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Metal Halide Perovskite/Chalcohalide Heterojunctions for the Photoinduced Oxidative Coupling of *p*-Substituted Thiophenols

Anna Cabona, Stefano Toso, Alejandro Cortés-Villena, Ignacio Rosa-Pardo, Mirko Prato, Michele Ferri, Julia Pérez-Prieto,* Ilka Kriegl,* Liberato Manna,* and Raquel E. Galian*



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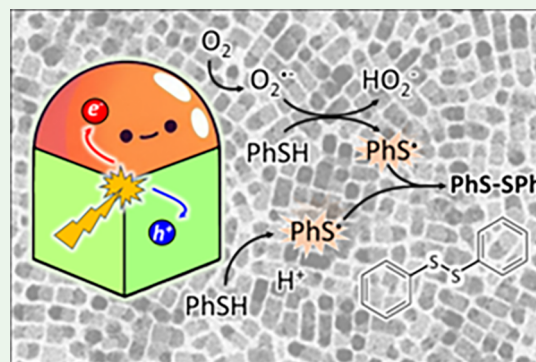
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Supporting Information

ABSTRACT: The introduction of a semiconductor–semiconductor junction is an effective strategy to enhance the photocatalytic performance of perovskite nanocrystal-based systems. Herein, we optimized the synthesis of $\text{CsPbX}_3/\text{Pb}_4\text{S}_3\text{Y}_2$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$) perovskite/chalcohalide heterostructures, whose band alignment can be tuned by the halide composition. As a proof-of-concept, we evaluated the photooxidative coupling of *p*-substituted thiophenols at room temperature, under visible light, in air, and without a sacrificial electron donor. Notably, $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ achieved up to 94% selectivity toward disulfide (*p*- OCH_3 thiophenol with a turnover number of 14 300), highlighting the crucial role of the type-II heterojunction in promoting charge separation and efficient electron delocalization across the junction.

KEYWORDS: heterostructure, photocatalysis, heterojunction, perovskite, chalcohalide



Colloidal nanocrystal heterostructures (HSs) are nanoparticles composed of at least two distinct materials sharing an interface^{1,2} exhibiting properties that can be distinct from their individual components. Semiconductor–semiconductor HSs are especially promising for light-harvesting applications,³ as both domains can absorb light and generate electron–hole pairs. Proper band alignment at the heterojunction can enhance charge separation and reduce recombination,⁴ making these architectures attractive for photocatalysis.⁵

HSs based on lead halide perovskites have emerged as promising photocatalysts,⁶ as they combine tunable band gaps⁷ and the intrinsic defect tolerance⁸ of CsPbX_3 with the additional electronic tunability of heterojunctions. Indeed, significant progress has been achieved using CsPbBr_3 nanocrystals as photocatalysts for organic transformations.⁹ However, improving the photocatalytic performances of metal halide perovskites, beyond their intrinsic instability under thermal and humid conditions,¹⁰ requires addressing several crucial factors such as their optical absorption properties, the generation and separation of photogenerated charge carriers, and the surface reaction kinetics. A highly promising strategy to enhance charge separation efficiency is coupling perovskites with a secondary semiconductor. This combination allows for an improved surface reaction rate through advanced configurations, such as type-II, Z-scheme, and S-scheme heterojunctions.¹¹ In this context, $\text{CsPbX}_3/\text{Pb}_4\text{S}_3\text{Y}_2$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$) perovskite/chalcohalide epitaxial HSs, initially reported by some of the authors,¹² have recently

emerged as promising photocatalysts, where strong interfacial coupling enhances charge separation.¹² For instance, Pradhan et al.¹³ recently demonstrated that $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ HSs outperform CsPbBr_3 nanocrystals (NCs) in CO_2 photo-reduction due to suppressed radiative recombination and efficient charge transfer across the heterojunction.

Most perovskite-based heterostructure photocatalysts reported in the literature present a nonepitaxial interface between the two semiconductors,¹⁴ where the benefits of the architecture mainly rely on the heterojunction type rather than on interface quality.¹⁵ In contrast, the proposed perovskite/chalcohalide $\text{CsPbX}_3/\text{Pb}_4\text{S}_3\text{Y}_2$ HSs present several advantages over the reported HSs: (a) an epitaxial interface, which enables a potentially defect-free junction, thereby reducing the probability of recombination centers; (b) a type-II heterojunction, with efficient electron delocalization across the nearly isoenergetic conduction bands of both semiconductors; and (c) a dimer morphology that could improve the number of effective contact points with the substrate.

