Collective excitation of plasmon-coupled Au-nanochain boosts photocatalytic hydrogen evolution of semiconductor

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Localized surface plasmon resonance (LSPR) offers a valuable opportunity to improve the efficiency of photocatalysts. However, plasmonic enhancement of photoconversion is still limited, as most of metal-semiconductor building blocks depend on LSPR contribution of isolated metal nanoparticles. In this contribution, the concept of collective excitation of embedded metal nanoparticles is demonstrated as an effective strategy to enhance the utilization of plasmonic energy. The contribution of Au-nanochain to the enhancement of photoconversion is 3.5 times increase in comparison with that of conventional isolated Au nanoparticles. Experimental characterization and theoretical simulation show that strongly coupled plasmonic nanostructure of Au-nanochain give rise to highly intensive electromagnetic field. The enhanced strength of electromagnetic field essentially boosts the formation rate of electron-hole pair in semiconductor, and ultimately improves photocatalytic hydrogen evolution activity of semiconductor photocatalysts. The concept of embedded coupled-metal nanostructure represents a promising strategy for the rational design of high-performance photocatalysts.

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Enhancing the efficiency of semiconductor photocatalysts is of paramount importance for realizing more efficient conversion of solar energy in artificial photosynthesis\textsuperscript{1–3}. Integrating a plasmonic metal nanostructure with a semiconductor has been found as a promising alternative to improve the efficiency of conventional architectures\textsuperscript{4–11}. The enhanced photo-reactivity is attributed to the localized surface plasmon resonances (LSPRs) of plasmonic metal, in which confined free electrons oscillate with the same frequency as the incident radiation, giving rise to intense, highly localized electromagnetic fields\textsuperscript{12–16}. However, plasmonic enhancement of photoconversion is still limited, far from reaching the theoretical maximum efficiency of plasmonic metal–semiconductor\textsuperscript{12,17}. To advance this emerging method, some basic problems, such as the architectures and fabrication strategies of plasmon building blocks, need to be carefully reconsidered.

Three major energy transfer mechanisms between plasmonic metals and semiconductors have been proposed in the past decade: light scattering, hot electron injection, and plasmon-induced resonance energy transfer\textsuperscript{10–18,20}. A big challenge is how to design a plasmonic metal–semiconductor heterostructure for offering great possibility in enabling above three major plasmonic energy transfer mechanisms. Primarily, the proximity of semiconductor to plasmonic metal should be one of important factors to improve the energy transfer. It is not only because the plasmonic hot electrons need an interfacial transfer through overcoming a Schottky barrier, but also the distance could significantly lower the plasmon-induced resonance energy transfer from the metal to the semiconductor\textsuperscript{12,21–23}. The localized electromagnetic fields of plasmonic metal are spatially non-homogenous. The highest intensity is at the surface of the plasmonic metal and decreasing exponentially distance from the surface\textsuperscript{24–26}. Much closer to the plasmonic metal, more electromagnetic fields can be captured. However, most of current researches based on a nanostructure with isolated metal particles dispersed on semiconductor surface. The proximity of semiconductor to the electromagnetic fields of plasmonic metal is limited for such architectures.

In addition, enhancing the local intensity of plasmon-induced electromagnetic fields is another crucial factor for maximizing efficiency of plasmonic metal–semiconductor. We have known that it partly depends on the competence of particle nature, including the composition, size, and shape\textsuperscript{27–31}. While the collective behaviors of dense metal nanoparticles to the plasmonic enhancement is still unclear. Although some physical research show that strongly coupled metallic nanostructures would generate much higher electromagnetic fields at the adjacent spot, what kind of architectures would be effective for the semiconductor photocatalyst systems is still unknown\textsuperscript{32–34}. It should be simultaneously considered the spatial arrangement of semiconductor and plasmonic metals. It would significantly depend on a rational design of plasmonic metal–semiconductor building blocks.

