Atomically dispersed Ni in cadmium-zinc sulfide quantum dots for high-performance visible-light photocatalytic hydrogen production

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Catalysts with a single atom site allow highly tuning of the activity, stability, and reactivity of heterogeneous catalysts. Therefore, atomistic understanding of the pertinent mechanism is essential to simultaneously boost the intrinsic activity, site density, electron transport, and stability. Here, we report that atomically dispersed nickel (Ni) in zincblende cadmium–zinc sulfide quantum dots (ZCS QDs) delivers an efficient and durable photocatalytic performance for water splitting under sunlight. The finely tuned Ni atoms dispersed in ZCS QDs exhibit an ultra-high photocatalytic H2 production activity of 18.87 mmol hour⁻¹ g⁻¹. It could be ascribed to the favorable surface engineering to achieve highly active sites of monovalent Ni(I) and the surface heterojunctions to reinforce the carrier separation owing to the suitable energy band structures, built-in electric field, and optimized surface H2 adsorption thermodynamics. This work demonstrates a synergistic regulation of the physicochemical properties of QDs for high-efficiency photocatalytic H2 production.

INTRODUCTION

The design of catalysts with suitable chemical and physical properties is essential for many energy conversion and storage technologies, such as water electrolysers, photocatalytic water splitting, metal-air batteries, and fuel cells. Introducing active single atoms into the catalysts has been the most widely used strategy to tune the electronic structure of the catalysts to optimize their intrinsic activities, electronic transport, active site densities, and stability (1–3). Furthermore, downsizing catalyst particles or clusters to single atoms is highly desirable for maximizing catalytic efficiency. It has been well recognized that the isolated active atoms singly dispersed in matrices can maximize the efficiency of atom utilization (hence, single-atom catalysts) in acidic (4) and alkaline (5) hydrogen evolution reaction (HER) (6), electrochemical reduction of CO2 (7), CO oxidation (2), etc.

The structurally uniform and well-defined single atomic sites in a simple structure provide atomic-level insight and the corresponding catalytic reaction mechanism (2, 8, 9). However, it is still a big challenge to understand the catalytically active center in “atomic interfaces” (typically with different charges or even different chemical identities) (7) within higher complexities. Obviously, the identification of an active site structure with more sophisticated functionalities is crucial for catalytic reactions that simultaneously require different kinds of functional active sites. Grimaud and Xu et al. (10) found that substituting Al of inactive but low-cost CoAl2O4 with a small amount of Fe can activate the preoxidation of Co and optimize the O 2p level of oxide for greater structural flexibility to facilitating the surface reconstruction of CoAl2O4. They revealed that on the reconstructed surface, the Fe substitution facilitates a two-step deprotonation process, which leads to the formation of active oxygen sites at a low overpotential and thus greatly promotes the oxygen evolution reaction (OER) (10). The Cd1-xZnxS solid solution rather than bare CdS and ZnS demonstrated efficient photocatalytic properties for hydrogen (H2) evolution in the presence of sacrificial electron donors. Its photocatalytic activities can be optimized by adjusting the x value for achieving appropriate band structure for the photocatalytic H2 production (11–13). Xu and Wang et al. (14) also unveiled the accurate amount of catalytically inactive Zn2+ incorporating into CoOOH that can give rise to oxygen nonbonding states with different local configurations, which is critical to regulating the OER mechanism. They found that if two neighboring nonbonding oxygens with the partially filled O(2p) band can hybridize their oxygen holes without sacrificing metal-oxygen hybridization substantially, the OER proceeds via the lattice oxygen oxidation mechanism pathway on the metal oxyhydroxides, discovering that Zn0.2Co0.8OOH has optimum activity (14). Identification of active site structures is even more vital for the photocatalytic H2 production through water splitting driven by visible light because of their complex multiple reaction processes: from light harvesting to charge (electron and hole pairs) excitation, further to photocatalyst surface engineering for both HER and OER (15–17). Therefore, it is critical to investigate the efficiency of the introduced single atoms on a per-atom basis and further systematically evaluate the electronic and structural properties of the photocatalysts to realize synergistic integration of photocatalytic constituents into a functional heterostructure. One of the challenges to unveil the synergistic effect of the single atoms with their coordinating elements is the irregular structure of the bulk catalysts, resulting in the different exposed facets with anisotropic physical and chemical properties.

In contrast to the elusive irregular bulk materials, here we use a crystallographic and structural chemistry design approach to manipulate the atomically dispersed nickel (Ni) in zincblende cadmium–zinc sulfide quantum dots (ZCS QDs), maximizing the photocatalytic properties for water splitting driven by visible light. The colloidal QDs, such as ZnS-coated InP QDs (15) with tunable bandgap and versatile surface properties, remain among the most promising photocatalysts for the HER. Here, experimental investigation and theoretical density function theory (DFT) calculations revealed that with continuous adjustment on the concentration of atomically dispersed...
Ni, the anisotropy of different crystalline facets [(111) and (110)] of the ZCS QDs can be fine-tuned. In particular, the (111) facets consisting of isolated, high-density, low-valence Ni(I) as verified by the x-ray absorption fine structure analysis (XAFS), electron energy-loss spectroscopy (EELS) spectra, etc., show a highly catalytic activity for HER. Furthermore, surface heterojunctions due to the different exposed crystal planes [(111) and (110)] in the same phase maximize the charge carrier separation. Meanwhile, the built-in electric field (BIEF) can further facilitate the charge carrier migration to the surface, leading to enhanced electronic conductivity. Together with proper surface H₂ adsorption thermodynamics on the atomically dispersed Ni(I) active sites, the optimized Ni₀.03125Zn₀.25Cd₀.75S QDs achieved a remarkable photocatalytic H₂ production rate of 18.87 mmol hour⁻¹ g⁻¹. This work could pave a new avenue for the synergistic modulation of the physicochemical properties of nanocrystals to substantially improve their performances for various applications, e.g., catalysis, electronics, and optoelectronics.

RESULTS AND DISCUSSION
Phase structures and morphology
Stoichiometric ZCS QDs were synthesized through the hot injection approach, using metal chloride and thioacetamide (TAA) as precursors and oleylamine (OLA) as the reducing and stabilizing agent. The field emission scanning electron microscopy (FESEM), the high-resolution transmission electron microscopy (HRTEM), and the high-angle annular dark field scanning TEM (HAADF-STEM) images were used to identify the morphology of the as-prepared QDs. It shows that the monodisperse ZCS QDs with the uniform tetrahedral shape and a narrow size distribution (~8.5 nm) were obtained (fig. S1, A to D). They exhibit an equilateral triangle shape with a 60° angular parietal, and the fast Fourier transform (FFT) plots can be indexed as (111) crystal planes of the zincblende structure (fig. S1, E to G). The ZCS QDs are enclosed by (111) facets, as identified by the angles of the simulated outlines of the triangular pyramids sitting on the tetrahedral facets together with the HAADF-STEM (fig. S1, H to L). After dispersing Ni into ZCS QDs, we obtained four NiₓZCS (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs. All these QDs are monodisperse (with an average size of ~8.0 nm). They self-assemble to form a superlattice structure (fig. 1, A₁ to D₁ and A₂ to D₂, and fig. S2, A to H), as confirmed by the regular hexagonal arrangement FFT patterns (insets of Fig. 1, A₁ to D₁). The low polydispersity in size can be ascribed to the temperature-dependent release of reactive sulfur species from TAA and the optimized reactivity. As calculated (fig. S4, O to S), with Zn and Ni substitute, the Td symmetry of the [Cd₄S₄] tetrahedron is preserved, but the atomic relaxation results in an isotropic elongation of the four Cd─S bonds, indicating that the [Ni/ZnS₄] tetrahedron experiences a local inward relaxation with shorter Ni─S and Zn─S bond length (~2.33 Å) than the original Cd─S bond (~2.53 Å). It implies the effect of the atomically dispersed Ni on the volume shrinkage of the supercell along with increasing Ni content.

