Quasi-solid-state self-assembly of 1D-branched ZnSe/ZnS quantum rods into parallel monorail-like continuous films for solar devices

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Translating the extraordinary optoelectric properties of colloidal quantum rods (QRs) into functional devices requires multiscale structural control to preserve the nanoscale attributes as well as to introduce micro- and macroscale interactions between the building blocks. Self-assembly of anisotropic QRs into ordered nanostructures can tailor the photovoltaic properties of the QRs, such as in light absorption, and charge separation and transfer. However, it remains a challenge to assemble anisotropic nanomaterial into centimeter-sized, multilayered continuous films that retain nanoscale properties in the fabricated macroscopic devices. We have developed a quasi-solid-state self-assembly of randomly oriented nanostructures for overcoming this challenge, demonstrated by the re-assembly of randomly packed ZnSe/ZnS QRs into aligned and ordered parallel monorails (PMs). These ZnSe/ZnS PMs show significant enhancement in photo-excited charge transport, boosting photocatalytic oxygen evolution rates and the enhancement of photoelectrochemical activities, with a photocurrent density of 18 μA/cm², 5 times higher than the parent random packing of ZnSe/ZnS QRs. The ZnSe/ZnS PMs enrich the p-n heterojunctions, which can modulate charge carrier separation and transport at the interfaces. The new method has applicability for re-assembling randomly packed films of anisotropic nanoparticles into ordered nanostructures. Importantly, the extraordinary photovoltaic-energy conversion behavior of the Type-I core/shell quantum materials illuminates the pathways for novel designed materials by tailoring the hierarchical structures at all scales.
1. Introduction

Ordering nanoparticle assemblies has significant opportunities for precision control of nanostructures in bulk materials [1]. Orienting the assembly of one-dimensional (1D) colloidal quantum rods (QRs) as such offers exciting possibilities for simultaneously maintaining quantum confinement in radial dimensions, tuning light absorption, and facilitating charge carrier transport in the axial direction for long-distance charge separations. This process has attracted considerable attention because of its potential to enhance the electronic [2], photonic [3,4], plasmonic [5,6] and magnetic [7] properties of quantum materials. Indeed, precise control of the alignment of nanocrystals in an ordered structure provides a simple pathway towards the fabrication of solution-processed photoelectronic devices including photodetectors [8], polarized light-emitting diodes [9,10] and bio-sensors [11]. The most widely employed methods for fabricating aligned and ordered 1D colloidal nanocrystals use an air-liquid interface or a fluid flow driving force, such as the electric field-assisted assembly of CdS nanorods [12], mechanical rubbing alignment of CdSe/CdS seeded-rods [13], assembling vertically aligned pristine TiO$_2$ nanorods [14], and the drop-casting assembly of CsPbX$_3$ perovskite nanowires into films [15]. However, fabricating large-size, multilayered, yet well-aligned QRs that are connected “side to side” and “head to tail” for manufacturing photovoltaic (PEC) devices is challenging.

The self-assembly of colloidal semiconductor nanocrystals is highly dependent on their capping surface ligands, which not only serve as coordinating solvent for nanocrystal morphology control, but also are critical to stabilize the dispersion of colloidal nanocrystals [16–18]. Such ligands can also play a pivotal role in the self-assembly process when the nanocrystals are incorporated into solid-state devices. However, the ligands, whether they are hydrophobic as-synthesized or are hydrophilic through ligand-exchange, exhibit insulating properties and entail surface defects [19]. Therefore, removing the surface ligands on the nanocrystals via thermal annealing is required for enhanced photovoltaic energy conversion efficiency of a nanocrystal-formed thin-film device and improving catalytic activity [20]. This thermal annealing postprocessing is underexplored, particularly in the low-temperature processing regime immediately above the melting temperature of the ligand.

In the anthropocene era of concern for the environment, photo- and photoelectro-catalytic applications urgently require the development of heavy-metal-free zinc-based quantum materials, which also have the low-cost advantage [21,22]. However, for photoelectrochemical applications, being wide-bandgap semiconductors, zinc-based quantum materials such as ZnS$_{31}$ Se$_{3}$, aloyed quantum rods [23] and Zn$_n$Sn$_{2n}$ nanowires [24] can only act as a co-catalyst or photo absorber. In photocatalysis, zinc-based quantum materials are usually combined with other nanosized noble metal or bulk semiconductors to serve as a co-catalyst [21, 25], or merely function as a photosensitizer or absorber in the presence of sacrificial agents [26–28] such as ZnSe/ZnS core/shell nanorods with Ni(NO$_3$)$_2$ [28]. Clearly, the direct and facile in-situ synthesis of zinc-based quantum materials with desired heterostructures for photocatalytic and photoelectrochemical applications remains a challenge.