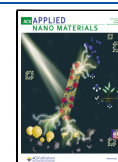
Despite this potential, their application in organic transformations in nonpolar media remains largely unexplored. To

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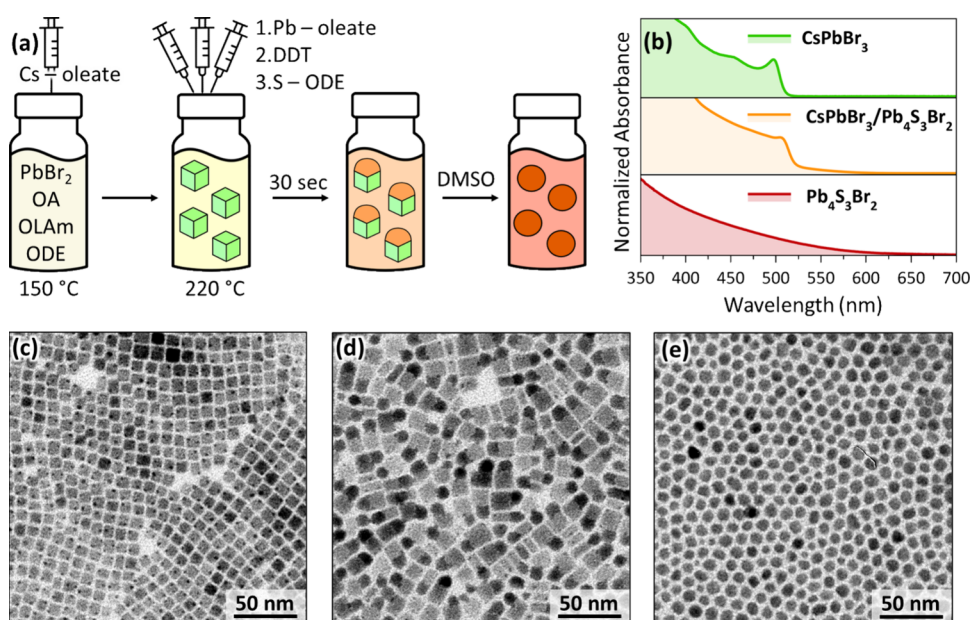


Figure 1. Synthesis of CsPbBr₃/Pb₄S₃Br₂ HSs. (a) Scheme of the synthetic route used to obtain CsPbBr₃ NCs and CsPbBr₃/Pb₄S₃Br₂ HSs, followed by selective etching of the perovskite domain to isolate free-standing Pb₄S₃Br₂ NCs. (b) Absorption spectra of CsPbBr₃ NCs (green), CsPbBr₃/Pb₄S₃Br₂ HSs (orange), and Pb₄S₃Br₂ NCs (red). (c–e) TEM images of CsPbBr₃ NCs (c), CsPbBr₃/Pb₄S₃Br₂ HSs (d), and Pb₄S₃Br₂ NCs (e).

address this gap, we investigate the band alignment of three different CsPbX₃/Pb₄S₃Y₂ (X, Y = Cl, Br, I) HSs, as interfacial energy level matching is crucial to designing an effective photocatalyst for specific target reactions.

Based on this knowledge, we selected the oxidative coupling of thiophenols into disulfides as a proof-of-concept reaction to directly assess how the use of a semiconductor–semiconductor heterostructure catalyst enhances the photocatalytic performance. This model transformation, relevant across (bio)-chemistry¹⁶ and industry,¹⁷ enables direct evaluation of the advantages of semiconductor heterojunctions over single-phase nanocrystals. Compared to conventional methods, this photocatalytic approach offers a milder and more sustainable alternative, avoiding overoxidation and simplifying purification.¹⁸ To assess the photocatalytic activity of the CsPbX₃/Pb₄S₃Y₂ HSs in the oxidation of *p*-thiophenols, we compared their reactivity against their individual components (CsPbX₃ and Pb₄S₃Y₂ NCs). Among all HSs we tested, CsPbBr₃/Pb₄S₃Br₂ showed the highest yield (81%) and selectivity (87%), outperforming stand-alone NCs and suggesting efficient charge separation at the interface. These results were attained in only 90 min upon 450 nm illumination, a significantly shorter time than that in previous studies with perovskite-based photocatalysts.¹⁹ These results underscore the pivotal role of heterojunction configuration in enhancing charge separation and photocatalytic performance.