Depth profiling of the crystal structure and electronic structure was carried out using x-ray photoelectron spectroscopy (XPS). The atomic ratios of Ni/Zn/Cd on the surface are 3.13%:28.18%:68.69%, 9.50%:26.71%:63.79%, 11.75%:23.23%:65.02%, and 12.65%:21.53%:65.82% for NiₓZCS (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs, respectively, as measured by XPS. The metal versus S ratio was confirmed to be around 62%:38%, indicating the loss of the S on the surface. The dangling S on the (111) crystal plane of zincblende presents a much higher activity, implying their instability [-2 eV higher surface energy of (111) facets with dangling S than the one without dangling S]. The high-resolution XPS results of Zn 2p and Cd 3d agree well with the truncated tetrahedral architecture (fig. S2X). Therefore, the as-prepared NiₓZn₀.25Cd₀.75S₁₋ₓ QDs are enclosed by the (111) and (110) facets only. Figure S3 shows more detailed shape evolution images of the NiₓZCS QDs along [111], [100], [110], and [112] orientations, confirming the role of Ni in the evolution of the enclosed facets. For comparison, the bare CdS and ZnS QDs were also synthesized through the same process. They also present the uniform size distribution and the tetrahedral morphology (fig. S2, Y and Z). As characterized by FESEM, HRTEM, and HAADF-STEM, it confirms the uniform size, surface morphology, and crystallography of the as-prepared NiₓZCS QDs. Furthermore, the clearly identified anisotropy crystal facets of the NiₓZCS QDs could present the tunable electron structure to tune the photocatalytic activity.

To gain deeper insight into the phase structures of the bulk and surface compositions of the NiₓZCS QDs, inductively coupled plasma mass spectrometry (ICP-MS), energy-dispersive x-ray spectroscopy (EDS), the Rietveld refinement x-ray diffraction (XRD) patterns, and the selected area electron diffraction (SAED) analyses were explored. ICP-MS and EDS measurements confirm that the chemical compositions of NiₓZCS QDs are close to the molar ratio of Ni, Zn, and Cd in the initial solution (table S1). Owing to the similar covalent radii of Ni, Zn, and Cd (121, 131, and 148 pm, respectively), Zn and Ni can readily substitute Cd within the NiₓZCS QDs, which was confirmed by the calculated lowest free energy of the substitute dopants (fig. S4, A to G, and table S2). Moreover, the formation energy of an impurity Ni is 0.45 eV in the Ni₀.125ZCS when nickel chloride is used as Ni source, implying the high solubility of Ni in the ZCS matrix. This is also identified by the Rietveld refinement XRD patterns (fig. S4, H to L). The lattice parameters decreased from 5.712 Å for bare ZCS QDs to 5.706, 5.694, 5.665, and 5.631 Å for NiₓZCS (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs, respectively, which is well consistent with the DFT calculation results and Vegard’s law plot (fig. S4, M and N) (20). The main XRD peaks [(111), (220), and (311)] continuously shift toward higher angles without phase separation along with increasing Ni content, indicating the homogeneous structure of the NiₓZCS solid solutions (fig. S4l). As calculated (fig. S4, O to S), with Zn and Ni substitute, the Td symmetry of the [Cd₄S₄] tetrahedron is preserved, but the atomic relaxation results in an isotropic elongation of the four Cd─S bonds, indicating that the [Ni/ZnS₄] tetrahedron experiences a local inward relaxation with shorter Ni─S and Zn─S bond length (~2.33 Å) than the original Cd─S bond (~2.53 Å). It implies the effect of the atomically dispersed Ni on the volume shrinkage of the supercell along with increasing Ni content. The SAED ring patterns are consistent with XRD results (fig. S4, T to W). Together with the ICP-MS and EDS measurements, it elucidates the solid solution feature of the as-prepared NiₓZCS QDs, which could benefit the electron conductivity for their catalytic applications.
the values reported for the divalent Zn and Cd in pure metal sulfides (fig. S5, A and B) (21, 22). Two subpeaks in S 2p 3/2 XPS spectra (Fig. 2A) can be ascribed to the lattice S 2− (at ~161.1 eV) and the oxidized states of S (at ~163.2 eV), respectively (23). The gradually decreased subpeak at ~162.9 eV indicates the lower oxidization of surface S along with increased concentration of Ni in Ni$_x$ZCS QDs. This is consistent with the geometry evolution of the Ni$_x$ZCS, because more (110) facets increase the Bader charge of surface S [−0.92 to −0.96 V for (110) facets and −0.85 to −0.91 V for (111) facets, table S3]. The Ni 2p XPS profile shows the main peaks of Ni 2p 3/2 and Ni 2p 1/2 at ~855.3 and ~872.6 eV, respectively (Fig. 2B) (24). The former main peak can be ascribed to the direct charge transfer from the nearest-neighbor S 2p to Ni core hole (25, 26). The Ni 2p XPS profile shows the main peaks of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ at ~855.3 and ~872.6 eV, respectively (Fig. 2B) (24). The former main peak can be ascribed to the direct charge transfer from the nearest-neighbor S 2p to Ni core hole (25, 26). It can be fitted into a doublet (~855.6 and ~856.9 eV, peaks 1 and 2) with the increased Ni concentration, which is related to the two different photoemission channels: e.g., a single Ni site screened by a shift of electron density from the surrounding nearest-neighbor S 2p (peak 1) and a nonlocal effect from an adjacent cation occupancy (peak 2) (27). Here, peak 2 can only be ascribed to the adjacent Ni cation occupancy, which is evidenced by the local density of state (LDOS) of the Ni, Zn, Cd, and S in the Ni$_x$ZCS (fig. S5, C to F). The d10 metals Cd and Zn show a tight and localized DOS at the bottom edge of the valence band (VB) in Ni$_x$ZCS crystals and do not participate in bonding. Only Ni 3d levels occupied the top of the VB and bottom of the conduction band (CB), together with substantial S 2p charge-transfer character to form the bandgap. It indicates that Ni 2p3/2 peak 2 can only be derived from the adjacent Ni nonlocal effect. Thus, owing to the low Ni concentration within Ni$_0.015625$ZCS and Ni$_0.03125$ZCS QDs, the adjacent Ni nonlocal screening is eliminated, resulting in the broader peak 2 within Ni 2p3/2 peaks, which is hard to distinguish, compared with the ones in the higher Ni doping levels samples. Furthermore, the 2p$^3$3d$^8$ state associates with the satellite feature, leading to the broad peak at ~863 eV, which agrees with the single metal site character even for very dilute Ni (28). Such broad satellite peak also decreased in Ni$_x$ZCS QDs within less Ni because of the less Ni d-d nonlocal screening transitions (25, 26), confirming the low-level Ni distribution within the Ni$_0.015625$ZCS and Ni$_0.03125$ZCS QDs. As revealed by the XPS, the Ni atoms are highly uniformly distributed within the Ni$_x$ZCS QDs host crystals, which can benefit the usage of Ni active sites.

To further probe the local hybridization states of Ni in the Ni$_x$ZCS QDs on high spatial resolution down to the nanometer level, the L-edge EELS was collected to measure the Ni dipole transitions from 2p orbitals to unoccupied 3d orbitals. The L-edge EELS was recorded to evaluate the local electron distributions and magnetic moments of Ni (Fig. 2C) (29, 30). The L$_y$/L$_x$ white-line ratio of Ni is increased from 1.124 for Ni$_0.015625$ZCS to 1.21 for Ni$_0.03125$ZCS, 1.420
for Ni$_{0.0625}$ZCS, and 1.573 for Ni$_{0.125}$ZCS QDs, indicating the gradually lowered occupied Ni d orbit and more unpaired electrons (enhanced magnetic moments) within Ni (29, 30). We studied the anisotropy crystal facets of the orthorhombic nonpolar (110) surface and hexagonal polar (111) surfaces of the Ni$_x$ZCS to reveal the local electronic structure of Ni in Ni$_x$CZS QDs. As confirmed by both surface energy and experimental M:S molar ratio results (XPS and EDS, table S1), the metal cations on the polar (111) surface...
coordinate with three S rather than four. The relaxed top MS (M = Ni, Zn, and Cd) layers of both (111) and (110) crystal planes appear corrugated with respect to the bulk termination, and all cations in the outermost layer tend to downshift toward the inner layer (S tends to upshift) (Fig. 2D and fig. S5, G and H). The Ni and Zn ions become almost coplanar with their three coordinated S atoms (Cd even further downshifts to form the invagination pyramid), and shorter M–S bond lengths (−2.25 Å for both Zn–S and Ni–S and −2.48 for Cd–S) were achieved. The (111) surfaces displayed a flatter feature (almost parallel to the ab plane) than the (110) ones (−137° to the ab plane). Being consistent with the Bader charge [0.95 to 0.98 for (110) and 0.54 to 0.58 for (111) facets] and the unpaired electron number of Ni [1.61 to 1.69 for (110) and 0.95 to 0.99 for (111) facets], the magnetic moments of Ni atoms were calculated to be 1.61 to 1.69 μB for (110) facets and 0.95 to 0.99 μB for (111) facets (table S4). These results unveil that the Ni in the (111) facets shows one unpaired electron with a 3d⁹, S = 1/2 electronic configuration and monovalent oxidation state, whereas the Ni in (110) facets features two unpaired electrons and a 3d⁸, S = 2/2 electronic configuration. Therefore, as characterized by the Ni EELS spectra, the higher L₂/L₁ white-line ratio derived from more Ni dipoles transitioning from 2p to 3d orbits can be ascribed to the more unoccupied Ni 3d orbits on the (110) facets. Meanwhile, as unveiled by the EELS, the unpaired electrons on the (110) and (111) facets can contribute to more interaction with the H.