Herein, we introduce melting ligand-facilitated re-assembling of solid-state, randomly distributed, branched ZnS (short arm)-ZnSe (long arm) quantum rods (referred to as ZnSe/ZnS QRs), into ZnSe/ZnS parallel monorails (ZnSe/ZnS PMs) for photocatalytic and photoelectrochemical applications. The low-temperature annealing process not only removes the surface ligands, but also facilitates self-assembly of the nanorods via wetting, bubbling and dewetting of interfacial interactions, resulting in ligand dissociation and evaporation. The resulting PM film carries hierarchical structural ordering, from the QR core/shell architecture at less than 5 nm resolution, to the aligned monorail assembly with a periodicity of the width of the QRs. The precision control of the hierarchical material is achieved by: (a) the versatile chemistry of colloidal QRs synthesis, forming nanoscale heterostructures such as p-n heterojunction, and (b) the ordered assembly of the nanoparticles, which in this case accelerates the separation of the photogenerated electron-hole pairs and facilitates charge transport. Moreover, the obtained ZnSe/ZnS quantum rod PM film can be directly employed as photoanodes and photocatalysts for water oxidation, exhibiting highly efficient catalytic activities for oxygen evolution and enhanced PEC performance. This simple low-temperature annealing approach establishes a new strategy for transforming Type-I core/shell QRs into quantum-confined nanostructures with artificial p-n heterojunctions and dramatically enhanced electron-hole separation and charge transfer, improving the performance of colloidal quantum material devices.

2. Results and discussion

2.1. Core/shell quantum rods synthesis and controlled surface defects

The unique properties of the as-synthesized branched ZnS (short arm)-ZnSe (long arm) QRs (short hand: ZnSe/ZnS QRs) [16] motivated us to directly assemble them on the surface of fluorine-doped tin oxide (FTO)-coated glass substrates as a photoanode, as illustrated in Fig. 1a. In the branched ZnSe/ZnS QRs (Fig. 1b–e and S1 in Support Information (SI)), the wavefunction of both the lowest electron and the highest hole states resides in the main body of the ZnSe long rod, and the confinement of holes is strengthened by the formation of the ZnS branched shell. The incomplete shell growth of ZnS branches and the etching effect of 1-dodecanthiol precursor results in a defect-rich rough surface with abundant trapping states, as confirmed by the broad and longer wavelength emission [16,23,29]. Thus, surface trapping dynamics and charge transfer energetics in Type-I core/shell ZnSe/ZnS QRs can be directly utilized to manipulate photocatalytic efficiency [30, 31]. The construction of the heterostructure interface can directly affect the charge transfer and recombination processes. In particular, the ZnS branches comprised of both Zinc blende and Wurtzite polymorphs, provide numerous heterojunction points at the interface, benefiting the separation of electron/hole pairs and suppressing charge recombination [32,33]. In addition, 1-D hetero-semiconductor quantum rods may improve the charge carrier mobility through efficient hole migration and extraction with a low photocurrent generation threshold [34,35]. However, in thin film-based device applications, the advantage of 1-D nanorods in charge transport can only be manifested if they are assembled into aligned and connected rails. Such an alignment also offers an opportunity for tailoring the exposed surface edge sites and defect vacancies.

2.2. Quasi-solid-state self-assembly of randomly packed nanorods

The self-assembly process involved three stages, as shown in Fig. 1a. The QRs covered with the 1-oleylamine ligand can be uniformly dispersed in non-polar chloroform. In the initial step of the self-assembly process (Fig. 1a), the branched ZnSe/ZnS QRs were suspended in chloroform and randomly dispersed onto the FTO surface of 0.5-cm diameter. SEM images indicate a random arrangement of the QRs, using a single drop of diluted solution (Fig. 1b). Using the HRTFM and HAADF, we could clearly identify the enriched ZnS branches on the ZnSe core (Fig. 1c, d), as illustrated by the cartoon in Fig. 1e. The separated distribution of ZnSe and ZnS in the heterostructure is confirmed by EDS elemental mapping (Fig. 1f).

