We report ripening of metal particles anchored on pyramid-shaped heterostructure nanocrystals. The 'intra-particle' ripening results in a large metal tip at one corner with the other three tips vanishing. Investigation reveals that the ripening and core/shell formation affects photocatalytic activities via the Fermi level change.

Metal nanoparticles deposited on the surface of semiconductor photocatalysts enhance their photocatalytic activity. With their surface partially coated with small metal particles, semiconductor colloids show enhanced photocatalytic performance in various reactions, such as water splitting,\textsuperscript{1,2} reduction of carbon dioxide,\textsuperscript{3} and degradation of phenol.\textsuperscript{4} The metal cocatalysts serve as both electron sinks and catalytic reaction sites, in which the metal/semiconductor interfaces facilitate the separation of the photo-generated electron and hole.\textsuperscript{5} Recently, a growing demand for the development of photocatalysts for energy applications has fueled the search for optimal metal–semiconductor combinations.\textsuperscript{6–8}

Colloidal lead selenide (PbSe) nanocrystal quantum dots have been used for photocatalysis under infrared irradiation.\textsuperscript{9} The growth of cadmium chalcogenide shell layers on a PbSe quantum dot provides electronic energy levels in the staggered offset (type II) configuration, which could offer a platform for efficient charge separation.\textsuperscript{10} In addition, the synthesis of “open”-structure heterostructure nanocrystals (HNCs), such as nanopyramids or nanotetrapods, is possible because of the anisotropy of the wurtzite CdS.\textsuperscript{14,15} Interestingly, when Au concentration increases (Au : HNC = 1200 : 1),\textsuperscript{13} four Au tips grow at the corners of pyramid HNCs (Fig. 1b). The selective growth at the corners is a consequence of the high reactivity of (111) planes of zinc blende CdS at pyramid tips (see Fig. S1, ESI†), which are atomically identical to the (001) planes of wurtzite CdS.\textsuperscript{14,15} Interestingly, when Au concentration increases (Au : HNC = 2300 : 1), one Au tip grows at the expense of the three other particles on each HNC (Fig. 1c and d). In the discussions that follow, we denote the ripened Au-tip HNCs as tAu–HNCs. The ripening appears to take place in an “intra-particle” fashion; namely, the Au atoms travel only within their host HNC, so each HNC ends up with one larger Au tip. This winner-take-all motif of Au tip ripening was previously observed in Au–CdSe nano-dumbbells, where asymmetric Au growth occurs at higher Au concentration.\textsuperscript{16,17} The Au tips undergo ripening in an “intra-particle” fashion because the host CdSe nanorods are considered to serve as electron conduction channels. Menagen \textit{et al.} later supported the idea by providing indirect evidence of the electron transfer through CdSe/CdS core/shell nanorods in the process of Au ripening.\textsuperscript{12}

The electron conduction model appears to explain the intra-particle ripening of Au in our system, shown in TEM images of Fig. 1. In an effort to eliminate ambiguity, we devised a simple...
experiment, in which a Cu wire coated with Au-tipped HNCs was immersed in the Au precursor solution and the Au reduction proceeded (Fig. 2a). Now, the electron would be able to travel “between” pyramid HNCs as the Cu wire serves as a charge carrier conduction channel. Fig. 2b and c shows TEM images of the product collected from the Cu wire before and after the ripening process. 2 nm of gold nanoparticles are evenly deposited on each pyramid HNC before the ripening process (Fig. 2b), while Au tips appear to undergo ripening (Fig. 2c). Note that some of the HNCs turned tip-free, while some HNCs have multiple Au tips (some with 3 tips). Now, the conductive channel between HNCs enables the “cross-particle” ripening, in which a larger Au tip on a HNC can grow at the expense of a smaller tip on another HNC. Fig. 3 illustrates the contrast between the Ostwald ripening processes with and without the Cu conductive substrate in our system. The impetus for the Ostwald ripening on conducting substrates derives from the difference in work function between the Au particles of different sizes.\(^{18}\)

When no conductive substrate was introduced, two primary changes in the Au tips occur as a result of the Ostwald ripening: (i) the number of Au tips attached on each HNC decreases (i.e., four to one), and (ii) the size of the remaining Au tip increases. Both of the changes could play a role in altering the photocatalytic activity. To elucidate the effects, we prepared several types of Au–HNC hybrid photocatalysts and tested their photocatalytic activity in the reduction of methylene blue (MB) under 785 nm light irradiation: pyramid-shaped PbSe/CdSe/CdS HNCs with no Au tips (denoted as HNCs), HNCs with 1.7 nm Au tips (Au–HNCs), and HNCs with ripened Au at one corner (rAu–HNCs). The concentration of MB in the MB–photocatalyst mixture was estimated from the absorption spectra: the optical density (OD) at 650 nm subtracted from the OD contributed by the photocatalysts. Typically, the absorption spectra of MB–photocatalyst samples show a peak at \(~650\) nm characteristic of MB, and the peak diminishes as a consequence of the photocatalytic reduction of MB (Fig. S2, ESI†). For example, in the case of Au–HNCs, 4 h of irradiation at 785 nm resulted in the reduction of 57% of MB versus 19% in the case of HNCs (Fig. 4a). Au tips serve as an electron sink and consequently facilitate charge separation at the semiconductor–metal interfaces.\(^9\)

In addition to the photocatalytic reduction of MB, we used our HNC-based hybrid materials for the photoreduction of metal salts to metal particles. First, we attempted photocatalytic reduction of AgNO\(_3\) using the PbSe/CdSe/CdS HNCs. As shown in Fig. 5a, \(~3\) nm...
sized Ag tips grew at the corners of the HNCs even when no reducing agent was used, after the HNCs and AgNO₃ mixture solution was placed under irradiation at 530 nm for 30 min. On the other hand, almost no Ag particles were reduced in the dark (Fig. S3a, ESI†). Under room light, 1–2 nm sized Ag tips were grown on the pyramid-shaped HNCs (Fig. S3c, ESI†). This indicates that Ag tip growth occurs more rapidly through photoreduction than Ag cation exchange.¹⁹,²⁰ Interestingly, other reports claim that cation exchange occurs more rapidly through photoreduction than Ag cation exchange.¹⁹,²⁰

In conclusion, we have demonstrated that varying geometries of Au and Ag tips on the pyramid-shaped PbSe/CdSe/CdS HNCs influence the photocatalytic activity of the hybrid composites. The Ostwald ripening and subsequent photoreduction of metal salts in the presence of free-floating HNCs enable the versatile control of metal tips with geometric configurations ranging from ripened single metal tip to core/shell metal nanoparticles. rAu–HNCs have larger single Au tips per HNC, as opposed to four smaller tips in the case of Au–HNCs. The ripening of the metal tips on pyramid-shaped HNCs reduced the photocatalytic activity of HNCs. The work function could be controlled through the core/shell metal tip growth via alternating photoreduction. The control of the Fermi level of metal tips would enable the improved photocatalytic conversion particularly when the reaction steps involved multiple intermediates (e.g., CO₂ conversion).

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Notes and references

13. Au:HNC denotes the ratio of the number of Au atoms to that of HNCs. See ESI† for the description of the estimate detailed.