The first synthetic protocol developed for CsPbBr₃/Pb₄S₃Br₂ HSs relied on perovskite nanoclusters as precursors, which were reacted with a sulfur source to obtain the product.¹² While producing well-defined heterostructures, this protocol has a low reaction yield, hampering extensive testing. Therefore, we here optimized an alternative published protocol,¹³ using preformed CsPbBr₃ nanocrystals reacted with lead oleate, 1-dodecanethiol (DDT), and sulfur in 1-octadecene (S-ODE). This approach significantly increases the yield (130 mg/batch), albeit at the cost of a less controlled

morphology and a higher fraction of stand-alone CsPbBr₃ nanocrystals (~20–25%, quantified by analyzing more than 500 NCs from TEM images). Figure 1a is a scheme of the protocol, where CsPbX₃ NCs synthesized via a hot-injection method²⁰ are immediately reacted, without purification, with the chalcogenide precursors injected at 220 °C. “Free-standing” CsPbX₃ NCs (used later as a reference) were obtained by interrupting the synthesis after the first step, while Pb₄S₃Y₂ nanocrystals were recovered by selective etching of the perovskite domain in the corresponding HSs using dimethyl sulfoxide (DMSO).²¹ Figure 1b shows the typical optical absorption spectra of the HSs and isolated NCs for the X = Y = Br case, with characteristic absorption features of the perovskite highlighted in green and the broad and featureless absorption of Pb₄S₃Br₂ NCs in red. As expected, the HSs absorption spectrum combines both features of the free-standing NCs. Representative TEM images of the three samples are displayed in Figure 1c–e (see Figures S1–S3 for additional characterization data).

The presence of two independent semiconductor domains allows for some tuning of the band gap to target specific reactions, in principle expanding the scope of HSs as photocatalysts. For instance, replacing PbBr₂ with PbCl₂ in the reaction yields CsPbCl₃/Pb₄S₃Cl₂ HSs (Figure 2a,b) with only minor adjustments to the synthesis required (see Experimental Methods in the Supporting Information and Figures S4–S7). Conversely, the direct synthesis of CsPbI₃/Pb₄S₃I₂ HSs was unsuccessful, probably due to the increased lattice mismatch of CsPbI₃/Pb₄S₃I₂ compared to the Br and Cl analogues.¹² However, CsPbI₃-based HSs can still be obtained via halide exchange from CsPbBr₃/Pb₄S₃Br₂ HSs, as shown by us in a previous work.¹² Due to the low ionic mobility in the perovskite domain, such a reaction primarily affects the perovskite domain,¹² resulting in CsPbI₃/Pb₄S₃Br₂ HSs (Figure 2c,d and Figure S8). The exchange was tracked by the redshift of the perovskite absorption onset, while the

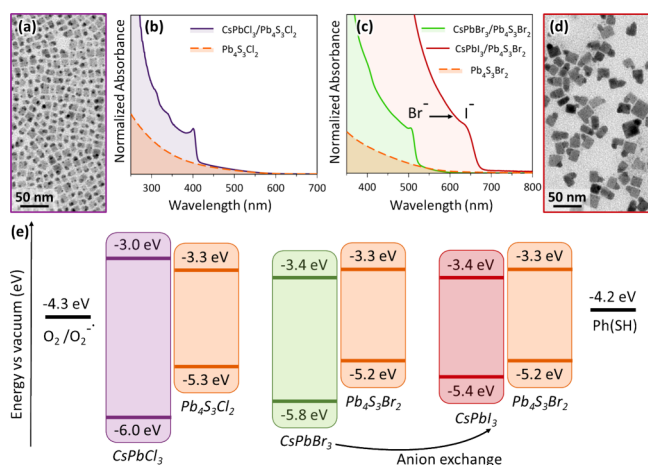


Figure 2. Synthesis of HSs and band alignments. (a) TEM image of CsPbCl₃/Pb₄S₃Cl₂ HSs. (b) Absorption spectra of CsPbCl₃/Pb₄S₃Cl₂ HSs (purple line) and Pb₄S₃Cl₂ chalcogenides NCs (orange line). (c) Absorption spectra of CsPbBr₃/Pb₄S₃Br₂ HSs (green line), CsPbI₃/Pb₄S₃Br₂ HSs obtained from them by halide exchange (red line), and Pb₄S₃Br₂ chalcogenides NCs (orange line). (d) TEM image of CsPbI₃/Pb₄S₃Br₂ HSs. (e) Band alignments of the valence band (VB) and conduction band (CB) of different HSs, compared with the highest occupied molecular orbital (HOMO) of thiophenol (PhSH) and the reduction potential of O₂ to superoxide anion.

contribution from the chalcogenides domain remained essentially unchanged (Figure 2c).

