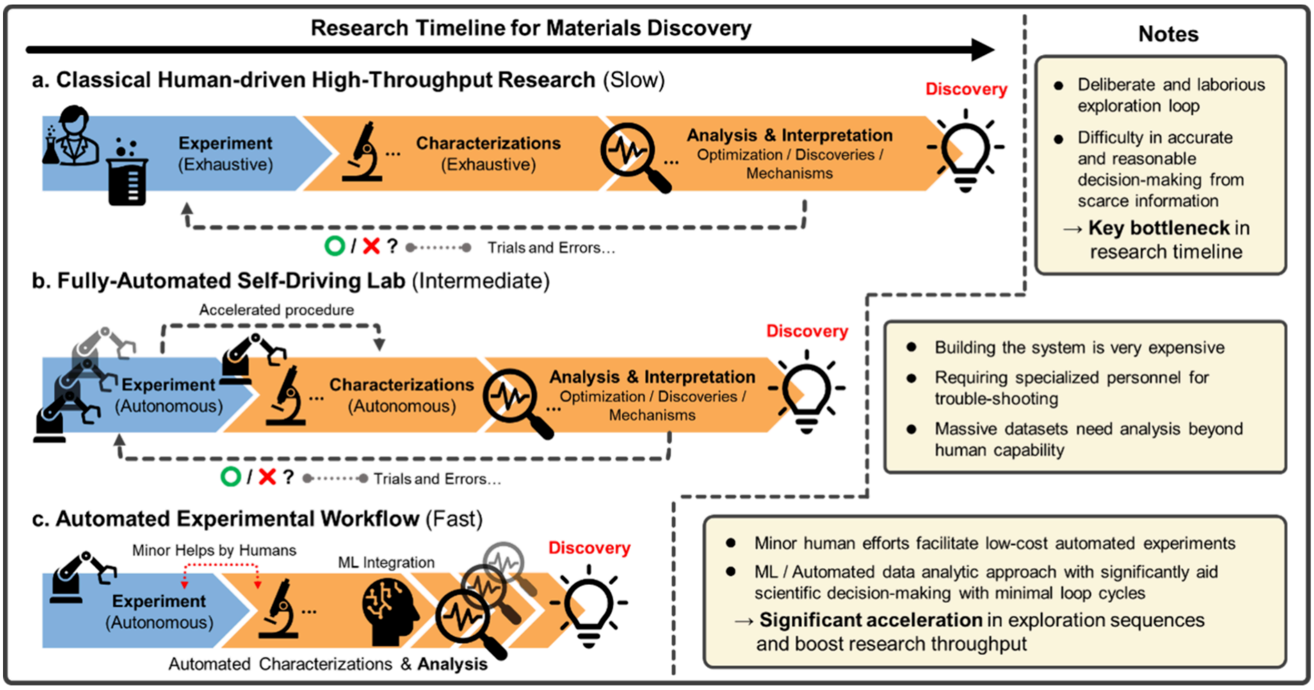

Figure 3. Schematic comparison of three distinctive experimental workflows for materials discovery: (a) classical workflow driven by humans, (b) fully automated self-driving lab, and (c) automated high-throughput experimental workflow.

during material synthesis and application. Therefore, understanding and mitigating these toxicity concerns are crucial for alternatives to lanthanide-based HPs.

Given the current state of Pb-free HPs, it is evident that a judicious selection of nontoxic ions at A- and B-sites within the perovskite structure is imperative. The expansive array of elements in the periodic table provides an extensive platform for the exploration of functional Pb-free HPs with diverse functionalities. Presently, only a few limited numbers of Pb-free systems align with the requirements outlined in Figure 1 for photocatalysis testing, necessitating more extensive explorations of materials with investigation for functional materials discovery. Moreover, there exists a critical demand for the identification and synthesis of new functional, nontoxic HPs that are economically viable, facile to produce, and serve as efficient photocatalysts. Hence, systematic, and multidimensional approaches are necessary for materials explorations with adherence to initial screening criteria such as a narrow band gap, minimal charge carrier recombination, and robust stability.

Unfortunately, the classical exploration workflow based on trial-and-error experiments and analysis consumes substantial time budgets in materials discovery. Such limited conditions, as well as the research budget for materials explorations, make the systematic and extensive materials discovery sequence extremely challenging.[21,56−58] This not only causes researchers to inevitably rely on the serendipitous discovery of scarce material candidates but also results in sluggish explorations, creating significant bottlenecks within the research timeline.