In this contribution, considering both the strength and transfer of plasmonic energy, a plasmonic building block that embedding a strongly plasmon-coupled metal nanostructure is fabricated. Au-nanochain (a strongly plasmon-coupled metal nanostructure) is built into Zn\textsubscript{0.67}Cd\textsubscript{0.33}S semiconductor (denoted as Au-chain@Zn\textsubscript{0.67}Cd\textsubscript{0.33}S, x = 0.67). Visible-light-driven hydrogen evolution rate of Zn\textsubscript{0.67}Cd\textsubscript{0.33}S can be boosted to 16,420 μmol h\textsuperscript{−1} g\textsuperscript{−1} by the Au-nanochain. The apparent quantum efficiency can reach 54.6% at 420 nm. All these results are obtained without additional cocatalysts. The contribution of Au-nanochain to the enhancement of photoconversion is 3.5 times increase in comparison with that of conventional isolated Au nanoparticles. A systematic investigation is carried out to clarify the dependence of the photocatalytic performance on the spatial arrangement of plasmonic metal in the metal–semiconductor building blocks. Both the theoretical simulation and experimental characterization shows that Au-nanochain could give rise to much higher local electromagnetic field than that of isolated Au nanoparticles when excited by the incident light. It essentially increases the formation of the electron–hole pair on the nearby semiconductors and causes a high reactivity. The concept of embedding coupled-metal nanostructure in semiconductors represents an efficient way to enhance the solar energy conversion efficiency.

Results

Preparation and structural analysis of Au-nanochain-containing sample. Au-chain@Zn\textsubscript{x}Cd\textsubscript{1−x}S (x = 0.67) was prepared by a hydrothermal method. Figure 1a illustrates the preparation procedures of the heterostructure from ions. Firstly, L-cysteine solution was mixed with Zn(NO\textsubscript{3})\textsubscript{2} or Cd(NO\textsubscript{3})\textsubscript{2} to form the stable complexes of cysteine-Zn\textsuperscript{2+}/Cd\textsuperscript{2+}. Next, Au colloids with uniform particle size of 15 nm was added to the freshly prepared cysteine-Zn\textsuperscript{2+}/Cd\textsuperscript{2+} solution under vigorous stirring. Finally, the cysteine-Zn\textsuperscript{2+}/Cd\textsuperscript{2+}-coupled Au colloids were transferred into Teflon-lined stainless-steel autoclaves and maintained at 130 °C for 6 h. The Au colloids were prepared by reducing HAuCl\textsubscript{4} with sodium citrate in an aqueous solution (see details in the “Methods” section and Supplementary Figs. 1 and 2). The measured elemental composition of Zn/Cd from inductively coupled plasma (ICP) spectroscopy is closely to the concentration of Zn\textsuperscript{2+}/Cd\textsuperscript{2+} used during the synthesis. Transmission electron microscopy (TEM) image shows the spatial arrangement of Au nanoparticles in Au-chain@Zn\textsubscript{0.67}Cd\textsubscript{0.33}S (Fig. 1b). Au nanoparticles connect with each other forming a chain shape. Some branches can be observed in the image, but all the Au nanoparticles are closely packed. Zn\textsubscript{0.67}Cd\textsubscript{0.33}S grows around the Au-nanochains and wrapped them completely. No porous structure can be found in the images. High-resolution transmission electron microscopy (HRTEM) image (Fig. 1c), clearly shows the fringe of 0.24 nm, which is ascribed to the face-centered cubic (fcc) Au (111). While another set of lattices with periodic spacing of 0.31 nm are assigned to cubic Zn\textsubscript{0.67}Cd\textsubscript{0.33}S (101) lattice planes. Two sets of reflections can be observed in selected area electron diffraction (SAED) patterns (Fig. 1b inset). High-angle annular dark-field (HAADF) image and energy-dispersive X-ray spectroscopy (EDXS) mapping images (Fig. 1d), could also clearly depict the arrangement of Au nanoparticles, while Zn, Cd, and S are homogeneously distributed on Au-chain@Zn\textsubscript{0.67}Cd\textsubscript{0.33}S.