The combination of these strategies enables the various CsPbX₃/Pb₄S₃Y₂ HSs to cover the whole visible spectrum (Figure 2e). The band alignment and redox properties of “free-standing” CsPbX₃ and Pb₄S₃Y₂ NCs were characterized by combining optical absorption spectroscopy, to determine the optical band gap, with ultraviolet photoelectron spectroscopy (UPS) and ambient pressure photoemission spectroscopy (APS), to establish the position of the valence band (VB) edge with respect to the vacuum level (Figures S9–S13). While the literature is rich in reports on the band positions of CsPbX₃,²² very limited experimental data are available for Pb₄S₃Y₂ chalcogenides.^{21,23} Our results confirm the current computational predictions,^{23,12} highlighting that the band gap of lead chalcogenides is only minimally affected by the halide composition, likely due to the band edge states being predominantly derived from Pb²⁺ (conduction band) and S²⁻ (valence band) orbitals.²³ We also confirmed the type-I and type-II band alignments predicted respectively for CsPbCl₃/Pb₄S₃Cl₂ and CsPbBr₃/Pb₄S₃Br₂ HSs, which explains the photoluminescence quenching observed in both systems. Notably, for the CsPbBr₃/Pb₄S₃Br₂ HSs the conduction band edges of the two materials are closely aligned in energy (−3.4 eV for CsPbBr₃ and −3.3 eV for Pb₄S₃Br₂), thus facilitating electron delocalization across the HSs.

According to the energy levels estimated for CsPbX₃/Pb₄S₃Y₂ and the HOMO value for thiophenol (−4.2 eV, calculated from cyclic voltammetry, Figure S14), the CsPbBr₃/Pb₄S₃Br₂ HSs present optimal band levels to perform the photocatalytic reaction. In the case of CsPbCl₃/Pb₄S₃Cl₂ HSs, the type-I alignment would lead to a competitive nonradiative recombination in the chalcogenide domain, limiting charge separation, while CsPbI₃/Pb₄S₃Br₂ HSs require an additional halide exchange step in the synthesis without offering a sensible advantage over CsPbBr₃/Pb₄S₃Br₂ HSs.

Based on these considerations, we selected as a benchmark the photooxidation of PhSH (**1a**) to disulfide (**1b**) catalyzed by CsPbBr₃/Pb₄S₃Br₂ HSs under 450 nm LED excitation (Scheme 1) without an external sacrificial electron donor, as discussed in detail later (see Experimental Methods, Figures S15 and S16, and Table S1).

Scheme 1. Standard Conditions for the Photooxidative Coupling of *p*-Substituted Thiophenols

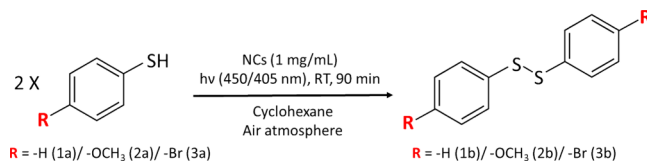


Table 1. Standard Conditions^a Using Different Solvents for the Photooxidative Coupling of Thiophenol

Entry	Solvent	Conversion (%)	1b Yield (%)	Selectivity (%)
1	Cyclohexane	93.0	81	87
2	Cyclohexane/CH ₂ Cl ₂ (1:1)	98.0	76	76
3	Hexane	88.0	57	65
4	CH ₂ Cl ₂	100.0	33	33