To expedite the investigation of both existing and novel Pb-free HP NCs in photocatalysis, this Perspective promotes the incorporation of automated workflows and machine learning (ML). Time-sensitive issues necessitate high-throughput solutions. This strategy encompasses the fast synthesis of materials and the identification of efficient photocatalysts for specific target reactions by screening a diverse range of catalysts.

HIGH-THROUGHPUT AUTOMATED SYNTHESIS AND CHARACTERIZATION FOR Pb-FREE HPs

The conventional experimental workflow for the discovery of novel and functional materials has historically constituted the predominant approach for the development of new materials, with "*fortuitous*" discoveries that have served as an additional facet of the exploration well-representing the sequence of photocatalytic materials discovery. Understanding of material functionalities hinges predominantly on the meticulous characterizations, a process known for its intensive labor and time demands as well as the expensive costs. The resulting scarce information on materials and functionality spaces subsequently causes difficulty for appropriate decision-making to drive the exploration. As a consequence, the overall process becomes sluggish, rendering significant bottlenecks within the research timeline (Figure 3a).

The remarkable advances in recent robotic systems provide an opportunity to build fully automated laboratory platforms. This realizes rapid and precise high-throughput (HT) combinatorial synthesis of a multitude of inorganic and hybrid organic−inorganic materials under control. Utilization of these state-of-the-art autonomous experimental platforms manifest the full exploitation of combinatorial chemistry, shedding light on accelerating photocatalyst discovery from fundamentals to functionalities (Figure 3b). Also, overcoming the synthesis challenges (time-consuming, laborious, human error, and resource-intensive) using autonomous platforms can even widen researcher's perspectives on the photocatalyst candidates from the classical oxides to unexplored Pb-free halide platforms. In fact, HT automated experimentation has been facilitating the synthesis and screening of large molecular libraries containing a large number of organic compounds ever since its introduction 40 years ago to speed up drug research. This method has changed the paradigm of pharmaceutical research from focusing on single compounds to focusing on an immense collection of compounds, since the essential feature of HT is to replace the single compound in the chemical reaction with mixtures of compounds. This makes it possible to synthesize a huge library of novel materials in a single process.

However, substantial practical challenges lie in the meteoric costs to establish infrastructure and specialized personnel/scientists who can troubleshoot, all of which cannot be easily achieved in general. Moreover, massive amounts of the produced data sets need to be analyzed, which is the most important (and time-consuming) stage in materials exploration but far beyond human capability. Thus, even with the accelerated experimentation utilizing such state-of-the-art, high-cost research infrastructure, the overall timeline for materials discovery cannot be significantly accelerated (Figure 3b).

Here, integration of machine learning (ML) or automated analytical functions into the HT experimental workflow can render an effective breakthrough. From the large and complex data sets, those algorithms can effectively discover latencies that are hard to catch for humans or easily visualize the global trends in the system. This subsequently facilitates and accelerates proper decision-making in an explorative workflow, which is an ideal strategy in photocatalysis explorations. Note that though not fully automated, minor human assistance still efficiently connects the fragmented sequence in an overall high-throughput experimental workflow consisting of relatively cheap characterization tools. This further allows for technoeconomic platforms providing broader access to scientists while not compromising the overall exploration timeline (Figure 3c), thus realizing genuine "accelerated materials discovery".[59] Such state-of-the-art research workflows are now exhibiting their utility in various research fields not only for organic synthesis and pharmaceutics but also for materials sciences including HP-based optoelectronics. From an industrial perspective, such efficient expedition of the processing parameters also contributes to curtailing the costs and labor for commercialization and ubiquitous realization of sustainable and renewable photocatalysis applications in the future.

Within the domain of HT automated synthesis methods, various approaches are considered based on factors such as material type, desired properties, and available resources. For HP materials, a few automated experiment platforms already exist, including fully automated robotic laboratories employing Bayesian optimization (BO) workflows,[60−62] microfluidic systems based on modular platforms guided by ensemble neural network (ENN) exploration,[63] and micropipetting robotic methods leveraging our expertise as well.[64−66] These strategies efficiently drive materials explorations, effectively discovering the optimal point for the best functionalities or disentangling the fundamental phenomena associated with the optoelectronic applications in an accelerated way.

