Summary

Photocatalysis represents a promising approach for the sustainable conversion of solar energy into valuable chemical products, enabling green energy storage in the form of chemical bonds. In the search for efficient and cost-effective photocatalysts, colloidal nano-semiconductors have emerged as attractive candidates due to their tunable electronic properties, size control, and favorable charge-carrier dynamics upon illumination. However, these nanomaterials also present significant challenges in design and synthesis, and several improvements are required to achieve efficient photocatalytic performances. One open challenge is enhancing the accessibility of photoinduced charge carriers that drive photochemical reactions. One possible strategy to address this issue is to employ heterostructures composed of two different materials connected at an interface. In such systems, suitable band alignment can promote charge separation, increase carrier lifetimes, and improve their availability for surface reactions.

This thesis aims to explore the rational design, synthesis, and application of selected heterostructures. Particular attention is given to metal halides, which are currently at the forefront of colloidal chemistry research. Heterostructures based on these materials are promising due to the appealing optoelectronic properties of the metal halide domains. However, these hybrid architectures pose significant design and synthetic challenges. Within this framework, three case studies are presented, each defined by distinct design, synthetic, and photocatalytic challenges.

Chapter 4 evaluates the feasibility of forming an epitaxial $CsPbBr_3$@AgBr core@shell heterostructure by first assessing structural compatibility at the interface. This analysis was performed with Ogre, a python-based package for predicting epitaxial interfaces between ionic materials. The workflow generated atomistic models of several interface configurations, verifying that the two materials are epitaxially compatible along multiple lattice directions, a key requirement for core@shell architectures. Guided by these predictions, we developed a hot-injection synthesis protocol. Unexpectedly, this approach produced the inverse architecture, consisting of an AgBr core and a $CsPbBr_3$ shell. Nevertheless, this outcome is consistent with the epitaxial predictions, with the difference likely originating from chemical reactivity considerations.

Chapter 5 evaluates the practical advantages of epitaxial semiconductor-semiconductor heterostructures for photocatalysis. Although $CsPbX_3/Pb_4S_3Y_2$ heterostructures have been reported previously, we optimized a two-step direct synthesis to improve the reaction yield, which is crucial for enabling systematic photocatalytic testing. Different halide combinations were made accessible by post-synthesis halide exchange reactions, allowing access to a broader range of band alignments, which were characterized by spectroscopic techniques. Photocatalytic performances were demonstrated using thiophenol coupling as a model reaction. For this specific process, we found that the type II $CsPbBr_3/Pb_4S_3Br_2$ heterostructure delivered the highest product yield, outperforming stand-alone nanocrystals of the two materials. This enhanced activity is attributed to effective charge separation at the heterojunction upon illumination.

Finally, Chapter 6 presents a novel heterostructure, $Bi/Bi_{13}S_{18}Br_2$, that was obtained by introducing a mild reducing agent during the synthesis of the semiconductor chalcohalide $Bi_{13}S_{18}Br_2$ to achieve the in-situ reduction of metallic bismuth. These heterostructures adopt a distinctive bell-like morphology, which motivated an investigation of the growth mechanism using a combination of X-ray diffraction and advanced electron microscopy techniques. The proposed growth mechanism indicates that the initial nanorods play a dual role, acting first as heterogeneous nucleation templates for metallic Bi nucleation, and then as a material reservoir for the further growth of the chalcohalide domains via Ostwald ripening. Finally, the photo(electro)catalytic performance of the resulting nanobells was evaluated in dye degradation and CO_2 reduction reactions. Consistently with the $CsPbX_3/Pb_4S_3Y_2$ heterostructures discussed in Chapter 5, the enhanced activity is attributed to the intimate coupling between the two domains, which promotes effective charge separation under illumination.

Overall, this thesis demonstrates how the rational design of epitaxial heterostructures, guided by interfacial compatibility and chemical tunability, can enhance photocatalytic performance through effective multi-domain coupling. At the same time, the work highlights the synthetic and mechanistic challenges that naturally emerge when translating interface design into the experimental realization of complex, functional nanomaterials.