Theoretical simulation. Three-dimensional finite difference time domain (FDTD) method is used to simulate the near-field distributions of isolated and coupled nanoparticles (Fig. 1e and Supplementary Figs. 3–5). The total field scattered field (TF/SSF) source is used in simulation. The incident wavelength is 520 nm. The grid spacing is 0.5 nm. The radius of gold nanoparticle is 7.5 nm. Figure 1e shows the electric field distributions of Au nanoparticles with different interparticle distances. When distance decrease from 20 to 2 nm, the strength of electromagnetic fields increase at least one order of magnitudes at hot spot area. It demonstrates that Au-nanochain can give rise to highly intense and localized electromagnetic fields when excited by incident light of the appropriate polarization.

Photocatalytic performance. Photocatalytic test of Au-chain@Zn\textsubscript{0.67}Cd\textsubscript{0.33}S under visible light (≥420 nm) gives an activity of 16,420 μmol h\textsuperscript{−1} g\textsuperscript{−1} for hydrogen evolution (Fig. 1d). It is about 20 times of commercial CdS (830 μmol h\textsuperscript{−1} g\textsuperscript{−1}) and 3.3 times of pure Zn\textsubscript{0.67}Cd\textsubscript{0.33}S (5020 μmol h\textsuperscript{−1} g\textsuperscript{−1}) prepared with the same method as Au-chain@Zn\textsubscript{0.67}Cd\textsubscript{0.33}S. It should be
noted that all these catalytic results are obtained in the absence of any additional metal or metal oxide as a cocatalyst on the surface of semiconductor. Under the optimized reaction conditions, the apparent quantum efficiency of Au-chain@Zn0.67Cd0.33S can even reach to 54.6% under 420 nm illumination (Supplementary Fig. 6). This efficiency is obviously higher than most of literature results, and keeps leading in the tests free of cocatalysts (Supplementary Table 1). The high efficiency should attribute to the strongly coupled nanostructure of Au-nanochain embedded into the semiconductor.

**Influence of the spatial arrangement of plasmonic metals.** For systematic investigation of the dependence of the photocatalytic performance on the spatial arrangement of plasmonic Au, two other samples Au-iso@Zn0.67Cd0.33S (Au nanoparticles separately embedded into Zn0.67Cd0.33S, see Supplementary method and Supplementary Figs. 7 and 8) and Au-surf@Zn0.67Cd0.33S (Au nanoparticles post loaded on the surface of Zn0.67Cd0.33S, Supplementary method and Supplementary Figs. 7 and 9) were also prepared. Au-iso@Zn0.67Cd0.33S and pure Zn0.67Cd0.33S were prepared with a hydrothermal method, which is the same as Au-chain@Zn0.67Cd0.33S. Figure 2a shows the X-ray diffraction (XRD) patterns of Au-chain@Zn0.67Cd0.33S, Au-iso@Zn0.67Cd0.33S, Au-surf@Zn0.67Cd0.33S as well as pure Zn0.67Cd0.33S. All the samples exhibit six diffraction peaks at 2θ = 25.1°, 26.8°, 28.4°, 44.0°, 48.1°, and 52.1°, which can be assigned to (100), (002), (101), (110), (103), and (112) planes of hexagonal wurtzite Zn0.67Cd0.33S (ICPDS No. 40-0835)\(^3\). The diffraction peaks of Au nanoparticles cannot be detected in the XRD patterns, due to the low concentration and the highly dispersed state of Au nanoparticles in the samples. N\(_2\)-adsorption results (Table 1) show that the specific surface areas of three Au-containing samples are all at about 40 m\(^2\) g\(^{-1}\), which is just a little higher than that of pure Zn0.67Cd0.33S (36.1 m\(^2\) g\(^{-1}\)). The isotherms (Supplementary Fig. 10) shows that all these samples are non-porous materials, which is consistent with that of TEM results.