In the context of HT techniques,[67] parallel synthesis involves creating a material library on a solid support, such as a glass slide or silicon chip, where each distinct area contains a different material composition. Robotic synthesis techniques utilize automated systems for precise and controlled reagent dispensing.[68] Flow synthesis,[69] employing continuous reactant flow through microfluidic channels, facilitates rapid synthesis and optimization of reaction conditions. Inkjet printing,[70] using an inkjet printer for precise material deposition, allows for intricate patterns and composition gradients. Combinatorial mixing and spotting involve presynthesized components mixed in various ratios and spotted onto a support to generate a diverse library.[71] Solution-phase combinatorial synthesis[72] involves a well-plate-based pipetting method that controls the dilution process and also the endmember concentrations. The room temperature-based solution-processing method offers scalability, making it an excellent choice for industrial-level production of Pb-free NCs. This method is not only compatible with synthesis but also aligns seamlessly for cocatalyst loading, compositional engineering, morphology regulation, and surface engineering. Besides, HT methods also offer a pathway to modify the morphology of Pb-free HP NCs via altering the synthesis parameters, thereby optimizing their photocatalytic performance. This could include facet engineering and the creation of active surfaces. These modifications can enhance the photocatalytic efficiency and extend the diffusion length of charge carriers.

Our group specializes in synthesizing various HP materials, including 3D, 2D, and quasi-2D materials and their nanocrystals, using HT pipetting robots for solar cell and light-emitting diode (LED) applications.[59,71−73] The recent study by our group has significantly contributed to the advancement and precision in the synthesis, specifically focusing on examining the effects of antisolvents in synthesizing double HPs.[65] These pipetting robot-based techniques stand out for their precision, speed, and efficiency, providing consistent results while minimizing errors and contamination compared to conventional nonrobotic methods. Additionally, they are easy to use, cost-effective, and support large-scale manufacturing without compromising sensitivity to solvent choices and synthesis steps. Data acquisition and analysis capabilities facilitate the optimization of absorption and emission properties and later screening.

Using our HT pipetting robot,[74,75] it is possible to synthesize at least 2400 materials per a day. Such a large chemical space can be preliminarily explored via consecutive automated HT optical spectroscopy (e.g., UV−isible absorption and photoluminescence spectroscopy) as proxy characterizations. Through automated analysis of the large data set, this allows one to assess the key information on the materials (e.g., narrow band gap, high stability, and charge carrier recombination rate) to screen the promising candidates for photocatalysts. Additionally, HT experiments allow us to understand the surface chemistry of the Pb-free HP NCs upon ligand engineering, which holds substantial promise owing to the sensitivity of their photophysical properties to their surface chemical environment. Ligands on the NC surface not only dictate the shapes, sizes, crystallographic phases, and even functionalities (i.e., colloidal and phase stability, emission characteristics, and surface reactivities) but also regulate the growth behaviors of the NCs. The density of these ligands on the surface can also be a critical parameter, as a high ligand density can potentially diminish the photocatalytic activity. Additionally, encapsulation emerges as another viable surface engineering technique aimed at stabilizing and reducing surface defects of these materials. This technique further underscores the potential of HT synthesis in refining the performance of Pb-free HPs by focusing on surface interactions, thus contributing to the broader quest for superior photocatalytic materials.

HT catalytic activity tests on the robot-synthesized set of material libraries are also feasible via delicate integration of electrochemical characterizations or a quantitative gas-phase detection system. Furthermore, the state-of-the-art HT