In the second stage, the suspension was added dropwise onto the FTO glass eight times. The chloroform evaporated immediately at room temperature, and the QRs formed a thick solid film of randomly packed ZnSe/ZnS QRs. The solid interlayers between the rods shown in Fig. S2a are the excessive 1-oleylamine, which is the QR surface capping agent in the original reaction solution. In this stage, the QRs are randomly packed with the film being a composite of ZnSe/ZnS QRs and solidified 1-oleylamine (Fig. S2b).
In the third stage, when the film of the randomly packed QRs was annealed at 350 °C under N2 gas for 0.5 h, the 1-oleylamine started to volatilize and mobilize under a stream of the inert gas. Finally, 1-oleylamine was removed with concomitant assembling of the QRs into PMs, as shown in Fig. 1g-m. The inset photos in Fig. 1a show the color changes of the ZnSe/ZnS photoanodes from whitish to brownish before and after the annealing process, which exhibit improved light absorption.

The 1-oleylamine in the melt state plays a crucial role in facilitating the self-assembly process through colloid–colloid, colloid–substrate, and colloid–solvent interactions [36]. Fig. 1g reveals that the thin film of ZnSe/ZnS PMs are covered with ‘craters’ of 2–3 µm diameter on the FTO substrate surface, and the cross-sectional SEM image (Fig. 1h) presents the sharp junctions between two ‘craters’. The film morphology suggests that micrometer-sized bubbles were likely generated during the annealing treatment. The sharp ‘ridges’ around the craters were formed by the aligned upward-pointing QRs, indicating kinetic-driven assembly under ligand evaporation near its boiling temperature. Furthermore, the aligned single QR can still be clearly observed from the cross-section of the film, as shown in Fig. 1i and j. In the magnified SEM image (Fig. 1j), the assembled quantum rods are connected head-to-tail like railways. Because the ‘railway tracks’ are assembled side-by-side, though closely together, but visually distinctive, we name the structure as ‘paralleled monorails’ (PMs). The PMs are not all straight, but have curves, which agrees with the previous report that one-dimensional (1-D) nanostructure with large aspect ratios can be bent during assembly [15]. Furthermore, the cross-section SEM images of PMs present a thinner and more compact contact layer on FTO substrate than the QRs (Fig. S3). In addition, several twisted positions in the sides of the PMs have high-density contacts at the sides and edges of the rods, as fully contacted 1-D assemblies. The low-temperature annealing process provides a straightforward approach for fabricating photoanodes directly from the crude colloidal QR random assembly to PMs without ligand exchange.

We employed liquid phase-frequency modulation atomic force microscopy (FM-AFM) to check the spacing between the ZnSe/ZnS QRs (Fig. 2a and b) in the parent random packing. Fig. 2a shows that individual branched quantum rods can be resolved by the FM-AFM. According to the corresponding height profiles, the spacing between the rods is around 20 nm, which falls within the working range of the monolayer ligand interaction and capillary forces [Fig. 2c and d] [36]. Interestingly, compared with the samples in air, the quantum rods appear swollen in the water phase (Fig. 2b), indicating strong interactions between the quantum rods and the water phase. This also explains the less resolved height profile of the quantum rods, 2 nm in Fig. 2b and d in comparison to 6 nm in Fig. 2a and c. This phenomenon is likely associated with the intense electrostatic interactions between the hydrophobic long-chain 1-oleylamine ligand coordinated on the quantum rods and water molecules [38].

Thermal annealing at a temperature slightly below the boiling point of the ligand significantly changes the interparticle positioning. In Fig. 2e, the quantum rods are stacked in “side to side” and “head to tail” arrangements. The HRTEM image (Fig. 2f) shows that the gap between two paralleled rods is 2.2 nm. The HRTEM images also clearly show the high crystallinity of the ZnSe/ZnS PMs with clear lattice fringes (Fig. 2g and Fig. S4). As marked by the yellow dashed line, the distance between the two lattices in the assemblies is less than 0.5 nm. Furthermore, FFT analysis of the whole area in Fig. 2g presents an ordered alignment in the crystallographic diffraction, corroborating a Wurtzite structure of the ZnSe/ZnS QRs. Remarkably, distinct lattice reflections can be observed, which indicate a highly ordered arrangement of the parallel monorails. We conducted a closer analysis of the selected area, which further reveals the atomic configurations of the parallel monorails in bending structures, Fig. 2h. As labeled, the distances between two lattice fringes are 0.33 and 0.32 nm, corresponding to the (100) and (002) planes of Wurtzite ZnSe and ZnS, respectively. The restrained crystal lattice spacings revealed a slight shrinkage of the (002) and (100) planes of rods in comparison with the standard wurtzite ZnSe reference (PDF#15-0105) [23]. In addition, several twisted positions in the sides of the
single unit matrix can be ascribed to the bending crystalline interface and provide direct evidence of the strain control behavior in the assemblies of crystalline particles (False-color HRTEM image in Fig. S5).