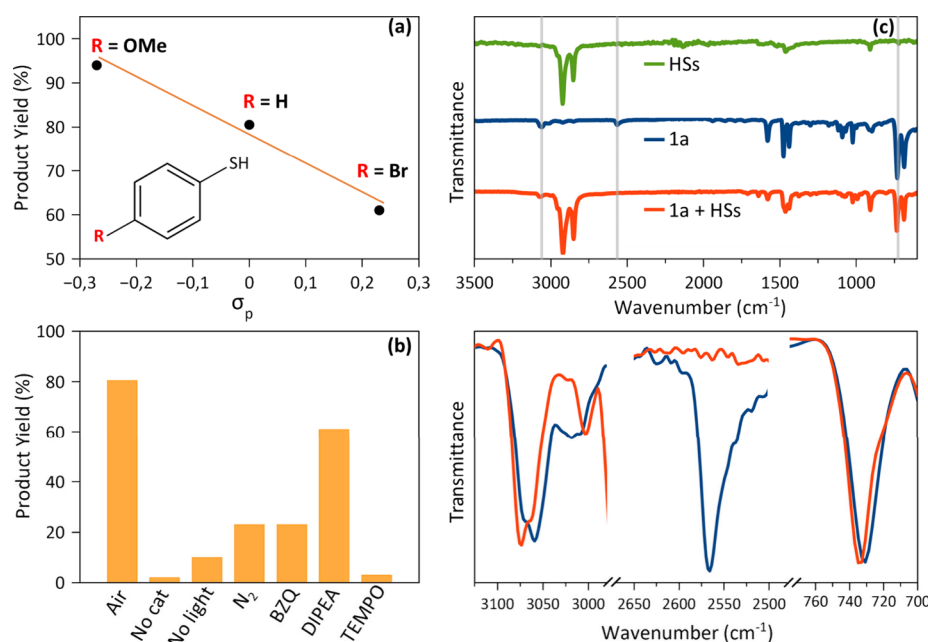
^aConditions: thiophenol (0.034 mmol), CsPbBr₃/Pb₄S₃Br₂ HSs (1 mg) in 1 mL of solvent after 90 min of irradiation ($\lambda_{\text{max}} = 450 \text{ nm}$) at 20 °C in air. Yields are determined by GC-MS using biphenyl as the internal standard.

Preliminary solvent screening showed that cyclohexane gave the highest yield (81%, Table 1 and Figure S17), outperforming hexane likely due to structural features that enhance the solvation of both nanoparticles and substrate, improving photocatalyst–substrate interactions.²⁴ A 1:1 CH₂Cl₂/cyclohexane mixture gave a high yield (76%) but lower selectivity, which is unfavorable for further photocatalytic investigations. In contrast, the photoreaction carried out in CH₂Cl₂ yielded an even lower yield (33%). This was attributed to the partial anion exchange between Br[−] in the perovskite domain and Cl[−] ions from CH₂Cl₂ as a result of the C–Cl bond cleavage, as previously reported by Wu et al. (Figure S18).¹⁹ These results highlight that reaction kinetics depend also on substrate diffusion and solvation energy, with the solvent influencing substrate adsorption on the NCs surface and consequently the S–S bond formation.

The photocatalytic activity of the HSs was compared with single-component CsPbBr₃ and Pb₄S₃Br₂ NCs, using 1 mg of photoactive material (estimated by TGA analysis, Figure S19). Although HSs and single-component NCs photocatalyzed the reaction (Table 2), both the product yield and the selectivity were significantly improved for CsPbBr₃/Pb₄S₃Br₂ HSs; this can be ascribed to the effective charge separation induced by the electronic junction in the HSs. Control experiments conducted in the absence of the photocatalyst or light resulted in only 2% or 10% **1b** yields, respectively, further confirming the photocatalytic activity of the HSs. The turnover number (TON) and turnover frequency (TOF) were determined according to the method previously reported by some of the authors.²⁵ The HSs exhibited the highest photocatalytic performance, with a TON of 14 300 and a TOF of 9560, while significantly lower values were obtained for the CsPbBr₃

Table 2. Standard Conditions Using Different Photocatalysts (Bromide-Based) for the Coupling of Thiophenol and *p*-Substituted Thiophenols