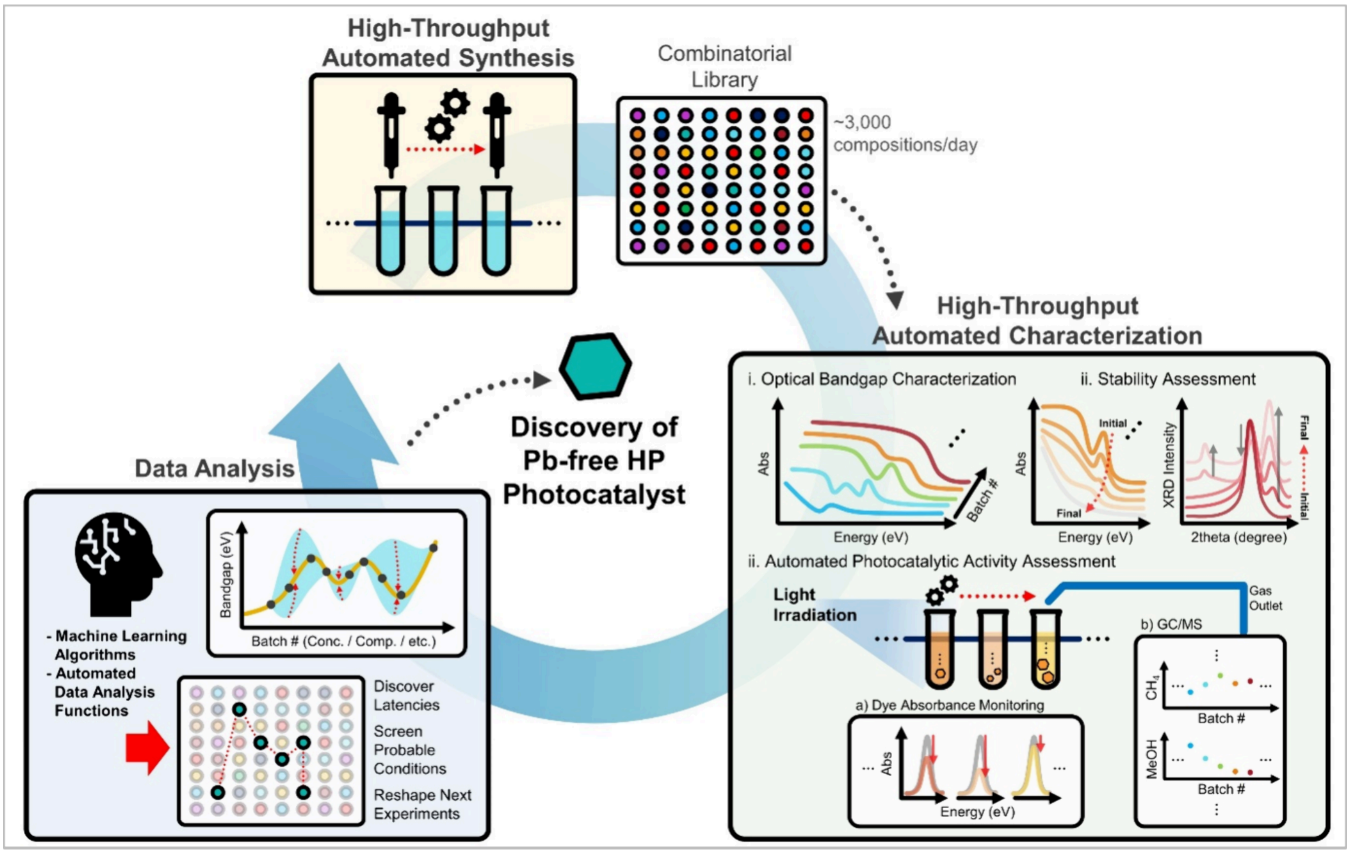

Figure 4. Schematic showing a closed-loop workflow for the high-throughput (HT) automated exploration of Pb-free hybrid perovskites (HPs). HT automated synthesis using a pipetting robotic platform generates a combinatorial library of Pb-free HPs. Subsequently, HT characterizations including automated UV−vis-absorption spectroscopy provide proxy information, including band gap or stability of materials, that can be utilized for materials screening. Time-dependent optical (absorption spectra) and structural characterizations (X-ray diffraction patterns) further hint at comprehensive phase transformation phenomena. Furthermore, automated photocatalytic activity tests are conducted on a large number of compositions/libraries using integrated HT analytical techniques. Machine learning (ML) and/or automated data analysis approaches allow not only for mapping the characteristic optical behaviors but also for effective visualization of latencies in the spaces of the synthesized materials library from the collected data set.

automated X-ray diffraction characterization allows for exploring crystallographic information in large compositional space, which not only to quantifies the stability but also hints to the surface facet engineering of the photocatalytic materials. Photocatalytic reproducibility cycles of the synthesized library can also be tested automatically using pipetting robots within one day or a few hours, compared to the weeks or months required for traditional nonrobotic experiments.