Consistent with the FFT, X-ray diffraction (XRD) patterns (Fig. 2i) suggest that the ZnSe/ZnS QRs are self-bent on the substrate along the principal axis. The (002) peak shown in the original QRs random packing after chloroform evaporation (blue line) disappeared on the PMs counterpart (red line), indicating that the ZnSe/ZnS PMs assemble in a “lay down” rather than “standing” mode on the FTO surface [39]. Furthermore, the (101) peak intensity increases for ZnSe/ZnS PMs, suggesting an average diagonal position of the ZnSe/ZnS QRs on the FTO substrate, in agreement with the SEM images (Fig. 1h). In addition, the (101) peak shows a shift of 0.37°, potentially due to the relaxed crystal lattices after annealing [40]. The XRD pattern proves high structural stability of the individual QRs during the self-assembly process. It is worth noting that, after the self-assembly process, the PMs retain the properties of individual QRs without being fused into a bulk material (Fig. 2 and Fig. S6). The stability of QRs under the low-temperature annealing process is crucial for performing the reorganization in the solid-state and maintaining the quality of the discrete particles.

To understand the fate of the surface ligands, we employed the NEXAF spectra in C K-edge to reveal the dipole transitions from C 1s core states to 2p-derived electronic states. Fig. 2j shows a sharp peak at 285.4 and a broad peak at 292.5 eV, which are attributed to the transitions from C 1s to π* C–C and σ* C–C states, respectively [41]. Compared with the ZnSe/ZnS QRs, the reduced unoccupied densities of ZnSe/ZnS PMs states indicate the occurrence of charge transfer at the many-body interfaces [42]. The peaks at ~288.0 and ~289.0 eV can be assigned to the π* C–C and σ* C–O resonances, respectively [41]. The shift of the unoccupied densities from 288.0 to 289.0 eV represents a decrease of the oxidized C environment, suggesting partial removal of 1-oleylamine, which would create more active sites for water oxidation. These features also demonstrate the strong coordination interaction between the organic ligand and ZnSe/ZnS.

2.3. Quasi-solid-state self-assembly mechanism

Thermodynamically, the anisotropic one-dimensional rods prefer to stay in an ordered orientation at a higher density to achieve the lowest free energy of a homogeneous solution [43,44]. Mathematical modeling further revealed that relatively longer rods tend to be better oriented than short rods due to the volume fraction and short-range effect [43]. Interactions between two 1-D rods are the primary driving force for self-assembly. Solvent evaporation or de-wetting during the annealing process can introduce a variety of forces in action throughout the process, namely van der Waals (vdW) forces among the particles, steric repulsions between the hydrophobic tails of the ligands, capillary forces, depletion forces, and Coulomb forces between surface charges or electric dipoles. Thus, a careful control over the evaporation kinetics and inter-particle forces at the interfaces (gas-solid, liquid-liquid, liquid-gas, or liquid-solid interfaces) can facilitate nanoparticle self-assembly into ordered structures [36,45]. We propose the mechanism of the self-assembly during the three stages shown in Fig. 3.

According to the morphology changes displayed in Fig. 2 and S3, we can easily determine the interaction ranges by identifying the ZnSe/ZnS QRs/PMs sizes and spacing. In the first process (from Fig. 3a to b), the ZnSe/ZnS QRs are homogeneously dispersed in chloroform. Upon the initial dropcast deposition onto the FTO slide, the QRs form a random packing without any particular ordered feature, which is likely due to the fast evaporation of chloroform and its low viscosity. After 8 times of repeated dropcasting, the random packing of QRs achieves sufficient density, where the interparticle distance is close enough for the various long-range forces to be at play (Fig. 3b and c).

During the annealing process (Fig. 3a–d), the excessive 1-oleylamine on the QR evaporated, thereby inducing interaction forces in the nanometer range (10–100 nm), including capillary forces, van der Waals interactions, and monolayer surfactant interactions. From the above TEM and AFM characterizations, the self-assembly between two rods starts at a distance around 12 nm and finishes with a spacing ranging from 2.2 to 0.5 nm. Firstly, it is the capillary force that drives the assembly process. According to Eq. S1, the capillary force (1-oleylamine
coated NRs in chloroform) is about $-1643.26 \text{nN}$, which is higher than the capillary force of chloroform evaporation. Then, for the side-by-side rods with small spacing, the potential ($V_{vdw}$) of the van der Waals interactions can be calculated by Eqs. S2-S4 (See SI), which is around $3.31 \times 10^{-5} - 66.2 \times 10^{-5} \text{nN}$. Therefore, the capillary force from ligand melting and evaporation acts as the primary driving forces for the self-assembly.