Figure 2b, c shows the X-ray photoelectron spectroscopy (XPS) of Au-chain@Zn0.67Cd0.33S, Au-iso@Zn0.67Cd0.33S, Au-surf@Zn0.67Cd0.33S, and pure Zn0.67Cd0.33S. All these four samples exhibit similar surface chemical state of Cd and Zn. The surface Zn/Cd ratios of these samples are all close to 2.0 (Table 1), which is just a little higher than their values in the bulk. It should be noted that no signal of Au can be detected on the surface of Au-chain@Zn0.67Cd0.33S, Au-iso@Zn0.67Cd0.33S, and Au-surf@Zn0.67Cd0.33S (Table 1 and Supplementary Fig. 11), confirming that Au nanoparticles in these two samples are embedded completely into the Zn0.67Cd0.33S semiconductor.

Figure 3a shows the Raman spectroscopy of Au-chain@Zn0.67Cd0.33S, Au-iso@Zn0.67Cd0.33S, and pure Zn0.67Cd0.33S. Two typical Raman scattering peaks of wurtzite Zn0.67Cd0.33S can be observed in the spectroscopy, which are the first (ILO) and second (2LO) band of longitudinal optical (LO) phonon modes at 295 and 598 cm\(^{-1}\), respectively\(^3\). The intensity of Raman signals follows the order of Au-chain@Zn0.67Cd0.33S > Au-iso@Zn0.67Cd0.33S > Au-surf@Zn0.67Cd0.33S > Zn0.67Cd0.33S.
According to the principle of surface-enhanced Raman spectroscopy (SERS), the enhancement of signals relies on the received plasmon-induced local electromagnetic field from metal nanostructures. XRD and XPS have shown that Zn_{0.67}Cd_{0.33}S in all these samples possess nearly the same structure and surface properties. So, compared with pure Zn_{0.67}Cd_{0.33}S, the enhancement of Raman signals in Au-containing samples should be ascribed to the plasmon-induced local electromagnetic field of Au nanostructures. The field received by Zn_{0.67}Cd_{0.33}S follows the order of embedded Au nanochain > embedded Au nanoparticles > surface Au nanoparticles. UV–vis spectra further confirm above results (Fig. 3b). In comparison with pure Zn_{0.67}Cd_{0.33}S, Au-containing samples show a red shift of absorption edge, which are due to the influence of LSPRs from Au nanostructure. This shift originates from the change of optical properties of Zn_{0.67}Cd_{0.33}S affected by the electromagnetic effect of Au LSPR, while not a simple addition of absorption of Zn_{0.67}Cd_{0.33}S and Au LSPR. Both Raman and UV–vis results provide the experimental evidences that embedded Au-nanochain has greatest impact on the excitation of Zn_{0.67}Cd_{0.33}S. It should originate from the electromagnetic properties of interacting Au nanoparticles in close mutual proximity. In brief, the interaction energy can be described with $V \propto \frac{p_1p_2}{r^3}$, where $p_1$ and $p_2$ are the magnitudes of the dipole moments and $r$ is the inter particle distance. This interaction energy is considerably stronger in the case of nearly adjacent Au nanoparticles.

### Table 1 Texture properties and the atom contents on the surface of various samples

| Samples                  | $S_{BET}$ (m² g⁻¹) | XPS spectra results |
|--------------------------|--------------------|---------------------|
|                          |                    | Zn (at.%)           |
|                          |                    | Cd (at.%)           |
|                          |                    | Au (at.%)           |
| Zn_{0.67}Cd_{0.33}S     | 36.1               | 30.89               |
| Au-surf@Zn_{0.67}Cd_{0.33}S | 40.1           | 30.47               |
| Au-iso@Zn_{0.67}Cd_{0.33}S | 41.3           | 31.26               |
| Au-chain@Zn_{0.67}Cd_{0.33}S | 40.9           | 31.72               |
| Zn_{0.67}Cd_{0.33}S     | 30.89               | 15.45               |
| Au-surf@Zn_{0.67}Cd_{0.33}S | 31.26           | 15.72               |
| Au-iso@Zn_{0.67}Cd_{0.33}S | 30.47           | 14.87               |
| Au-chain@Zn_{0.67}Cd_{0.33}S | 31.72           | 15.81               |
| Zn_{0.67}Cd_{0.33}S     | 0                  | 0.14                |
| Au-surf@Zn_{0.67}Cd_{0.33}S | 0                | 0.14                |
| Au-iso@Zn_{0.67}Cd_{0.33}S | 0                | 0.14                |
| Au-chain@Zn_{0.67}Cd_{0.33}S | 0                | 0.14                |