We have expertise in unsupervised machine learning programs, facilitating the study of time- and composition-dependent optical properties of synthesized libraries of high-performance materials. This method exploits non-negative matrix factorization (NMF) in multivariate statistical analysis.[76] Hence, the amalgamation of HT synthesis, characterization, and machine learning-assisted data analysis can enable automation to reduce delays and guide discovery by defining parameters and conditions for new experiments based on previous photocatalytic experimental results. Overall, such HT automated experimental workflow, where the HT synthesis, necessary characterizations, and data analytic functions are harmonized with each other, can accelerate the discovery of functional photocatalytic Pb-free HP NCs (Figure 4).

Specifically, HT synthesized and characterized Pb-free hybrid perovskite NCs necessitate concomitant HT photocatalytic experimentation. However, the incorporation of HT photocatalysis into the workflow is contingent upon the comprehensive requirements encompassed within the requirements of photocatalysis. Specific photochemical reaction requisites dictate the automation and integration of HT photocatalysis, wherein the experimental setup diverges depending on the nature of the targeted process; for instance, the experimental configuration for organic dye degradation will differ from that tailored for water splitting and CO_2 reduction.

■ AUTOMATION OF HIGH-THROUGHPUT PHOTOCATALYTIC CHARACTERIZATION

The advancement of photocatalysis relies heavily on efficient and insightful HT characterization methods, coupled with robotic automation for accelerating photocatalyst research and development. The conventional photocatalytic approach typically entails quantifying the photodegradation of a single organic pollutant dye compound in individual jacketed beakers, necessitating the laborious photodegradation kinetic studies, separation of photocatalysts, and extended photocatalytic operation times. Through the use of HT techniques, the number of photocatalytic reactions can be accelerated enormously.

Researchers have studied a few of the popular photocatalysts (mainly metal-oxides) via HT automation-based photocatalysis characterization. For example, Dai et al. utilized a CCD imaging analysis system and a photocatalytic reactor under UV light irradiation.[77] Through the screening of various catalyst libraries, they identified that the WO_3 and Nb_2O_5-codoped TiO_2 catalyst demonstrated significantly enhanced photodegradation efficacy in the breakdown of 1,6-hexamethylenediamine compared to pure TiO_2.[78] Potgieter et al. have used a HT technique for the synthesis and exploration of up to 96 heterogeneous catalysts on glass plates and a 3D-printed 96-well plate.[79] They accomplished this by transforming nanodroplets on a glass plate, and subsequent heat treatments led to the formation of metal oxide catalysts. Reaction rates for each catalyst were then calculated to screen for the most active catalyst. Motz et. al performed combinatorial synthesis method to generate 646 cobalt complexes of the type $[Co(LL)_2pyCl]$ as promising new water reduction cocatalysts for hydrogen evolution.[80] They found that alkyl-substituted glyoximes were necessary for hydrogen evolution via water splitting and showed increased activity when paired with ligands containing strong hydrogen-bond donors. Bi et. al used a 96-well microplate HT method for photocatalytic reaction using a range of organic pollutants (i.e., methyl orange, methylene blue, terephthalic acid, and *b*-nicotinamide adenine dinucleotide coenzyme).[81] They were screened through direct spectrophotometric and spectrofluorometric measurements. The photocatalytic conversion of pentacene on the HT synthesized $(SrTiO_3)_{1-x}(LaAlO_3)_x$ library was carried out by K-cell evaporation in ultrahigh vacuum.[82]

The aforementioned studies have primarily focused on metal-oxide-based materials, which are considered inefficient photocatalysts due to the rapid recombination of charge carriers caused by detrimental defects, as explained in the preceding sections. Nevertheless, the significant research gap concerning the unexplored systematic photocatalytic activity of Pb-free HPs serves as motivation for us to employ such integrated HT analytical techniques similar to those used for metal-oxides in investigating photocatalytic activity of Pb-free HPs.