Another important factor to be considered is the surfactant monolayer-induced interaction and attraction [45]. The solvophilic ligands behave as ligand brushes, effectively overcoming the repulsive force and the double-layer electrostatic force between the rods in the assembly process within a small distance [36,45,47]. Two parallel quantum rods with long-alkyl chain ligand brushes, which benefit from the anisotropic 1D shape effect, can be considered in the cross-section assembly of two particles. In a good solvent, the interactions between these two approaching particles coated by end-grafted monolayer ligands can be studied using the self-consistent field theory (SCFT) [46, 48]. Such an intermediate state becomes significant by pushing forward the last nanometers before being finally removed the solvent. The surfactant monolayer-induced force is between 0.5 and 2 nm spacing, Fig. 2g and Fig. S4. As shown in Fig. 3c and f, the “side to side” stacking of QRs in Stage 3 provides the stress for further “head to tail” alignment along the principal axis to form a paralleled monorail arrangement. Consequently, all the interactions allow the rods to form a compact structure to avoid the gaps between individual quantum rods, and such a close-packed assembly can facilitate fast charge transport between the QRs.

2.4. ZnSe/ZnS PMs optoelectrical conversion capacity

The UV–vis absorption of ZnSe/ZnS PMs is enhanced in the range of 320–580 nm in comparison to ZnSe/ZnS QRs, as shown in Fig. 4a. The bandgap of ZnSe/ZnS QRs is determined by a Tauc Plot to be at 454 nm, corresponding to 2.25 eV, whilst that of ZnSe/ZnS PMs is shifted to 3.25 eV.
2.18 eV. This red shift in the band edge as well as enhanced absorption established increased inter-rod interactions in the aligned and closely packed ZnSe/ZnS PMs. The photoelectric properties of ZnSe/ZnS PMs and random packing QRs without annealing are evaluated with photoelectrochemical and photocatalytic water oxidation. Fig. 4b and Fig. 5a and b compare the linear sweep voltammetry (LSV) curves of the samples under the chopped light irradiation, which show an intense light-dependent anodizing current of ZnSe/ZnS, confirming that the anodizing capacity over PMs is more robust than that over QRs in a neutral electrolyte. Similarly, the photochemical currents (J) of both single components ZnSe and ZnS PMs anodes under different potentials are higher than those of their respective QRs counterparts (Fig. S7a and S7b). Consequently, the different degrees of the negative shift of the onset potential over the PMs photoanodes suggests improved water oxidation kinetics [23]. The amperometric current-time (i-t) curves of the photoanodes, recorded under chopped light irradiation (100 m W cm\(^{-2}\)) are shown in Fig. 4c. The ZnSe/ZnS PMs photoanode presents a distinct improvement in the photocurrent density under respective open-circuit potentials and different bias potentials as compared to ZnSe/ZnS QRs. With increasing applied bias potential to 0.4 V, the absolute photocurrent density of ZnSe/ZnS PMs photoanode reached 18.3 μA/cm\(^2\), 5 times higher than that of ZnSe/ZnS QRs (3 μA/cm\(^2\)), suggesting efficient electron-hole separation and transportation abilities of PMs. The removal of ligands and the PM assembly of QRs during annealing significantly increases the interfacial contacts between the QRs, and between QR and electrolyte, thereby, facilitating the charge transfer and the interfacial reductive actions, as reflected by the enhanced photocurrent densities. At a constant bias voltage of 0.4 V, the photocurrent of PMs decreases noticeably with the duration of illumination time (Fig. 4c), indicating an increased probability of charge recombination in the self-assembled film when charge density increases. This phenomenon may be determined by the inherent weak electrical conductivity of ZnSe/ZnS. Charge carriers generated within the top layer of the film would take longer to reach the underlying FTO, hence are more likely to recombine before being collected. This feature can be examined by the transient time (t\(_0\)) from the equation [48],

\[ t_0 = (I_t - I_0)/(I_{in} - I_0) \tag{1} \]