The localized coordination environments of induced Ni within Ni₅ZCS QDs crystals were confirmed by the XAFS (Fig. 2, E to M). All four K-edge Ni x-ray absorption near-edge structure (XANES) spectra present the prepeak at ~8348 eV (peak A in Fig. 2E), suggesting the dipole-forbidden but quadrupole-allowed transition and the 3d empty metal states and 4p orbit hybridization of the Ni central atoms (31). Furthermore, along with the increase of Ni in Ni₅ZCS QDs, the pre-edge peak intensity increased (inset of Fig. 2E), indicating the more empty p component in p-d hybridized orbits. These are consistent with the EELS spectra that presented more (110) facets, resulting in the less occupied p component. Figure S6 simulated the XANES of NiS₄ (x = 6, 4, and 3) complexes to study their symmetrical dependency. The shoulder near 8348 eV appears in the sixfold coordinated NiS₄ octahedron (O₆), fourfold coordinated NiS₄ tetrahedra (T₄), threefold coordinated NiS₃ triangular pyramid, and the trigonal planar complex (C₃v), but not in the square planar complexes (C₄v) (32). For NiS₄ O₆ symmetry, the e₉ (dₓ²−ᵧ₂ and dₓz−yₑ) mainly contributes to the electric dipole and quadrupole transitions, whereas for the NiS₄ T₄, it mainly comes from the ɛ₂g (dₓ²−y², dₓz, and dᵧz) (fig. S6, A to C). Losing one more axial to form the threefold coordinated NiS₃ triangular pyramid, it presented a more intense pre-edge peak, mainly contributed by eₓ₂ and the intensity increased along with the Ni moving toward the planar center, reaching the maximum with the trigonal planar complex (C₃v). This is consistent with the pre-edge peak intensity changing from Ni₄₋₀.₃ZCS to Ni₀₋₀.₅ZCS QDs. These transitions can serve as a fingerprint for identifying the trigonal planar Ni-S₄ (25, 29). After calculation of the two shells [NiS₅M₁₂ and NiS₆M₀ for (111) facets and NiS₅M₇ for (110) facets, fig. S6D], the calculated XANES of NiS₅M₁₂ presented the highest white line (1s → 4p dipole transfer) and NiS₆M₀ mainly contributed to the prepeak (1s → 3d transfer). The experimental XANES of Ni₅ZCS QDs shows higher white line intensity than Ni foil and NiS. The intensities were enhanced with increased Ni in Ni₅ZCS QDs, confirming the Ni₅ZCS QDs mixed with the threefold coordinated NiS₃ and fourfold coordinated NiS₄ tetrahedra (T₄). Furthermore, the XANES edge positions of Ni₅ZCS QDs lie between those of Ni foil and NiS, indicating that their oxidation state is between 0 and +2 (inset in Fig. 2E). This also confirms the Ni mixed with the threefold coordinated NiS₃ and T₄ symmetry as demonstrated in Fig. 2D. Figure 2F displays the Fourier transform (FT) k³χ(k) of the phase-uncorrected extended x-ray absorption fine structure spectra (EXAFS). The FT k³χ(k) of Ni foil displays peak at 2.15 Å, corresponding to Ni-Ni interaction and does not appear in any of the Ni₅ZCS QDs, confirming isolation of Ni in Ni₅ZCS QDs. The main peak at ~1.58 Å of Ni₅ZCS QDs is attributed to the scattering interaction between Ni and the first shell S (Ni-S). Figure 2G and fig. S6 (E to G) show the four-shell fitted FT k³χ(k) EXAFS spectra of Ni₀₋₀.₃ZCS QDs and Ni₀₋₀.₅ZCS (x = 0.015625, 0.0625, and 0.125) QDs, respectively. It is well matched with DFT-optimized (111) and (110) facet crystals (inset of Fig. 2G and table S5 summarize the fitting results). The wavelet transform plot of Ni foil shows the maximum at around 7 Å⁻¹ (Fig. 2H), corresponding to Ni–Ni bonding, while for NiS, there are two wavelet transform plot maximal centers, related to Ni–S (5 Å⁻¹) and Ni–Ni (7 Å⁻¹) bonding, respectively (Fig. 2M). The maximum wavelet transforms of Ni₅ZCS QDs are all around 5 Å⁻¹ (Fig. 2, I to L), aligning with Ni–S bonding only. All these XAFS results elucidate that the Ni coordinates with the threefold S on (110) and (111) surfaces and fourfold S within the T₄ symmetry, suggesting the different localized electron structures on the surface, profiting the tunable catalytic property, as illustrated in Fig. 2N. Furthermore, DFT calculations on surface energy and the adsorption energies of OLA on the crystal planes (fig. S3, I and J) were applied for disclosing the morphology evolution on Ni₅ZCS (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs, as shown in fig. S3 (E to L).

The sub-ångström-resolution aberration-corrected HAADF-STEM and corresponding STEM-EDS spectrum were conducted to observe the highly uniformly distributed Ni atom within the Ni₅ZCS host crystals. The clean surfaces and edges of the Ni₅ZCS QDs can be observed by the HAADF-STEM (Fig. 3, A to D). The STEM-EDS elemental mapping of the Ni₀₋₀.₃Ni₀₋₀.₃ZCS QDs readily reveals the homogeneous distribution of Ni, Zn, Cd, and S in the integrated QDs (Fig. 3, E to H). HAADF images represent the projection of atoms along the incident beam direction. Therefore, the sub-ångström-resolution aberration-corrected HAADF-STEM images of Ni₅ZCS (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs along the [111] zone axis with different intensities for atomic columns (Fig. 3, I to L) were used to characterize the dispersion and configuration of the Ni/Zn and Cd atoms on the basis of Z-difference of the individual heavy atoms (33). The individual Ni atoms occupy exactly the positions of the Cd and/or Zn atoms within the surface of Ni₅ZCS QDs without the interstitial sites, which is comparable with the simulated Ni-substituted scanning tunneling microscope (STM) image of the (111) surface of Ni₀₋₀.₃ZCS (Fig. 3M). The line profiles (Fig. 3N) of the (111) surface of Ni₀₋₀.₃ZCS marked in Fig. 3J, showing different intensities, could identify the different elements (higher intensity represents Cd-rich atomic columns and lower intensity denotes Zn/Ni-rich atomic columns). The measured distances between two adjacent atoms (Fig. 3N) can be fitted with the relaxed Ni₅ZCS crystals (fig. S6, H to J). The atomically resolved HAADF-STEM confirms the uniformly distributed Ni, Zn, and Cd in the as-prepared Ni₅ZCS QDs, which can profit the catalytic properties.
Photocatalytic performances of H₂ production