The incorporation of HT analytical techniques represents a highly effective strategy for expediting the screening and optimization of photocatalysts based on Pb-free HPs. In photocatalysis, key HT analytical techniques that can be seamlessly integrated with HT synthesis include cyclic voltammetry, fluorescence spectroscopy, Kelvin probe force microscopy (KPFM), gas chromatography−mass spectrometry, infrared spectroscopy, and micro-Raman spectroscopy. In particular, gas chromatography and mass spectrometry play a pivotal role in the precise analysis of byproducts and intermediates arising from photochemical reactions (CO_2 reduction and CH_4 conversion), providing valuable insights into the selectivity and efficiency of the photocatalyst. Fluorescence spectroscopy facilitates real-time monitoring of photoinduced electron and energy transfer events, offering a dynamic perspective on photocatalytic performance in water splitting for H_2 evolution. KPFM contributes spatially resolved information at the nanoscale regarding changes in surface photovoltages, aiding in the elucidation of the surface activity of photocatalysts. Absorbance and photoluminescence spectroscopy reveal information about charge carrier generation and recombination in the photoinduced charge carriers of photocatalysts. Meanwhile, Raman spectroscopy provides vibrational information, elucidating the chemical changes during photocatalysis.

The integration of these HT analytical techniques with HT synthesis robots establishes a seamless and efficient workflow in photocatalysis (Figure 4). HT automated photocatalytic characterization offers rapid feedback on the success of photochemical reaction strategies and provides critical information such as catalyst loading and alteration of the pH of the reaction for further optimization.

INTEGRATION OF MACHINE LEARNING (ML) IN A HIGH-THROUGHPUT AUTOMATED EXPERIMENTAL WORKFLOW

HT automated synthesis of Pb-free HP photocatalysts generates extensive data sets that often surpass the analytical capabilities of traditional methods. The understanding of these data presents a significant challenge in identifying and leveraging intricate structure−property relationships crucial for photocatalysis. Here, ML emerges as a transformative tool offering advanced capabilities in feature selection, interpretation, prediction, and optimization. These functionalities are integral to dissecting and utilizing the complex interplay within photocatalytic materials.

In bridging the methodologies of HT synthesis and ML with our core objective, we concentrate on applying these techniques in the development and optimization of lead-free halide perovskite materials for photocatalysis. The HT approach systematically varies compositions and processing conditions to generate a diverse array of lead-free perovskite materials. Screening these materials through photoluminescence spectroscopy, UV−vis spectroscopy, and X-ray diffraction allows us to assess their structural and optical properties, including band gap energy, and stability, factors vital to their photocatalytic efficiency and practical viability. A pivotal element in data analysis could be the implementation of Bayesian optimization (BO) to interpret the data from UV−vis spectroscopy. BO is adept at determining which material compositions should be adjusted to achieve optimal band gap energies. This method efficiently navigates the complex parameter space of material compositions, identifying changes that can lead to enhanced photocatalytic performance and material stability.

Additionally, to address the stability aspect, ML methods such as nonnegative matrix factorization (NMF) can be employed. NMF excels in analyzing data patterns related to material degradation, providing valuable insights into improving the lifespan of our perovskite materials. Through the integration of SHAP (Shapley additive explanations), the synthesis parameters can be further fine-tuned, ensuring that both the band gap energy and material stability are optimized to enhance the photocatalytic activity. This approach, merging HT synthesis with sophisticated ML analysis like BO and NMF, enables us to methodically explore and refine the properties of lead-free perovskite materials, leading to the development of efficient and durable photocatalysts for applications such as CO_2 reduction and water splitting.

The ML algorithms can extend beyond predicting basic properties to encompass other correlated factors such as the stability of hyperparameters (HPs) in catalytic performance. Xu et al. utilized ML to search for ABX_3 ferroelectric perovskites with the desired properties. A ML workflow and the sure independence screening sparsifying operator (SISSO) were used to construct the regression models to predict the specific surface area (SSA), band gap (E_g), Curie temperature (T_c), and dielectric loss ($\tan \delta$) of ABO_3-type perovskites.

They found 20 potential ferroelectric perovskites for photocatalysis, ferroelectric semiconductor, and water splitting applications.[83]

For instance, the HT workflow is pivotal in unraveling the pathways of photocatalytic evolution, providing a foundational understanding of the interplay between composition and performance. ML augments this process by enabling more precise predictions compared with random sampling methods. It offers a cost-effective and efficient strategy for assessing photocatalytic activity based on discernible material properties. Density functional theory (DFT) can be employed for HT screening of perovskite-like structures for photocatalysis based on their stability and bandgaps using HSE06 Hartree−Fock/DFT hybrid functional calculations. Other specific ML algorithms like random forests, gradient boosting machines, and support vector regression (SVR) are particularly adept at managing the high-dimensional data from these HT experiments.[84−86] These algorithms excel in feature selection and reduction, making them crucial for handling data sets with numerous variables, as often encountered in HT studies. Random forests, for example, can provide the advantage of handling classification and regression tasks. Gradient boosting machines are highly effective in dealing with missing data and nonlinear relationships, which is essential in interpreting complex photocatalytic systems. Other deep learning methods, including neural networks, are also invaluable for identifying complex patterns within these data sets.[87,88] These models are suited for extracting hierarchical features and identifying correlations in large-scale data. These approaches are particularly beneficial for rapidly identifying promising lead-free perovskite photocatalysts for applications like CO_2 reduction and water splitting.