where \(I_0\) and \(I_0\) represent the photocurrent densities at the beginning and endpoint of the light illumination, respectively (Fig. 4c) with \(I_t\) the photocurrent density at time \(t\), and the transient time \(t_0\) is defined as the decay time when \(\ln t_0 = -1\). The transit time of ZnSe/ZnS PMs is 6.15 s for the photocurrent density under 0.4 V bias condition, while ZnSe/ZnS QRs show near-zero decay time. The extraordinary long decay time of the PMs demonstrates the self-assembled aligned structure results in a dramatic improvement in charge separation and recombination suppression [49–51]. Moreover, as shown in Fig. 5c and d, under the same mass loading and annealing conditions, the PM assembly of ZnSe and ZnS quantum rods exhibited higher photocurrent densities than the ZnSe and ZnS QRs counterparts, respectively. This set of experiments illustrate the versatility of both the metal-ligand facilitated self-assembled method and the advantage of the PMs structure in charge carrier harvesting. The annealing treatment also strengthens the adhesion between the nanocrystals and FTO substrates as confirmed by Fig. S3, which facilitates further film characterization and application studies [23,52]. All the PMs present significantly enhanced anodic photocurrent densities with the order of ZnSe/ZnS > ZnSe > ZnS.

The photo-response of the ZnSe/ZnS PMs and QRs were further analyzed under wavelength-resolved light irradiation, Fig. 4d. The measurement was conducted at a bias potential of 0.4 V under continuous monochromatic light irradiation with a 1 nm/s scanning step from 340 to 600 nm. After subtracting the dark current density, the photocurrent response decreased gradually with the redshift of the light wavelength, consistent with the UV–vis absorption of the ZnSe/ZnS QRs and PMs (Fig. 4a). However, particularly in the wavelength ranging from 300 to 350 nm, a significantly improved current density in the PMs is observed, although the UV–vis absorption spectra of the QR film and the PMs are at similar levels. This is a strong evidence showing that the PMs packing of the ZnSe/ZnS quantum rods significantly improves the charge transfer. Accordingly, the monochromatic incident photon-to-current conversion efficiency (IPCE) of the as-prepared electrodes in the same electrolyte buffer were calculated based the equation [52]:

\[ \text{IPCE} = (1240 \times I_d/\lambda) \times 100 \% \tag{2} \]

where \(\epsilon\) is the dielectric constant of ZnSe (8.9) and ZnS (9.2) and \(e_0\) is the electron charge (1.602 × 10\(^{-19}\) C). Based on this equation, the calculated charge carrier densities are 2.96 × 10\(^{21}\) cm\(^{-3}\) for ZnSe/ZnS QRs and 5.11 × 10\(^{21}\) cm\(^{-3}\) for ZnSe/ZnS PMs. Considering the exact same slope value of the tangents drawn from the MS linear region of the n-type ZnSe, the \(N_d\) in the ZnSe body shows nearly no changes before and after the annealing, as shown in Table 1. The annealing process would not change the carrier density within the ZnSe body. As the p-type ZnS and p-n junction are mostly localized at the branches or the interface of the rods, the self-assembled aligned close packing would mainly affect the physicochemical form of ZnS by connecting the ZnS branches and the p-n junctions between QRs, thereby facilitating an increase of carrier density of this part. Such a structure also confirms the synergistic effect of ZnSe/ZnS p-n junction with a sufficient charge layer, leading to the enhanced charge carriers under light irradiation [55]. More significantly, the flat band potential (\(E_{fb}\)) derived by the MS plots shows a positive flat band shift of 0.53 V (V vs. RHE) from ZnSe/ZnS QRs (−0.61 V) to ZnSe/ZnS PMs (−0.08 V) in the n-type ZnSe region, suggesting decreased bending degrees of the band edges of ZnSe, which promotes charge transfer at the ZnS/ZnSe junction [56,57]. This will be illustrated in the following discussion and Fig. 5f.

We used electrochemical impedance spectroscopy (EIS) to clarify the diffuse layer resistances on the anodes under light and dark conditions. As shown in Fig. 4g, the high-frequency zone reflects the charge transfer limiting process, which is related to the charge transfer resistance (Rct) at the contacting interface with double-layer capacitance (CPEDl) (Rs is the solution resistance). Under light irradiation, ZnSe/ZnS PMs exhibit a reduced charge-transfer resistance with a smaller radius in a linear

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flat band potential ((E_{fb}))</th>
<th>Charge carrier density ((N_d))</th>
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<tbody>
<tr>
<td>ZnSe/ZnS QRs n-type region</td>
<td>−0.61 V</td>
<td>1.58 \times 10^{22} \text{ cm}^{-3}</td>
</tr>
<tr>
<td>ZnSe/ZnS PMs n-type region</td>
<td>−0.08 V</td>
<td>1.58 \times 10^{22} \text{ cm}^{-3}</td>
</tr>
<tr>
<td>ZnSe/ZnS QRs p-type region</td>
<td>1.63 V</td>
<td>2.96 \times 10^{21} \text{ cm}^{-3}</td>
</tr>
<tr>
<td>ZnSe/ZnS PMs p-type region</td>
<td>1.63 V</td>
<td>5.11 \times 10^{21} \text{ cm}^{-3}</td>
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direction than that of the ZnSe/ZnS QRs, confirming accelerated charge transfer at the electrode/electrolyte interfaces due to the removal of the organic ligand [39]. The reduced resistance also confirms the ordered alignment of ZnSe/ZnS PMs with the compact connection in both side and top sections, providing better conductive media for the charge transfer, as shown in Fig. S9 for EIS under dark conditions.