The activity in the visible-light–powered photocatalytic H₂ evolution of NiₓZCS QDs was evaluated (Fig. 4A). As comparison samples, the bare CdS and ZnS QDs have negligible visible-light photocatalytic activity with very limited H₂ production rates of 242 and 207 μmol hour⁻¹ g⁻¹, respectively. The ZCS QDs increase H₂ production rate to 1.50 mmol hour⁻¹ g⁻¹. The NiₓZCS QDs show a remarkable enhancement of the H₂ production rates. In particular, Ni₀.₀₁₅₆₂₅ ZCS QDs achieved a H₂ production rate of 13.74 mmol hour⁻¹ g⁻¹. With increasing Ni content, Ni₀.₀₃₁₂₅ ZCS QDs present the optimal photocatalytic properties and obtained the highest H₂ production rate of 18.87 mmol hour⁻¹ g⁻¹, exceeding that of bare CdS QDs by a factor of 78- and 2.7-fold superior activity over the 1.9 weight % (wt %) Pt-loaded CdS QDs (6.88 mmol hour⁻¹ g⁻¹). The stability of the optimized Ni₀.₀₃₁₂₅ ZCS QDs was further tested by cycling photocatalytic experiments (Fig. 4B). No substantial deterioration of photocatalytic activity was observed during cycling. A further increase in the Ni content led to deterioration of photocatalytic performance. Ni₀.₀₆₂₅ZCS and Ni₀.₁₂₅ZCS QDs delivered a H₂ production rate of 12.11 and 6.97 mmol hour⁻¹ g⁻¹, respectively. The stability of the as-prepared Ni₀.₀₃₁₂₅ ZCS QDs was further confirmed by the post-characterization via the STEM, EXAFS, and XPS after the cycling test (fig. S7). It can be seen that after the cycling test, the Ni₀.₀₃₁₂₅ ZCS QDs still preserve the truncated tetrahedra shape with the well-defined crystalline feature (fig. S7, A to C). The QDs also mainly exposed with the (111) facets as verified by their corresponding FFT pattern analyses (fig. S7, D to F, taken from marked areas in fig. S7C). As confirmed by the high-resolution Ni 2p spectra of Ni₀.₀₃₁₂₅ ZCS QDs after the cycling test (fig. S7G), the sharp Ni 2p3/2 peak and the broad satellite peak at ~863 eV associated with the 2p3d⁸ state...
agree with the single metal site character (28). Furthermore, the Ni K-edge XANES spectra and the corresponding EXAFS FT ($k^2 \chi(k)$) spectra of Ni$_{x}$ZCS QDs (fig. S7, H and I) after the cycling test are comparable with those of the fresh sample, identifying the Ni state as well as the surface composition as stable under photocatalytic conditions.

The light-harvesting capability, charge separation and transfer ability, and surface redox reactions were studied to understand the intrinsic photocatalytic property of Ni$_x$ZCS QDs. Ultraviolet-visible (UV-vis) diffuse reflectance spectra show that the ZCS QDs have an absorption edge (~465 nm) between those of bare ZnS and CdS QDs. After Ni dispersion, a continuous red shift of the absorption edges can be observed (~469, ~476, ~500, and ~528 nm for Ni$_x$ZCS QDs ($x = 0.015625, 0.03125, 0.0625, and 0.125$), respectively, Fig. 4C). The bandgap of ZCS QDs was measured to be 2.75 eV, while Ni$_x$ZCS QDs have gradually decreasing bandgaps of 2.72, 2.67, 2.56, and 2.42 eV, respectively (Fig. 4D). The calculated band structures of bulk CdS, ZnS, and ZCS are shown in fig. S8 (D to F), with bandgaps of 2.41, 3.53, and 2.71 eV, respectively, which are well consistent with the experimental results (Fig. 4D) and the previous reported results (11–13). They are larger than the values