The combination of a high-throughput workflow with advanced characterization methods, such as absorbance, PL spectroscopies, and high-throughput photoreactors,[89,90] enriches the data set available for ML analysis (Figure 4). ML algorithms adeptly interpret alterations in the morphology and functionality of photocatalysts under diverse reaction conditions, including various illumination scenarios. This capability is vital for a nuanced understanding and optimization of catalytic performance, ensuring more effective and sustainable photocatalytic processes. Within the ML frameworks, feature engineering plays a critical role in dissecting photocatalytic properties. Techniques like SHAP provide sophisticated interpretations of the significance of various features, including light intensity, catalyst loading, irradiation time, and reaction concentration.[64,84,91] These insights are instrumental in refining photocatalyst design and operational parameters, leading to enhanced efficiency and efficacy.

Incorporating ML into the experimental workflow transforms the approach to problem-solving and decision-making in automated experimental setups. A closed-loop workflow, integrating ML with high-throughput synthesis and characterization methods, accelerates the exploration of photocatalysis. This enables a deeper understanding of the physical and chemical properties of photocatalysts and facilitates the efficient optimization of material parameters to achieve desired functionalities such as enhanced CO_2 reduction and water splitting efficiency. Currently, the Bayesian optimization (BO) method is being employed to navigate low-dimensional parameter spaces, including aspects like composition, ligand selection for nanocrystal growth, and antisolvent choice.[92,93] Alongside BO, Gaussian processes are leveraged for BO, and dimensionality reduction techniques like PCA play a critical role in visualizing and interpreting the complex data from HT experiments.[94] However, a traditional BO approach often faces limitations, notably, its inability to incorporate prior information. To address this, the integration of physics-based machine learning (ML) methods has become increasingly relevant.[95,96] These ML methods enhance the tuning and testing phases of the models. Utilizing ML in this capacity enables researchers to quickly iterate and refine materials, paving the way for significant breakthroughs in sustainable energy technologies.

The incorporation of ML also involves the consideration of intricate variables, such as defect density, which can exert an impact on the macroscopic photocatalytic mechanism and prove challenging to regulate through environmental factors in practical experimental settings. These latent variables and observational biases should be considered when employing ML models to gain a profound comprehension of efficient catalysts.

■ OUTLOOK

In the realm of cutting-edge research, photocatalysis stands at the forefront, poised to undergo a transformative journey with the synergistic fusion of machine learning (ML) techniques and advanced high throughput (HT) methodologies. The future holds the promise of unveiling a metamorphosis in the field as it confronts the challenges that have impeded its progress. At the core of this evolution is the critical quest for efficient and sustainable photocatalysts, particularly in applications like water splitting, conversion of greenhouse gases (CO_2, and CH_4), and other environmental remediation. The existing photocatalysts exhibit inefficiencies and drawbacks, hindering their utility in achieving long-term goals. To overcome these challenges, there is an urgent need to discover novel materials and swiftly assess the photocatalytic properties of existing ones. However, this exploration cannot compromise on factors such as toxicity (Pb-based materials), cost (metal-based catalysts), or complexity in synthesis (metal-oxide or oxide-perovskite).

From this perspective, Pb-free HP NCs have emerged as potential photocatalysts of this era. Their exploration not only addresses the shortcomings of current photocatalysts but also aligns with the goals of sustainability. Pb-free perovskites boast properties such as great light absorption, ambient stability, and nontoxicity, positioning them as captivating candidates for the catalytic spectrum of photocatalysis. To accelerate the synthesis and characterization of both existing and novel Pb-free HP NCs, this Perspective advocates the integration of high-throughput automated methods. This approach spans from identifying efficient catalysts for specific compounds to synthesizing and screening a wide array of catalysts. The combination of various spectroscopic and analytical methods within an HT framework establishes a robust foundation for ongoing exploration and innovation in environmental and energy research.