To test the photoelectric stabilities of the samples, we subjected the photoanodes under light irradiation and 0.4 V bias voltage for 150 min. The PMs-based photoanodes presented more substantial current densities than the QRs counterparts. As shown in Fig. 4h, a drastic reduction of the photocurrent occurs over the ZnSe/ZnS PMs photoanode under the first few chopped illumination, which is mainly due to the accelerated carrier recombination under a high bias voltage and the excessive accumulated hole-induced photo-corrosion of ZnSe/ZnS QRs surface under long-term irradiation. In contrast, only a slight decrease in photocurrent densities is observed over the ZnSe/ZnS QRs due to the shielding of the ligands. However, the photocurrent density is only 20% of that of PM counterpart under the stabilized condition. Interestingly, although the current density of ZnSe or ZnS PMS electrodes was relatively low (Fig. S10), they exhibited acceptable stabilities, which may be attributed to two possible reasons, (1) the consumption of sacrificial agents [S\(_2\)O\(_8\)]\(^{-}\) affects the turnover process of the [Ru(bpy)\(_3\)]\(^{3+}/3^+\) couple, and (2) quenching and decomposition of photosensitizer plays a direct role in the decreased water oxidation activity, which had been extensively demonstrated in previous works [59–62]. The results of photocatalytic oxygen evolution further proved that removal of the organic ligand and the oriented self-assembly could synergistically promote the water oxidation performance of PMs samples.

To gain further insight into the PEC performance promotion, we employed in-situ irradiation XPS spectroscopy to investigate interfacial charge transfer. According to Fig. 5a, ZnSe/ZnS PMs show a slight negative shift of 0.2 eV under UV, while ZnSe/ZnS QRs barely show any shifts under UV. Based on the electrostatic shielding effect, the weaker binding energy of ZnSe/ZnS PMs indicates a larger content of the photogenerated delocalized electrons compared with that of ZnSe/ZnS QRs [63]. These results provide direct evidence on the improved charge transfer in the PMs structures. High-resolution XPS spectra compare the binding environment of the samples before and after the PEC test of (b) Zn 2p, (c) S 2p, and (d) Se 3d. (e) Band gap alignment of ZnSe/ZnS PMs cathode. (f) Illustration of the electron and hole separation in ZnSe/ZnS QRs. (g) Schematic illustration of the water oxidation catalyzed by the ZnSe/ZnS PMs. (h) Illustration of the electron transportation in (h) ZnSe/ZnS QRs and (i) ZnSe/ZnS PMs. (j) Illustration of the electron and hole separation of ZnSe/ZnS PMs photoanode.