According to the principle of surface-enhanced Raman spectroscopy (SERS), the enhancement of signals relies on the received plasmon-induced local electromagnetic field from metal nanostructures. XRD and XPS have shown that Zn_{0.67}Cd_{0.33}S in all these samples possess nearly the same structure and surface properties. So, compared with pure Zn_{0.67}Cd_{0.33}S, the enhancement of Raman signals in Au-containing samples should be ascribed to the plasmon-induced local electromagnetic field of Au nanostructures. The field received by Zn_{0.67}Cd_{0.33}S follows the order of embedded Au nanochain > embedded Au nanoparticles > surface Au nanoparticles. UV–vis spectra further confirm above results (Fig. 3b). In comparison with pure Zn_{0.67}Cd_{0.33}S, Au-containing samples show a red shift of absorption edge, which are due to the influence of LSPRs from Au nanostructure. This shift originates from the change of optical properties of Zn_{0.67}Cd_{0.33}S affected by the electromagnetic effect of Au LSPR, while not a simple addition of absorption of Zn_{0.67}Cd_{0.33}S and Au LSPR. Both Raman and UV–vis results provide the experimental evidences that embedded Au-nanochain has greatest impact on the excitation of Zn_{0.67}Cd_{0.33}S. It should originate from the electromagnetic properties of interacting Au nanoparticles in close mutual proximity. In brief, the interaction energy can be described with $V \propto \frac{p_1p_2}{r^3}$, where $p_1$ and $p_2$ are the magnitudes of the dipole moments and $r$ is the inter particle distance. This interaction energy is considerably stronger in the case of nearly adjacent Au nanoparticles. FDTD simulations shown in Figs. 1c and 3c further match the change of spectroscopy observed experimentally. The adjacent nanoparticle pairs showing a hot spot in the junction for incident polarization along the interparticle axis, where the strength of electromagnetic field at least one order of magnitudes in comparison with that of isolated particles.
The enhancement of photocatalytic hydrogen evolution activity depended on the spatial arrangement of plasmonic Au nanostructure is shown in Fig. 4a. Compared with pure Zn$_{0.67}$Cd$_{0.33}$S (5020 μmol h$^{-1}$ g$^{-1}$), Au-surf@Zn$_{0.67}$Cd$_{0.33}$S and Au-iso@Zn$_{0.67}$Cd$_{0.33}$S enhance this activity to 8290 and 11,560 μmol h$^{-1}$ g$^{-1}$, respectively. The difference of these two samples is that isolated Au nanoparticles loaded on the surface for Au-surf@Zn$_{0.67}$Cd$_{0.33}$S and embedded in the body for Au-iso@Zn$_{0.67}$Cd$_{0.33}$S. The different enhancement of photocatalytic activity is mainly due to the the proximity of Zn$_{0.67}$Cd$_{0.33}$S to the electromagnetic field of plasmonic Au (Fig. 4b). Embedded structure facilitates the transfer of plasmonic energy from Au nanoparticle to the nearby Zn$_{0.67}$Cd$_{0.33}$S semiconductor. All these activities are much lower than that of Au-chain@Zn$_{0.67}$Cd$_{0.33}$S (16420 μmol h$^{-1}$ g$^{-1}$). The contribution of Au-nanochain to the enhancement of photoconversion is about 3.5 times increase in comparison with that of isolated Au nanoparticles. Under the similar reaction conditions, the apparent quantum yield is 14.2%, 28.7%, and 43.5% for these four samples, respectively (Supplementary Fig. 6). The enhancements of these apparent quantum yields are consistent with the H$_2$ evolution rate. The intensity and proximity of electromagnetic fields essentially affect the rate of e$^–$/h$^+$ formation in the Zn$_{0.67}$Cd$_{0.33}$S semiconductor. Figure 4c shows the photoluminescence (PL) spectra of above four photocatalysts. It is known that photoexcited electron and hole recombine each other through several processes, such as direct band-to-band coupling and/or shallowly/deeply trapped potential states$^{40-42}$. The intensity of the spectra can reflect the amount of electrons recombined with holes under emission of photons. It can be observed that Au nanochain significantly improves the emission signal of Zn$_{0.67}$Cd$_{0.33}$S, followed by isolated Au nanoparticles. Time-resolved PL measurements (Fig. 4d) show that the intensity of Au-chain@Zn$_{0.67}$Cd$_{0.33}$S decays much more slowly than that of other composite photocatalysts, and pure Zn$_{0.67}$Cd$_{0.33}$S, indicating a longer lifetime of electron–hole pairs in Au-chain@Zn$_{0.67}$Cd$_{0.33}$S. This longer lifetime should be correlated with both the increasing amount of electron–hole pairs and the presence of surfa-trapped states. Fitting results of Cd 3d XPS spectra show that there are certain amount of Cd species with low valent states on the surface of these four samples (Supplementary Fig. 16). Our previous work have shown that these Cd species act as the trap sites for photo-excited electrons and active sites for hydrogen evolution$^{40,41}$. In this case, a broad emission signal in the range of 450–650 nm can be observed. No obvious shift among the signals
of these samples should be mainly due to the similar crystal structure and surface properties of Zn$_{0.67}$Cd$_{0.33}$S semiconductor in these four samples. This broad emission peak indicates the presence of multiple radiation processes of excited electrons, including the emission from the band edge and the surface-trapped states. These trapped sites could play a more important role in sample of Au-chain@Zn$_{0.67}$Cd$_{0.33}$S. With the increase of electron–hole pairs formation, much more electrons could be trapped by these sites and effectively extend the lifetime of electron–hole pairs.