In tandem with these advancements, the narrative shifts toward the undeniable need for large, high-quality data sets in ML applications. The challenges, time-consuming nature, and substantial cost associated with obtaining structured data sets have long been obstacles. Additionally, the inherent bias within ML models, shaped by the prevalence of only successful outcomes in the reported data, poses a critical concern. The proposed solution lies in the widespread adoption of HT automated synthesis and characterization techniques, combining experimental and computational simulations to transcend the limitations of published data. Further enhancing the synergy, the integration of ML with data from *in situ* investigations, molecular dynamics simulations, and density functional theory is touted as a promising avenue.

This multidisciplinary approach is envisioned to unravel the intricacies of photocatalytic systems, fostering the development of novel strategies and materials. The inherent complexity of photocatalytic systems, previously challenging to characterize with simple descriptors, is poised to be tackled through advances in ML algorithms, enabling more intuitive and interpretable representations.

The climax of this narrative heralds the development of ML models capable of generating data, ushering in a new era of predictive accuracy. This capability not only facilitates the discovery of novel photocatalysts but also optimizes the photocatalytic processes. The convergence of advanced experimental techniques, computational simulations, and ML is set to revolutionize the field of photocatalysis, propelling it into an era of unprecedented discovery and innovation. The future of photocatalysis shines brightly, constrained only by the limits of imagination and the tools at our disposal.

AUTHOR INFORMATION

Corresponding Author

Mahshid Ahmadi − *Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering, The University of Tennessee−Knoxville, Knoxville, Tennessee 37996, United States;* orcid.org/0000-0002-3268-7957; Email: mahmadi3@utk.edu

Authors

Astita Dubey − *Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering, The University of Tennessee−Knoxville, Knoxville, Tennessee 37996, United States; Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany;* orcid.org/0000-0003-1666-3549

Sheryl L. Sanchez − *Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering, The University of Tennessee−Knoxville, Knoxville, Tennessee 37996, United States;* orcid.org/0000-0002-1485-3966

Jonghee Yang − *Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering, The University of Tennessee−Knoxville, Knoxville, Tennessee 37996, United States; Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea;* orcid.org/0000-0001-7013-6761

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.3c03186

Notes

The authors declare no competing financial interest.

Biographies

Dr. Astita Dubey earned her Ph.D. in Chemistry from Universität Duisburg-Essen in 2023, researching “Multifunctionality of doped Bismuth Ferrite nanoparticles”. She completed her Master’s at IIT Delhi in 2018, achieving the highest CGPA and securing a DAAD German fellowship for research at TU Hanover, Germany, focusing on “Lead halide perovskite nanocrystals”. Currently, she concentrates on catalysis, specifically “halide perovskites for photo/electro-catalysis”, utilizing “High Throughput Combinatorial Methods” and machine learning in her research.

Ms. Sheryl L. Sanchez is currently pursuing her PhD under the guidance of Dr. Ahmadi in the Department of Materials Science and Engineering at the University of Tennessee−Knoxville. She holds a Bachelor of Science in Chemistry, which she obtained from City College of New York in 2021. Her current research is focused on the high-throughput synthesis of inorganic perovskite nanomaterials, with a special emphasis on their applications in optoelectronics and photocatalysis. Additionally, she is exploring the integration of various machine learning techniques to enhance the understanding and design of these materials.

Dr. Jonghee Yang is now an assistant professor in the Department of Chemistry at Yonsei University, after working as a postdoctoral research associate in the Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering at the University of Tennessee−Knoxville. He received his Ph.D degree in Chemistry from Hanyang University, South Korea. His research is aimed at the high-throughput synthesis of perovskite nanomaterials and fundamental explorations of functional organic/inorganic semiconductors including perovskite materials using spatially resolved imaging techniques coupled with machine learning methods.

Dr. Mahshid Ahmadi is an assistant professor in the Department of Materials Science and Engineering at the University of Tennessee−Knoxville. She earned her Ph.D. from Nanyang Technological University, Singapore, in 2013. Her research focuses on the development of halide perovskites for optoelectronics, particularly utilizing automated high-throughput synthesis and characterization for material design, discovery, and optimization for clean energy applications. Additionally, her group concentrates on material characterization using spatially resolved techniques.

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