Entry	Variance	R Substituent	Photocatalyst	Conversion (%)	Product Yield (%)	Selectivity (%)
1	None	–H	CsPbBr ₃ /Pb ₄ S ₃ Br ₂	93.0	81 ± 1 ^a	87
2	None	–H	CsPbBr ₃	73.4	50 ± 4 ^a	72
3	None	–H	Pb ₄ S ₃ Br ₂	71.6	59 ± 4 ^a	86
4	Without photocatalyst	–H	-	19	2	-
5	Without light	–H	CsPbBr ₃ /Pb ₄ S ₃ Br ₂	51	10	-
6	Without light	–H	CsPbBr ₃	45	4	-
7	Without light	–H	Pb ₄ S ₃ Br ₂	40	7	-
8	In nitrogen	–H	CsPbBr ₃ /Pb ₄ S ₃ Br ₂	61	22	-
9	In nitrogen	–H	CsPbBr ₃	40	2	-
10	In nitrogen	–H	Pb ₄ S ₃ Br ₂	40	5	-
11	None	–OCH ₃	CsPbBr ₃ /Pb ₄ S ₃ Br ₂	100	94	94
12	None	–OCH ₃	CsPbBr ₃	100	86	86
13	None	–OCH ₃	Pb ₄ S ₃ Br ₂	100	93	93
14	None	–Br	CsPbBr ₃ /Pb ₄ S ₃ Br ₂	92	61	66
15	None	–Br	CsPbBr ₃	99	53	53
16	None	–Br	Pb ₄ S ₃ Br ₂	93	44	47

^aObtained from three independent measurements.**Figure 3.** Evaluation of different *p*-substituted thiophenols, different reaction conditions tested, and photocatalyst–substrate interaction. (a) Correlation between the electronegativity of the R substituent on thiophenol and the disulfide yield. (b) Product yield obtained from photocatalytic reactions tested under different conditions and in the presence of radical anions, holes, and radical scavengers. (c) Top: FTIR spectra of CsPbBr₃/Pb₄S₃Br₂ HSs (green trace), 1a (thiophenol, blue trace), and a mixture of CsPbBr₃/Pb₄S₃Br₂ HSs and 1a (red trace). Bottom: magnification of selected FTIR stretching regions highlighting differences between thiophenol (blue trace) and the HSs–thiophenol mixture (red trace).

(TON = 3680; TOF = 2460) and Pb₄S₃Br₂ nanocrystals (TON = 2070; TOF = 1380). Additionally, the CsPbBr₃/Pb₄S₃Br₂ HSs outperform other photocatalysts (Table S2) in terms of reduced reaction time with high TON and TOF numbers.

To investigate the influence of the *p*-substituent electronic properties on thiophenol reactivity, we selected two representative substrates: 4-bromothiophenol and 4-methoxythiophenol, bearing either an electron-withdrawing (–Br) or electron-donating (–OCH₃) group. As shown in Table 2, HSs again gave higher product yields than the single-component NCs. Notably, with 4-methoxythiophenol the yield of 2b was ca. 94% (Figure S20, Table 2, entry 11). This result is

consistent with the electron-donating nature of the –OCH₃ group, which increases the electron density of the aromatic ring, thereby enhancing its reactivity. Conversely, the –Br substituent, being more electron-withdrawing, makes the aromatic ring more electron-deficient, resulting in a lower reactivity (Figure S21, Table 2, entry 14). Electron-donating groups stabilize the thiyl radical by reducing the spin density at the sulfur atom, explaining the highest yield with *p*-OCH₃ thiophenol.²⁶ Figure 3a shows a clear correlation between the sigma value of the substituent (σ_p)²⁷ and the product yield for CsPbBr₃/Pb₄S₃Br₂ HSs, consistent with the electronic effects.

To elucidate the photocatalytic mechanism, several experiments with active trapping species were performed, employing

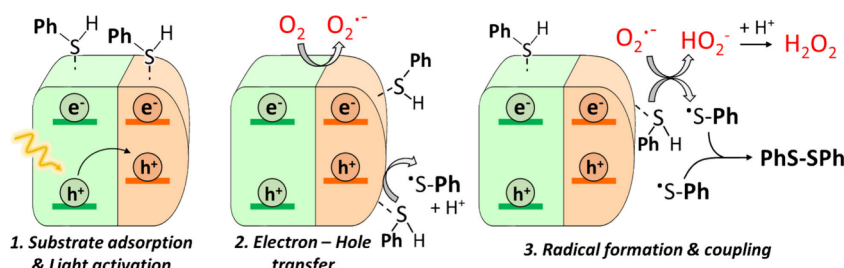


Figure 4. Proposed photocatalytic mechanisms for the oxidative coupling of thiophenol under aerobic conditions.