Discussion
The Au nanoparticles in Au-iso@Zn$_{0.67}$Cd$_{0.33}$S and Au-chain@Zn$_{0.67}$Cd$_{0.33}$S are wrapped well by Zn$_{0.67}$Cd$_{0.33}$S semiconductor. Little porous structure can be detected in these samples. So, the role of Au nanoparticles as a cocatalyst can be excluded. All the enhancements can be ascribed to the plasmonic effect of Au nanoparticles in the metal–semiconductor building blocks. In addition, the Au nanoparticles are protected by citric acid groups in the colloids aqueous solution and coupled with L-cysteine during the hydrothermal synthesis. There should be a non-conductive organic layer between Au nanoparticle and sulphide compound. It can be preliminarily verified by FT-IR measurement (Supplementary Fig. 17). This structure is suitable for the energy transfer from plasmonic Au to the semiconductor and could avoid the quenching of charge carriers on the surface of Au nanoparticles.

Combining all the above results, it can be concluded that the proximity and the spatial arrangement of plasmonic Au are two important factors affecting the photocatalytic performance. Firstly, the structure of embedding Au into the body of semiconductor effectively improves the proximity, facilitating the transfer and maximizing the use of electromagnetic energy from plasmonic Au to semiconductor (Fig. 4b). As for the isolated Au nanoparticle, theoretical simulation reported by Thomann et al. over 50 nm Au nanoparticles showed that the strength of electromagnetic field vary little whether the nanoparticle locates on the top or the bottom of the semiconductor. So, shorter distance between the semiconductor and plasmonic Au could realize more energy transfer. Secondly, the strongly coupled nanostructure of Au nanochain shows stronger capability of improving local electromagnetic energy field. The collective excitation of plasmonic metal facilitate much more plasmonic energy transfer from metal to the semiconductor. This energy enhances the formation rate and lifetime of e$^-$/h$^+$ pairs. Combined with quantum efficiency and stability measurements, it can further confirm that the coupled metal nanoparticles lead to an increase in lifetime of photo-excited electron–hole pairs. The significant enhancement of photocatalytic activity should origin from the collective behavior of these coupled metal nanoparticles, which is quite different from simple plasmonic effect of the isolated one. All these results show that embedding the plasmon-coupled metal nanostructure into semiconductor would be an effective strategy to fully take advantage of plasmonic energy.
It is known that Au nanochain is only one simple nanostructure with plasmon-enhancement effect. Considering a great deal of coupled metallic nanostructures has been reported in physics and nanoscience area, embedding different kinds of coupled nanostructure into semiconductor could further optimize the efficiency of photocatalysts. In addition, recombination of photoexcited electron–hole pairs is present in all semiconductor materials. Considering this recombination, the Au nanoparticle closer to the surface could favorize more charge carriers been utilized. Therefore, there should be an optimized depth of Au nanoparticle due to the balance of energy utilization (electron–hole pair formation) and charge carriers recombination. It correlates with both the nature of semiconductors and their crystallizations. Further work is still needed on the investigation of various kinds of coupled plasmonic metal nanostructure and optimizing the placement of these metal nanoparticles in the semiconductors.