![Figure 4. Photocatalytic performance and spectroscopy/photoelectrochemical characterization.](image)
calculated based on the generalized gradient approximation (GGA) exchange-correlation function, due to the underestimation by the GGA function (34). To gain insights into the charge separation and transfer mechanism induced by the Ni dispersion, the unfolded band structures were calculated (Fig. 4, G to J). For the bulk Ni\textsubscript{0.015625}ZCS crystals, both the CB minimum (CBM) and VB maximum (VBM) are found to be located at the Γ point of the Brillouin zone (BZ; fig. S8, A to C) with the direct bandgap transition. Along with the Ni doping level increase, the CB edge was reduced gradually. This indicates that Ni doping induced considerable energetic elevation of the CBM, which could contribute to narrowing the overall energy gap in the doped materials (2.49, 2.43, 2.38, and 2.31 eV for Ni\textsubscript{0.015625}ZCS, Ni\textsubscript{0.03125}ZCS, Ni\textsubscript{0.0625}ZCS, and Ni\textsubscript{0.125}ZCS, respectively), which is consistent with the Kubelka-Munk (K-M) results and the UV-vis spectra (Ni\textsubscript{0.03125}QDs have gradually decreasing bandgaps of 2.72, 2.67, 2.56, and 2.42 eV, respectively, Fig. 4D). The narrowed bandgap with Ni dopant has been reported by Thambidurai et al. (35), Zhang et al. (12), and Wu et al. (36). The strong Ni spin polarizations in Ni\textsubscript{x}Mott-Schottky plots and VB spectra (Fig. 4E and fig. S9, A to D). The Fermi level (\(E_F\)) and work function (\(\Phi\)) for the (111) facets are \(-2.99, -2.94, -2.88,\) and \(-2.83\) eV and \(\Phi = 5.96, 5.94, 5.92,\) and 5.8 versus vacuum level for the (110) facets of Ni\textsubscript{ZCS} (\(x = 0.015625, 0.03125, 0.0625,\) and 0.125), respectively. The values are \(-3.40, -3.33, -3.37,\) and \(-3.62\) eV (\(E_F\)) and 4.6, 4.48, 4.56, and 4.68 (\(\Phi\)) for the (111) facets, respectively. Accordingly, Fig. 5A shows the band edge (VBM and CBM) alignment of the (110) and (111) facets of Ni\textsubscript{ZCS}, demonstrating the typical type II (staggered) heterojunctions. Electrons in the (111) crystal planes with the higher Fermi levels tend to flow to the (110) crystal planes to flatten the Fermi levels. Therefore, the (110) facets here had considerable excess negative charges, whereas the (111) facets were electro positive to some extent. The adjustment of Fermi levels brought in the rearrangement of overall band structures (Fig. 5B), in which, to accommodate the flattened Fermi levels, both CBM and VBM of (110) parally shifted up, whereas CBM and VBM of (111) synchronously descended. Such rearranged band structures are consistent with the experimental Mott-Chottky plots and VB spectra (Fig. 4E and fig. S9, A to D). The CBMs of Ni\textsubscript{x}ZCS QDs were measured to be at \(-0.45, -0.98, -0.51,\) and \(-0.31\) V versus the standard hydrogen electrode (SHE) for Ni\textsubscript{ZCS} (\(x = 0.015625, 0.03125, 0.0625,\) and 0.125), respectively (Fig. 4E). The flattening of Fermi levels and electron flow could generate the BIEF between the (110) and (111) facets, forming a charge disequilibrium in the depth direction perpendicular to the interface (Fig. 5B). Furthermore, when evaluating the energy levels of the (110) and (111) facets of the same Ni\textsubscript{ZCS} (Fig. 5B), the difference in energy of the VB and CB between the (110) and (111) facets can be distinct. It suggests that the electron transfer from the (110) and (111) facets is feasible thermodynamically, leading to the accumulation of electrons on the (111) facets. Such spatial charge separation between the (110) and (111) facets is feasible due to their different energy levels, which is responsible for the formation of reduction and oxidation facets. Meanwhile, the opposite BIEF direction toward the electron flow markedly accelerates the migration of photoexcited electrons from the (110) to the (111) facets, whereas the immobilized positive holes near the (110)/(111) interface remain on the (110) facets because of the high repulsive force from the BIEF. It is worth noting that such synergetic effects of various coexposed facets in one crystal and balanced ratio of different exposed facets is crucial for the photocatalytic efficiency. The band bending of each facet of Ni\textsubscript{x}ZCS (\(x = 0.015625, 0.03125, 0.0625,\) and 0.125) and the BIEF are distinct owing to their different surface electronic structures, which is another factor affecting the spatial charge separation. The downward bent (110) VB and the upward bent (111) VB generate discontinuities at their interface, forming a barrier for holes to transfer from the (110) to the (111) facets, in spite of which the location of the (111) VBM is more favorable for hole migration. Thus, because of such favorable band structure and BIEF, photoexcited electrons could smoothly transfer from (110) to (111), whereas the holes stay within their respective facets. Such separated pathways could drastically increase the photoexcited charge carrier separation efficiency (37) as demonstrated by Fig. 5C. Moreover, owing to the different barrier height, the large offsets of VB and CB between the (110) and the (111) facets could enhance the driving force for the separation of photoexcited electrons and holes (38). Ni\textsubscript{0.03125}ZCS presented the largest \(\Delta E_{\text{CBM}}\) (\(-0.54\) eV), which is consistent with the most negative CBM as measured (Fig. 4E), indicating its strongest charge separation and hydrogen reduction capability. The \(\Delta E_{\text{CBM}}\) decreased to 0.35 eV for Ni\textsubscript{0.0625}ZCS. For Ni\textsubscript{0.125}ZCS, owing to the increased \(E_{\text{g}}\) of the (111) facets, both the CB and VB of the (110)/(111) interface generate discontinuities, impeding the transfer of both photoexcited electrons from (111) to (110) facets and holes from (110) to (111) facets. Such limited surface heterojunction cannot drive the charge pair separation. The charge carrier separation efficiency was validated by photoluminescence (PL) spectra (fig. S9E) and transient photocurrent (TPC) response. The strong recombination of electrons at the CBM and the holes at VBM produced a broad peak centered at \(-533\) nm. Ni\textsubscript{0.03125}ZCS QDs exhibit the lowest PL peak intensity, implying the most efficient charge carriers separation and transfer. The PL intensity of other QDs follow the sequence Ni\textsubscript{0.015625}ZCS QDs < Ni\textsubscript{0.0625}ZCS QDs < Ni\textsubscript{0.125}ZCS QDs < ZCS QDs < CdS QDs < ZnS QDs, suggesting a suppressed photoexcited charge carrier recombination. The TPC densities show the same trend (fig. S9f). The photocurrent response for Ni\textsubscript{0.03125}ZCS QDs gives the highest current density under intermittent visible-light illumination (fig. S9g), followed by Ni\textsubscript{0.015625}ZCS QDs, Ni\textsubscript{0.0625}ZCS QDs, Ni\textsubscript{0.125}ZCS QDs, ZCS, CdS QDs, and ZnS QDs. The surface charge-transfer efficiencies were measured by electrochemical impedance spectroscopy (EIS) (Fig. 4F). The semicircle diameters follow the sequence Ni\textsubscript{0.03125}ZCS QDs > Ni\textsubscript{0.015625}ZCS QDs > Ni\textsubscript{0.0625}ZCS QDs > Ni\textsubscript{0.125}ZCS QDs, also indicating much lower interfacial charge-transfer resistance of Ni\textsubscript{0.03125}ZCS QDs (table S6). All these results confirmed that doped ZCS QDs, especially the Ni\textsubscript{0.03125}ZCS QDs, show good interfacial charge carrier transfer and superior charge carrier separation ability.
Fig. 5. DFT calculation studies. (A) The calculated electronic band structures of (110) and (111) facets of Ni$_x$ZCS ($x = 0.015625$, 0.03125, 0.0625, and 0.125), CdS, and ZCS. (B) The band structure layouts after accommodation of Fermi levels. (C) Schematic diagram of the BIEF at the interface formed by (110) and (111) facets, contributing a surface heterojunction to reduce the electron-hole recombination. (D and E) Free energy of the hydrogen (H*) adsorption on different Ni, Zn, Cd, and S sites on the surface of (111) (D) and (110) (E) crystal planes of the Ni$_x$ZCS ($x = 0.015625$, 0.03125, 0.0625, and 0.125), CdS, and ZCS.
HER activity. The corresponding free energy change $\Delta G$ from (110) to (111), further enhancing the catalytic activity of the bond order of $\text{H}_2\text{O}$. The bonding nature of $\text{H}_2\text{O}$ on the Ni, Zn, and Cd species of Ni$_{0.03125}$ZCS (110) and (111) facets was further investigated by the projected densities of states (PDOS) (Fig. 6 and Fig. S12). For both (110) and (111) facets, the energy levels of Ni d orbits and $\text{H}_2\text{O}$ 1b$_1$ orbit are matched, leading to partial occupation of the formed d-1b$_1$ orbit (Fig. 6, A and C). The fragment orbit analysis provides more details of the interaction between Ni and $\text{H}_2\text{O}$ (Fig. 6, B and D). It shows that the spin-up Ni d$_z^2$ orbit on the (110) facet (Fig. 6B) and the spin-down Ni d$_x^2$ orbit on the (111) facet (Fig. 6D) can provide large exchange stabilization energy for the 1b$_1$ orbits of $\text{H}_2\text{O}$, forcing $\text{H}_2\text{O}$ to be of radical nature for hydrogenation. The partial 1b$_1$ orbit of $\text{H}_2\text{O}$ was enhanced above the Fermi level, leading to the antibonding orbit and lowering the O—H bonding energy level, which further weakens the H—O bond. Therefore, the more interaction and lower occupation of the 1b$_1$ orbit in $\text{H}_2\text{O}$ show a lower H—O bond order, which is responsible for the lower dissociation barrier than that of $^\dagger\text{H}_2\text{O}$. The crystal orbit overlap population (COOP) analyses (Fig. 6, E and F) also show that under the Fermi level, the Ni d$_z^2$ on the (111) facet presents more overlap population with both O and H to form the bonding feature. Meanwhile, H—O forms the antibonding feature, indicating the radical nature for hydrogenation. The d$_z^2$ orbit of Ni on the (110) facet only generated the bonding feature with O. The H forms the antibonding with Ni d$_z^2$ and H—O still bonds tightly. Obviously, the flatter crystal plane feature of the (111) facet more easily transfers electrons from the Ni d$_z^2$ orbit to the $\text{H}_2\text{O}$ 1b$_1$ orbit, weakening the H—O bond, lowering the bond order in $\text{H}_2\text{O}$, and facilitating the hydrogenation process. For both Zn and Cd, the d orbit mixes the 1b$_2$ orbit of $\text{H}_2\text{O}$ with much lower energy level (Fig. S12, A to D), which could not contribute a large amount of electron transfer from Zn and Cd to $\text{H}_2\text{O}$ (Fig. S12, E, F, H, and I). The corresponding COOP analyses also revealed their limited bonding feature with H and O (Fig. S12, G and J). Therefore, the Ni dispersion in Ni$_{0.03125}$ZCS QDs plays a crucial role in HER.

The triethanolamine (TEOA) interaction with the Ni$_{0.03125}$ZCS (110) and (111) facets was also studied to identify the H$_2$ evolution from TEOA (see Fig. S13). As shown by the charge density difference plots of TEOA adsorption on Ni$_{0.03125}$ZCS (110) and (111) (Fig. S13, B and C), both the (110) and (111) facets demonstrate strong charge transfer between Ni, Cd, and Zn sites with different H sites of TEOA (H$_1$, H$_c$, and H$_2$, which coordinated with O, C$_1$, and C$_2$ of TEOA, respectively, as shown in Fig. S13A). Besides the Ni, Cd, and Zn sites, their coplanarly coordinated S sites on (111) facets or their adjacent and in the same plane S sites on (110) facets also transfer the charge to the TEOA. Such interactions can be verified by the PDOS of Ni, Cd, and S on Ni$_{0.03125}$ZCS (110) and (111) facets together with different H sites of TEOA (H$_0$, H$_c$, and H$_2$, as shown in Fig. S13D, E, D, H, and I). For the bare TEOA, the H$_2$ shows the PDOS near the Fermi level, followed by H$_c$ and H$_0$, respectively (Fig. S13D), indicating their dehydrogenation ability from TEOA. For both (110) and (111) facets, the energy levels of Ni orbits and
Hc₁ and Hc₂ orbits are matched, leading to partial occupation of the formed Ni-Hc₂ and Ni-Hc₁ orbits (fig. S13, D and E). Their corresponding COOP plots (fig. S13, F and G) also show that under the Fermi level, the Ni on both (110) and (111) facets presents overlap population with Hc₁ and Hc₂ to form the bonding feature. In particular, the Ni on (110) facets shows more overlap population with Hc₁ than the one on (111) facets, which could be ascribed to the two unpaired electrons of Ni on (110) facets, contributing to more interaction with the H than that on (111) facets. Relative to Cd, Zn on (110) facets demonstrates the bonding feature with Hc₁ (fig. S13F), which could be ascribed to more matched energy levels of Zn orbits and Hc₁ on (110) facets (fig. S13D), while both Zn and Cd on (111) facets could bond with Hc₁ and Hc₂ (fig. S13G) due to their lower PDOS energy levels, which matches the Hc₂ and Hc₁ energy levels (fig. S13E). Meanwhile, because of the strong charge transfer between TEOA and coplanarly coordinated S sites with metals on (111) facets or in the same plane adjacent S sites to metals on (110) facets (fig. S13, B and C, S_{Ni}, S_{Cd}, and S_{Zn} represent the S coordinated with or adjacent to Ni, Cd, and Zn, respectively), the S PDOS of (110) and (111) facets together with H₂O, Hc₁, and Hc₂ were also