As shown in Fig. 4i, single component ZnS PMs, single component ZnSe PMs, and ZnSe/ZnS PMs showed increased oxygen evolution activities, as compared to the QRs counterparts. In addition, the photocatalytic oxygen evolution rates of all the catalysts decreased gradually, and the amount of generated oxygen plateaued at around 60 min. This can be attributed to two possible reasons, (1) the consumption of sacrificial agents [S\(_2\)O\(_8\)]\(^{-}\) affects the turnover process of the [Ru(bpy)\(_3\)]\(^{3+}/3^+\) couple, and (2) quenching and decomposition of photosensitizer plays a direct role in the decreased water oxidation activity, which had been extensively demonstrated in previous works [59–62]. The results of photocatalytic oxygen evolution further proved that removal of the organic ligand and the oriented self-assembly could synergistically promote the water oxidation performance of PMs samples.
Based on the performance and characterization evidence, we propose the mechanism of ZnSe/ZnS PMs towards photocatalytic and photoelectrochemical water oxidation, as shown in Fig. 5e–j. According to the bandgap energies of ZnSe and ZnS QRs in Fig. 5e, the conduction band (CB) of ZnSe is much lower than that of ZnS, while its valence band (VB) is slightly higher than that of ZnS [23]. As a result, the p-n junction with a Type-I band alignment provides a unique route to collect the trapped holes and suppress recombination of the electron-hole. Specifically, the photogenerated electrons would transfer from the CB of ZnS to CB of ZnSe, because of the potential difference and self-assembly induced band bending of ZnSe, and finally to the conductive FTO substrate (~0.45 V at NHE), while the holes would be trapped at the interface of ZnSe/ZnS p-n junctions. For energy distribution, abundant defects in the shell can allow the electrons to break the bandgap confinement and escape from the surface. The interface between the imperfect ZnSe branched shell and the ZnSe rod provides enriched p-n junctions to efficiently accelerate the charge transfer between the CB and VB of ZnSe and ZnS, facilitating the water oxidation reaction. As illustrated in Fig. 5f, due to the strong confinement of the 1D ZnSe long arm (main body rods) in the branched ZnSe/ZnS structure, the excited electrons are likely transferred to the tip of the ZnSe rods along the principal axis and be accepted by the sacrificial agent (S2O82−) in the photocatalysis test (Fig. 5g) or flow to the counter electrode along the external circuit in the PEC test (Fig. 5j). Simultaneously, the residual holes would migrate to the ZnSe/ZnS interface, and the junction between the branched ZnS and ZnSe body, to boost the water oxidation reaction. Such a unique charge carrier distribution significantly differs from previous core-shell quantum dots, rendering it of high utility in photocatalysis. The densely packed aligned quantum rods in PMs provide a superior packing structure for taking advantage of the electron-leaking property of the ZnSe/ZnS quantum rods. The side-to-side and head-to-tail close packing has significantly facilitated the charge transport. The narrower bandgaps in PMs, as determined by the UV–vis, reveals less confined electrons due to the high density packing of the quantum rods. As illustrated in Fig. 5h and i, the ZnSe/ZnS QRs with random arrangement would hinder the electron transfer between separated rods and across the empty resistant area, while the ZnSe/ZnS PMs allow efficient electron transfer through both ‘head-to-tail’ and ‘side-by-side’, likely due to electron tunneling. Thus, the ZnSe/ZnS PMs photooanode could promote charge mobility and significantly boost PEC performance.

3. Conclusion

We have demonstrated a quasi-solid-state self-assembly method for fabricating a macroscopic device with hierarchical ordering from anisotropic nanomaterials. In addition, we have shown the multi-functions of the surface ligands on nanomaterials, in stabilizing the colloidal suspension and inducing a melt state under the right condition, for then kinetics-driven self-assembly for fabricating ordered structures. With 1D branched ZnSe/ZnS quantum rods, we demonstrated the parallel monorail-structures formation on an FTO substrate from randomly packed solid-state ZnSe/ZnS QR by simple heat treatment at a temperature slightly below the boiling point of the surface ligand, 1-octylamine. The 1-oleylamine serves as a multifunctional unit for mediating the interfacial interactions, facilitating the kinetic-driven self-assembly involving ligand dissociation and evaporation. The rearranged quantum rods have “side-to-side” and “head-to-tail” alignment into parallel monorails.

The fabrication method accommodates nanoscopic architecture in a macroscopic material and imparts new properties into the assembly. Building on the unique property of ‘leaky-electrons’ of this untypical Type-I branched ZnS (short arm) – ZnSe (long arm) core/shell quantum rods, their self-assembled aligned PM packing modulates the band bending and facilitates electron transport. In addition, the ZnSe/ZnS QRs and PMs can be directly applied to photocatalytic and photoelectrochemical water oxidation applications, which is an unexpected behavior for conventional Type-I core-shell quantum particles. Compared with the ZnSe/ZnS QRs film, ZnSe/ZnS PMs with ordered hierarchical nanostructure show enhanced charge separation and transfer, reduced electronic resistance, and boosted photo-response and water oxidation activity. This work not only sheds light on the construction of hierarchically-ordered quantum materials through a quasi-solid-state self-assembly process, but also provides a new strategy for developing earth-abundant and eco-friendly photo(electro)catalysts for solar energy conversions.

Author contributions

D.C., H.Z., Q.L. and S.W. conceptualize the work. D.C. conducted the materials synthesis. H.Z. and D.C performed the photocatalytic and photoelectrochemical water oxidation applications. D.C. conducted the materials characterization and analysis. K.M., R.K., T.F. and D.C. performed the AFM. P.Z. and G.S. performed the In-situ XPS. D.C., L.Y. and Q.S. conducted the mechanism simulation. Q.L. and S.W. supervised the project. D.C., H.Z., S.W., Q.L., C.L.R., P.N.P. wrote the manuscript with contributions from all other authors. Y.G, N.T.N, G.J. and D.Z. revised the manuscript. All the authors discussed the results and commented on the manuscript.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the

References