1,4-benzoquinone (BZQ),²⁸ *N,N*-diisopropylethylamine (DIPEA),²⁹ and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), as shown in Figure 3b and summarized in Table S3. In the presence of BZQ, a well-known scavenger of superoxide anions ($\text{O}_2^{\bullet-}$), **1b** was obtained in 23% yield, which closely matches the yield observed under anaerobic conditions. Conversely, DIPEA, which is a hole (h^+) scavenger, led to a moderate reduction in yield (61%), suggesting that photogenerated holes also participate, albeit to a lesser extent, in the mechanism (as discussed below). When the reaction was performed in the presence of TEMPO as a radical scavenger, under both aerobic and anaerobic conditions, only negligible amounts of product were obtained (Figure 3b), suggesting the formation of thiyl radicals ($\text{PhS}^\bullet$). The detection of the TEMPO-PhS adduct by GC-MS analysis (Figure S22) confirmed the production of thiyl radicals as key intermediates in disulfide formation.

The surface chemistry of the photocatalyst also plays an important role in the overall photocatalytic activity. The possible thiophenol adsorption onto the NCs surface was investigated by Fourier transform infrared spectroscopy (FTIR), and the spectrum of the $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ -PhSH mixture was compared with those of the heterostructures and thiophenol alone (Figure 3c, top). In the $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ -PhSH mixture spectrum, the S-H band at 2565 cm^{-1} is absent, indicating interaction between thiophenol and the HSs. The C-S stretching band shifts from 730 to 735 cm^{-1} , and the C-H stretching peak at 3050 cm^{-1} shifts to higher energy ($\Delta\nu = 14\text{ cm}^{-1}$), reflecting changes in the chemical environment (Figure 3c, bottom). Similar shifts were observed for mixtures of PhSH and “free-standing” NCs, as well as in the case of *p*- OCH_3 and *p*-Br thiophenol (Figures S23–S26), in accordance with previous reports on organic molecule–perovskite interactions.³⁰ Collectively, these data support the adsorption of the different substrates onto the surface of the photocatalyst, which likely facilitates photogenerated charge transfer from the HSs to the substrate.

The proposed mechanism for the photooxidation of *p*-substituted thiophenols under aerobic conditions is represented in Figure 4. Once the contact between the photocatalyst and the substrate is established, upon visible-light illumination, the photogenerated holes migrate toward the $\text{Pb}_4\text{S}_3\text{Br}_2$ domain, while electrons are delocalized across the conduction band of the heterostructure. This partial charge separation can reduce charge recombination and thus enhance photocatalytic activity compared to the individual components. Under aerobic conditions, two parallel pathways might produce thiyl radicals: (i) photogenerated electrons from the conduction band of the heterostructure reduce O_2 to form a superoxide anion ($\text{O}_2^{\bullet-}$), which reacts with thiophenol, producing a thiyl radical ($\text{PhS}^\bullet$) and HO_2^- ; and (ii)

photogenerated holes react with thiophenol, also forming a thiyl radical ($\text{PhS}^\bullet$) and a proton (H^+). Subsequently, two thiyl radicals can couple to form the target disulfide product. As the intermediate HO_2^- is unstable, it can react with H^+ to produce H_2O_2 . These findings confirm the cooperative activity of both photogenerated charge carriers (electrons and holes) under aerobic conditions to produce thiyl radicals, thus improving the photocatalytic activity in the heterostructure. In a nitrogen atmosphere, there is only one pathway to produce thiyl radicals: the photogenerated electrons and holes interact with the thiophenol, leading to the formation of thiyl and hydrogen radicals, which after coupling produce the disulfide compound and molecular hydrogen (H_2 , identified by GC, Figure S27), respectively (Figure S28). Under both aerobic and anaerobic conditions, the coupling of two thiyl radicals leads to the formation of a disulfide product, which subsequently detaches from the photocatalyst surface due to a lower affinity and diffuses into the solvent.

The performance of the photocatalyst was evaluated after one photocatalytic cycle. XRD patterns recorded before and after the reaction confirmed the preservation of crystallinity of the HSs (Figure S29). The absorption spectrum of $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ HSs retained the perovskite band edge with a slight redshift and increased scattering (Figure S30), likely due to some nanocrystal aggregation caused by the partial removal of surface ligands during the photoreaction, as previously observed in C–C coupling with CsPbBr_3 NCs.²⁵ TEM imaging of the crude solution (Figure S31) revealed significant aggregation in part of the sample, but the heterostructure composition was preserved.