**Fig. 6. Electronic structure analysis.** Projected densities of states (PDOS) and schematic illustrations of 3d orbits of Ni on Ni₀.03125ZCS (110) (A) and (111) (C), 1s, 2s, and 2p orbits of the H₂O molecule, and their interaction within H₂O-Ni configuration. Tot represents the sum of PDOS of each orbits. (B and D) PDOS and schematic illustrations for the H₂O-Ni on Ni₀.03125ZCS (110) (B) and (111) (D) case and charge density differences of H₂O adsorption on Ni₀.03125ZCS (110) and (111) (cyan stands for holes and yellow stands for electrons). (B) and (D) also demonstrated the major interactions and energy levels of the molecular orbits of H₂O on Ni of (110) and (111) facets with correlation to the orbits from Ni and H₂O fragments. (E and F) Crystal orbit overlap population (COOP) for H₂O on Cd and Zn of Ni₀.03125ZCS (110) (A) and (111) (B) models. The balls in green, gray, purple, yellow, red, and white colors represent the Ni, Zn, Cd, S, O, and H atoms, respectively.
and contribute to the \( \text{H}_2 \) evolution. Therefore, the COOP between Ni on the (110) facets generates the strong bonding feature with \( \text{H}_2 \), \( \text{H}_2 \), and \( \text{H}_2 \), while S adjacent to Cd and Zn bonds well with \( \text{H}_2 \) than with \( \text{H}_2 \) and \( \text{H}_2 \). For the coplanarily coordinated S sites on (111) facets, their PDOS are pushed down, showing more matched energy levels with \( \text{H}_2 \). Therefore, it results in more bonding features between S and \( \text{H}_2 \) as shown in their corresponding COOP analyses (fig. S13K). Obviously, the flatter crystal plane feature of the (111) facets more easily transfer electrons to the TEOA orbit, weakening the \( \text{H}_2 \)–\( \text{C}_1 \) bond, lowering the bond order in TEOA, and facilitating the hydrogenation process. Furthermore, we also calculated the adsorption energy of TEOA on \( \text{Ni}_{0.03125} \)\( \text{ZCS} \) (110) and (111) facets. The results show that the adsorption of TEOA on (111) facets is much stronger than that on (110) facets (with the adsorption energy of \(-0.6 \) eV versus \(-0.2 \) eV), and the O–H bonds within TEOA are elongated more evidently on the (111) surface (0.99 Å) compared to that on (110) (0.97 Å). Therefore, the photogenerated holes on (111) facets can be more efficiently consumed by TEOA than on (110). The sequential oxidation of TEOA on (111) facets, induced by photogenerated holes, could produce acetaldehyde and diethanolamine on the basis of the reaction NR\(_2 \) \( \rightarrow \text{CH}_3 \text{CHO} + \text{HNR}_2 , (\text{R} = \text{C}_2 \text{H}_4 \text{OH}, \text{fig. S14A} ) \). (40–42). The COOP between N with \( \text{C}_2 \) of TEOA absorbed on (111) facets demonstrate a much weaker bonding feature compared with the bare TEOA and TEOA absorbed on (110) facets (fig. S14B). Oxidation of acetaldehyde and diethanolamine could produce hydrogen and contribute to the \( \text{H}_2 \) evolution. Therefore, the COOP between \( \text{H} \) sites on acetaldehyde and diethanolamine and Ni, Cd, and Zn on (111) facets were further calculated. It can be seen that there is no readily bonding feature between \( \text{H} \) sites on acetaldehyde with Ni, Cd, and Zn (fig. S14C) and \( \text{H} \) sites on diethanolamine with Zn (fig. S14D), while \( \text{H}_2 \) (H coordinated with Ni of diethanolamine), \( \text{H}_2 \), and \( \text{H}_2 \) form the bonding feature with Cd and Ni (fig. S14, E and F). Here, the systematic evaluation of electronic structures of the \( \text{Ni}_{0.015625} \)\( \text{ZCS} \) QDs actualizes the synergetic integration of photocatalytic constituents into a functional heterostructure to optimize the photocatalytic activity for HER.

**Conclusions**

In summary, we demonstrate a strategy to optimize the atomically dispersed Ni within the zincblende \( \text{Ni}_{x} \)\( \text{ZCS} \) QDs to maximize their efficient and durable photocatalytic performances for water splitting driven by sunlight. The fine-tuned atomically Ni-dispersed \( \text{Ni}_{x} \)\( \text{ZCS} \) QDs achieved an ultrahigh photocatalytic \( \text{H}_2 \) production activity of 18.87 mmol hour\(^{-1}\)g\(^{-1}\). The combination of the experimental investigation and DFT calculations revealed the mechanisms of achieving such high photocatalytic performances. These include (i) the favorable surface engineering of the as-prepared \( \text{Ni}_{0.03125} \)\( \text{ZCS} \) QDs with the highly active sites of monovalent Ni(II) on the (111) facets, (ii) the surface heterojunctions between the anisotropic (110)/(111) interface to reinforce the carrier separation owing to the BIEF, and (iii) appropriate surface \( \text{H}_2 \) adsorption thermodynamics. This work demonstrates a synergistic regulation of the physicochemical properties of QDs at the atomic level toward high-efficiency photocatalytic \( \text{H}_2 \) production. Therefore, the reported approach could provide an effective avenue for optimizing the accurate amount of the introduced heterogeneous elements into the catalysts to simultaneously boost the intrinsic activity, site density, electrical transport, and stability.

**MATERIALS AND METHODS**

**Synthesis of the \( \text{Ni}_{x} \)\( \text{ZCS} \) (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs**

The synthetic procedures for \( \text{Ni}_{x} \)\( \text{ZCS} \) (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs are as follows: the OLA (≥98%, Sigma-Aldrich) was firstly degassed under vacuum at about 100°C for 30 min. After cooling to room temperature, the Ni, Zn, and Cd chlorides (98%, Sigma-Aldrich) and TAA (≥99%, Sigma-Aldrich) were stoichiometrically dispersed in 5 ml of OLA, respectively. Then, Ar was bubbled through the solution for 30 min and followed by heating to certain temperatures (for Ni, Zn, Cd, and S, the temperature are 200°, 230°, 160°, and 90°C, respectively) to form a homogeneous and clear solution. After that, the resulting solutions were injected into a three-necked flask and the mixture was flash-heated to 220°C and aged at that temperature for 30 min, resulting in a colloidal solution. Ethanol (≥99%, Sigma-Aldrich), methanol (≥99.9%, Sigma-Aldrich), and chloroform (≥99.5%, Sigma-Aldrich) (2:1:4 in volume ratio) were added to precipitate the QDs. The precipitate was retrieved by centrifugation and was then redispersed in cyclohexane and subjected to another three rounds of purification. The obtained powders were redispersed easily in nonpolar solvents such as hexane, toluene, and cyclohexane.

**Structural and physical characterization**

The crystal structures and phases of the \( \text{Ni}_{x} \)\( \text{ZCS} \) (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs were examined by powder XRD (Bruker D8 Discover XRD) using Cu \( \text{K}_\alpha \) radiation. The morphology was characterized by FESEM (Zeiss Supra 55VP), and the details of the crystal structure of the \( \text{Ni}_{x} \)\( \text{ZCS} \) (x = 0.015625, 0.03125, 0.0625, and 0.125) QDs were identified by TEM and HRTEM (JEM-2011, JEOL). The images were collected by a Gatan charge-coupled device (CCD) camera in a digital format. Atomic resolved HRTEM images and EDS mapping were obtained by HAADF-STEM (JEM-ARM200F, JEOL) at an accelerating voltage of 200 keV and the Oxford EDS system. The energy resolution at the zero-loss peak was 0.3 eV. The spectra were acquired from thin regions of ~20 to 100 nm. Care was taken to ensure that samples were not damaged by the electron beam by applying liquid-nitrogen cooling. All operation and post-processing of the HAADF-STEM images were conducted by Digital Micrograph software. ICP-MS (Agilent 7500 Series) was used to quantify the elemental composition. EELS spectra were acquired with a Gatan 666 parallel EELS spectrometer attached to the JEM-ARM200F (JEOL) operated at an accelerating voltage of 200 keV. The energy resolution at the zero-loss peak was 0.3 eV. The spectra were acquired from thin regions of ~20 to 100 nm. Care was taken to ensure that samples were not damaged by the electron beam by applying liquid-nitrogen cooling. All operation and post-processing of the HAADF-STEM images were conducted by Digital Micrograph software. The white-line ratio on the EELS profile was calculated from the area under Ni L-edge each peak by eliminating the background intensity via a method suggested by Pearson et al. (43). XPS measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg \( \text{K}_\alpha \) radiation source. UV-vis diffuse reflectance spectra were collected for the dry pressed disk samples with a UV-vis spectrophotometer (LAMBDA 950 UV-vis/near infrared spectrometer, PerkinElmer)
using BaSO$_4$ as the reflectance standard at room temperature. Steady-state PL spectra were tested on a Varian Cary Eclipse fluorescence spectrometer at room temperature. The optical images were collected with a Canon EOS 660D camera. Here, the bandgaps of the samples were calculated by the K-M method on the basis of the UV-vis diffuse absorption spectra by the following equation (44)

$$\text{ahv} = A (\text{hv} - E_g)^{1/2}$$

where $a$, $h$, and $E_g$ are the absorption coefficient, the photon energy, and the direct bandgap, respectively; $A$ is a constant.

**XAFS measurements**

The XAFS spectra were collected at the 1W1B station of the Beijing Synchrotron Radiation Facility (operated at 2.5 GeV with a maximum current of 250 mA, Pt L$_3$-edge). XAFS measurements at the Ni K-edge were performed in fluorescence mode using a Lytle detector. All samples were pelletized as disks of 15-mm diameter with 1-mm thickness using graphite powder as a binder. All spectra were collected in ambient conditions.

**EXAFS analysis**

The acquired EXAFS data were processed by postedge background subtraction from the overall absorption and normalizing with respect to the edge-jump step using the ATHENA module implemented in the FEFFIT (45). Then, $\chi(k)$ data in the $k$-space ranging from 2.6 to 12.6 Å$^{-1}$ were Fourier-transformed to real ($R$) space using Hanning windows ($dk = 1.0$ Å$^{-1}$) to separate the EXAFS contributions from different coordination shells. The quantitative information can be obtained by the least-squares curve fitting in the $R$ space with an FT $k$-space range of 3 to 11.26 Å$^{-1}$. The backscattering amplitude $F(k)$ and phase shift $\Phi(k)$ were calculated using FEFF8.0 code (46).

First-principles scattering amplitudes and phase shifts for the photoelectron path of Ni-S and Ni-Cd(Zn) were calculated using Hartree-Fock “muffin-tin” potential accounting for the screened 1s hole of the absorbing Ni atom (47). To examine the effect of the second and third shells on the determined local structure of the absorbing atom, three series of fits were performed in $R$ space including one, two, and three coordination shells of Ni.

**Ni K-edge XANES spectra simulation within DFT framework**

The projected p state density of electronic states (pDOS) provided by DFT calculation of Ni$_x$S$_y$ ($x = 6, 4$, and $3$) complexes were compared with KXANES spectra since the K-absorption cross section $\sigma(\omega)$ ($\omega$ is the energy of x-ray photons) reflects mainly the energy structure of the empty p states on the absorbing Ni atom according to the dipole selection rule. To validate the application of the DFT method to the structural modeling of Ni$_x$S$_y$ ($x = 6, 4$, and $3$) complexes, their corresponding molecular orbital energy levels were analyzed. The dependence of $\sigma(\omega)$ and pDOS is established according to the Fermi’s Golden rule in the dipole and one electron approximations by the expression: $\sigma(\omega) = C |\langle \Psi_f | V | \Psi_i \rangle|^2 \rho_0(\omega + E_f)$, where $C$ is the constant coefficient, and $\Psi_i$ and $\Psi_f$ are the wave functions of the initial state of Ni atom and the final p symmetrical state with energy $E_f = \omega + E_1$, respectively. $\rho_0(\omega)$ is the pDOS at Ni atom, and $V$ is the operator of dipole transition. It can be seen that the fine structure of $\rho_0(\omega)$ or KXANES is determined mainly by the energy dependence of pDOS on the absorbing atom in assuming of the smooth energy dependence of the matrix element.

**Electrochemical measurement**

The surface charge-transfer efficiencies were investigated by the EIS measurements, which were carried out on a CHI 660C electrochemistry workstation with a standard three-electrode system using the synthesized Ni$_x$ZCS ($x = 0.015625, 0.03125, 0.0625, and 0.125$) QDs coated on F-doped SnO$_2$-coated glass (FTO glass) as the working electrodes, and a Pt wire and Ag/AgCl (saturated KCl) as the counter electrode and reference electrode, respectively. The working electrodes were synthesized as follows: 10 mg of the sample and 1 mg of naphthol (99%, as the binder, Sigma-Aldrich) were dispersed in 10 ml of ethanol. After sonification for several minutes to get the uniformly distributed precipitation solution, 1 ml of solution was dropped onto a 1 cm by 1.5 cm FTO glass electrode via a pipette. The obtained electrode was dried in an oven for 0.5 hours. All working electrodes studied were kept at a similar mass loading of 1 mg. For the TPC density measurement, Na$_2$S and Na$_2$SO$_4$ within the electrolyte worked as hole scavengers rapidly capturing the photoinduced holes on the surface of QDs, which can eliminate the surface charge recombination of QDs. Therefore, the collected TPC density reflects the charge separation efficiency in the bulk of the QD samples. The polarization curves were recorded in the abovementioned three-electrode system and the bias sweep range was from −0.4 to −0.9 V versus SHE with a step size of 0.005 V. The Mott-Schottky plots were also measured by the same three-electrode system using the synthesized Ni$_x$ZCS ($x = 0.015625, 0.03125, 0.0625, and 0.125$) QDs coated on FTO glass as the working electrodes without naphthol binder over an AC frequency of 1200 Hz in 0.5 M Na$_2$SO$_4$ aqueous solution. A 300-W xenon light with an UV-cutoff filter ($\lambda \geq 420$ nm) was applied as the light source.

**The experimental measurements of photocatalysis**

The H$_2$ evolution was characterized in a 50-ml Pyrex flask (sealed with silicone rubber septa) at ambient temperature and atmospheric pressure. Before the experiment, all glassware was rinsed carefully with deionized water. A Xe arc lamp (300 W) with a UV-cutoff filter ($\lambda \geq 420$ nm) was applied as a light source to trigger the photocatalytic reaction. The focused intensity on the flask was ca. 80 mW cm$^{-2}$. In the typical photocatalytic measurement process, 10 mg of photocatalyst was suspended with constant stirring in a mixed solution of TEOA and water (20 volume %, as a sacrificial reagent). Before irradiation, the suspension was sonicated and bubbled with argon gas for half an hour to remove residual and dissolved air and keep the reaction system under anaerobic conditions. During the irradiation process, 0.2 ml of gas was sampled intermittently through the septum, and the H$_2$ content was analyzed by a gas chromatograph (Clarus 480, PerkinElmer, TCD with Ar as a carrier gas and a 5 Å molecular sieve column). For comparison, the CdS QDs, ZnS QDs, and ZCS QDs and the Pt-CdS QDs were also measured for H$_2$ evolution. For loading the cocatalysts, 1 wt % Pt was deposited onto the surface of photocatalysts by the in situ photodeposition approach using H$_2$PtCl$_6$ ($\geq 37.5\%,$ Sigma-Aldrich) under Xe arc lamp (300 W) irradiation for 40 min.