To further validate our initial selection criteria for $\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ HSs, the photoreactions were performed also using Cl HSs (Table S4) and mixed I/Br HSs (Table S5). Employing $\text{CsPbCl}_3/\text{Pb}_4\text{S}_3\text{Cl}_2$ HSs, the observed trend is consistent with that found for the bromide analogue: the HSs outperform the individual NCs in both yield and selectivity. The slightly lower yield (70% versus 80%) obtained with the Cl HSs can be attributed to the type-I band alignment, which promotes nonradiative recombination and limits charge separation. The $\text{CsPbI}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ HSs, obtained via anion exchange, delivered the coupling product in 80% yield for **1b**, similar to that obtained with the bromide-based system, consistent with the band alignment. Nonetheless, in all cases, a reduction in the selectivity was observed.

In conclusion, we developed an optimized direct synthesis for semiconductor–semiconductor HSs ($\text{CsPbBr}_3/\text{Pb}_4\text{S}_3\text{Br}_2$, $\text{CsPbCl}_3/\text{Pb}_4\text{S}_3\text{Cl}_2$) and $\text{CsPbI}_3/\text{Pb}_4\text{S}_3\text{Br}_2$ via postsynthetic anion exchange, achieving tens-of-milligrams yields, above those of typical literature reports, and enabling extensive use in organic transformation photocatalysis. The chemical tunability of the perovskite allowed modulation of the band alignment,

systematically studied through optical and spectroscopic methods. Using *p*-substituted thiophenol coupling as a model reaction, the HSs outperformed the “free-standing” nanocrystals. Under aerobic conditions, the photogenerated electrons and holes produced thiyl radicals, enhancing the photocatalytic efficiency and exploiting the charge carrier separation at the heterojunction. This work establishes a versatile strategy for constructing semiconductor–semiconductor heterostructures. It demonstrates that the combination of type-II heterojunction engineering, surface chemistry, and the cooperative participation of photogenerated charge carriers to produce intermediate radicals is an effective approach for enhancing the photocatalytic performance of perovskite NCs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.5c05834>.

Experimental methods; characterization of the photocatalysts by TEM images, ABS/PL spectra, XRD patterns, UPS spectra, XPS spectra, Tauc plots, and TGA curves; product identification by GC-MS; FTIR spectra of different substrates and photocatalysts; and tables of different photocatalysts tested (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Julia Pérez-Prieto – Institute of Molecular Science, University of Valencia, 46980 Paterna, Valencia, Spain; orcid.org/0000-0002-5833-341X; Email: julia.perez@uv.es

Ilka Kriegel – Department of Applied Science and Technology, Politecnico di Torino, 10129 Turin, Italy; orcid.org/0000-0002-0221-3769; Email: ilka.kriegel@polito.it

Liberato Manna – Nanochemistry Department, Italian Institute of Technology, 16163 Genova, Italy; orcid.org/0000-0003-4386-7985; Email: liberato.manna@iit.it

Raquel E. Galian – Institute of Molecular Science, University of Valencia, 46980 Paterna, Valencia, Spain; orcid.org/0000-0001-8703-4403; Email: raquel.galian@uv.es

Authors

Anna Cabona – Nanochemistry Department, Italian Institute of Technology, 16163 Genova, Italy; Department of Applied Science and Technology, Politecnico di Torino, 10129 Turin, Italy; Institute of Molecular Science, University of Valencia, 46980 Paterna, Valencia, Spain

Stefano Toso – Nanochemistry Department, Italian Institute of Technology, 16163 Genova, Italy; Lund University, Division of Chemical Physics, 221 00 Lund, Sweden; orcid.org/0000-0002-1621-5888

Alejandro Cortés-Villena – Institute of Molecular Science, University of Valencia, 46980 Paterna, Valencia, Spain; orcid.org/0000-0001-6600-9209

Ignacio Rosa-Pardo – Institute of Molecular Science, University of Valencia, 46980 Paterna, Valencia, Spain; orcid.org/0000-0002-3662-2704

Mirko Prato – Materials Characterization, Italian Institute of Technology, 16163 Genova, Italy; orcid.org/0000-0002-2188-8059

Michele Ferri – Nanochemistry Department, Italian Institute of Technology, 16163 Genova, Italy; orcid.org/0000-0002-3862-6709

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsanm.5c05834>

Notes

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