**Theoretical calculations**

DFT calculations were performed using the Vienna Ab initio Simulation Package (48) on the basis of the GGA with the Perdew-Burke-Ernzerhof function as the exchange-correlation energy function. For the bulk crystals of Ni$_x$ZCS ($x = 0.03125, 0.0625$, and $0.125$), $2 \times 2 \times 2$ unit cells (relative to the face-centered cubic (fcc) zinblende
CdS unit cell, 4 Cd and 4 S atoms, respectively] with 64 atoms (with 1, 2, and 4 Ni atom substitution, respectively) were used for the crystal structure and electronic structure calculations. For the Ni$_{x}$ZCS, $4 \times 2 \times 2$ unit cells (relative to the fcc zincblende CdS unit cell, 4 Cd and 4 S atoms, respectively) with 128 atoms (with 1 Ni substitution) were used for the crystal structure and electronic structure calculations. We used the projector augmented wave potentials with 4s and 4p valence states for Cd, 3d, and 3s for Zn and Ni, and 3s and 3p for S with the cutoff energy of 500 eV. The conjugate gradient scheme is used to optimize the atom coordinates until the Hellmann-Feynman force is less than 0.01 eV Å$^{-1}$. The number of k-points was carefully optimized to achieve energy convergence, giving $2 \times 2 \times 2$ and $1 \times 2 \times 2$ Monkhorst-Pack BZ calculations for Ni$_{x}$ZCS ($x = 0.03125, 0.0625$, and 0.125) and Ni$_{0.015625}$ZCS, respectively. The $U$ term was taken into account with the GGA + $U$ approach (49). The $U$ for Ni was fitted to be 5.7 eV. Free energy of different substitutional, interstitial Ni dispersion species as well as the consideration of the S and Cd vacancies in the presence of Ni impurities were calculated on the basis of the energy differences between the Ni-dispersed crystals, for example, Ni$_{0.03125}$ZCS, $4 \times 2 \times 2$ unit cells (relative to the fcc zincblende CdS unit cell, 4 Cd and 4 S atoms, respectively) with 128 atoms (with 1 Ni substitution) were used for the crystal structure and electronic structure calculations. The total energy for the equivalent supercell containing only bulk ZCS.

Reactions for Ni$_{x}$ZCS QDs. Therefore, the final adsorption geometries in the (110) and (111) facets were calculated on the basis of the calculated band structures and the relation between the bandgap ($E_{g}$), work function ($\Phi$), and Fermi level ($E_{F}$): Work function ($\Phi$) = $E_{\text{vacuum}}$ − $E_{F}$.

### Reaction free energy

Three reactions were considered on (110) and (111) facets for evaluating their activities toward the HER and OER:

1. H* adsorption at the cations (M = Ni, Zn, or Cd) or anion (S) sites (i.e., the Volmer reaction)

   $H^+ + e^- + *(M \text{ or } S) \rightarrow H^*(M \text{ or } S)$

2. H$_2$O dissociation with HO* adsorbed at the cation or anion sites

   $H_2O + *(M \text{ or } S) \rightarrow HO^*(M \text{ or } S) + H^* + e^-$

3. H$_2$O dissociation with O* adsorbed at the cation or anion sites

   $H_2O + *(M \text{ or } S) \rightarrow O^*(M \text{ or } S) + 2H^* + 2e^-$

in which * represents an adsorption site on different facets of NixZCS QDs. Therefore, the final adsorption geometries in the above reactions were denoted as H*(M or S), HO*(M or S), and O*(M or S), respectively. The free energy for H* adsorption on each of the active sites of (110) and (111) facets [$\Delta G^i_{\text{H*}}(\text{M or S})$] was calculated according to the following equation with determination of zero-point energy (ZPE) ($\Delta E_{\text{ZPE}}$), entropy ($\Delta S$), and the pH in solution [$\Delta G_{\text{pH}}$] contributions

$$\Delta G^i_{\text{H*}}(\text{M or S}) = \Delta E^i_{\text{H*}}(\text{M or S}) + \Delta E_{\text{ZPE}} - \Delta S - \Delta G_{\text{pH}} + eU$$

where $\Delta E^i_{\text{H*}}(\text{M or S})$ is the adsorption energy of an H* at the M or S site, which can be calculated with

$$\Delta E^i_{\text{H*}}(\text{M or S}) = (E_{\text{H*}} - E_{\text{lab} - \text{OLA}} - n \cdot E_{1/2}/2)/n$$

in which the $E_{\text{lab}}$, $E_{\text{H*}}$, and $E_{1/2}$ are the energies of the slab before and after adsorbing with nH* and an H$_2$ molecule, respectively. $E_{1/2}$ is the energy of hydrogen molecules in the gas phase. As the vibrational entropy of H* in the adsorbed state is small, the entropy of adsorption of 1/2H$_2$ is the entropy of H$_2$ in the gas phase under standard conditions (39). $\Delta G_{\text{pH}} = -kTln(10 \times pH)$, where $T$ is the temperature and $k$ is the Boltzmann constant. $U$ is the potential equivalent to the $E_{\text{CBM}}$, related to the effect of photoexcitation in photocatalysts. Non-Nernstian dependence of the sulfide band edges with a slope of 33 mV pH$^{-1}$ has been considered (52). To determine the possible (110) and (111) surface terminations under the...
photocatalytic conditions, the free energy for reactions (ii) and (iii) was calculated on the basis of the following equations

$$\Delta G_{\text{HO}^*}^{\text{m or s}} = \Delta E_{\text{HO}^*}^{\text{m or s}} + \Delta E_{\text{ZPE}} - n(\Delta S + \Delta G_{\text{H2O}} - eU)$$

$$\Delta G_{\text{O}^*}^{\text{m or s}} = \Delta E_{\text{O}^*}^{\text{m or s}} + \Delta E_{\text{ZPE}} - 2n(\Delta S + \Delta G_{\text{H2O}} - 2eU)$$

where $\Delta E_{\text{HO}^*}$ and $\Delta E_{\text{O}^*}$ are the adsorption energies of HO* and O* on (110) and (111) surfaces, which were calculated as the following equations

$$\Delta E_{\text{HO}^*}^{\text{m or s}} = \left( E_{\text{ads HO}^*} + n \cdot E_{\text{H}/2 - E_{\text{slab}} - n \cdot E_{\text{H2O}}} / n \right)$$

$$\Delta E_{\text{O}^*}^{\text{m or s}} = \left( E_{\text{ads O}^*} + n \cdot E_{\text{H}/2 - E_{\text{slab}} - n \cdot E_{\text{H2O}}} / n \right)$$

$E_{\text{H2O}}$ and $E_{\text{O}^*}$ are the energies of adsorption geometries HO*(m or s) and O*(m or s), respectively. $E_{\text{H2O}}$ is the energy of a H2O molecule.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://advances.sciencemag.org/cgi/content/full/6/33/eaaz8447/DC1

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Acknowledgments

Funding: This original research was supported by the Australia Research Council, Commonwealth of Australia, the Australian Renewable Energy Agency (ARENA), University of Technology Sydney (UTS), through the Discovery Early Career Researcher Award (DECR A DE170101009), ARC Discovery Project (DP170100436), ARENA 2014/RND106, UTS Chancellor’s Postdoctoral Research Fellowship project (PRO16-1893), and UTS Early Career Researcher grant ECRGS PRO16-1304. We also acknowledge the use of the HAADF-STEM facility in the UOW Electron Microscopy Centre. Author contributions: D.W.S. conceived the research and carried out the synthesis, electrochemical tests, characterization, and the DFT calculations. J.R. performed the experimental measurements of photocatalysis. Z.W.Z. and C.C. conducted the x-ray absorption spectroscopy. Y.D.L., S.Z.Q., and G.X.W. discussed the overall research. D.W.S. conceived the project and drafted the manuscript. All authors discussed the experiments and the final manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 14 October 2019
Accepted 2 July 2020
Published 14 August 2020
10.1126/sciadv.aaz8447

Citation: D. W. Su, J. Ran, Z. W. Zhuang, C. Chen, S. Z. Qiao, Y. D. Li, G. X. Wang, Atomically dispersed Ni in cadmium-zinc sulfide quantum dots for high-performance visible-light photocatalytic hydrogen production. Sci. Adv. 6, eaaz8447 (2020).