In summary, Au-nanochain with strongly coupled plasmonic nanostructure was demonstrated to be an effective building block to enhance the photocatalytic performance of nearby semiconductor. The characteristic structure possesses junction or short distance between adjacent nanoparticles, which gives rise to highly intense and localized electromagnetic fields. The embedded structure facilitates the nearby semiconductor to capture the strong field. The maximum control and utilization of this electromagnetic field significantly improve the formation of electron–hole pairs in the semiconductor photocatalysts, and ultimately enhance photocatalytic hydrogen evolution. The construction of coupled-metal nanostructures within the semiconductors represents an efficient way to enhance the solar energy conversion efficiency.

Methods
All chemicals were analytic grade reagents and used without further purification. Purified water was used in all of the experiments.

Preparation of Au colloids.
Au colloids were prepared by a sodium citrate reduction method. Typically, an aqueous solution of HAuCl4 (0.25 mM, 100 mL) was heated to boiling, followed by the rapid addition of sodium citrate solution (0.5 M, 200 μL). The solution was kept boiling for another 15 min, producing a stable deep-red dispersion of Au nanoparticles with an average diameter of about 15 nm (see in Supplementary Fig. 1). The citrate-protected Au-colloids suspension (denoted as Au-Cit) was then cooled to room temperature for next use.

Preparation of Au nanochain embedded into Zn0.67Cd0.33S (denoted as Au-chain@Zn0.67Cd0.33S). Au-chain@Zn0.67Cd0.33S was prepared using a cysteine-assisted hydrothermal approach. Briefly, 100 mL L-cysteine solution (Cys, 60 mM) was mixed with Zn(NO3)2 and Cd(NO3)2 in a 1:0.3 molar ratio of Cys to Zn2+/Cd2+. The mixture was stirred for 30 min to form the stable complexes of cysteine-Zn2+/Cd2+. Then Au-Cit colloids (0.25 mM, 1 mL) was added to the freshly prepared cysteine-Zn2+/Cd2+ solution under vigorous stirring for 30 min, leading to a complete coupling between amine group of Cys and Au nanoparticles surface. Subsequently, the cysteine-Zn2+/Cd2+–coupled Au colloids were diluted to a total volume of 70 mL with deionized water and transferred into 100 mL Teflon-lined stainless-steel autoclaves. The autoclaves were maintained at 130 °C for 6 h and then cooled to room temperature naturally. The products were filtered and a photodiode was used in measurement.

Preparation of Au nanochain embedded into Zn0.67Cd0.33S (denoted as Au-chain@Zn0.67Cd0.33S). The number of reacted electrons

\[
\text{AQE}\% = \frac{\text{Number of reacted electrons}}{\text{Total number of incident photons}} \times 100 \tag{1}
\]

\[
\text{AQE}\% = \frac{2 \times \text{The number of evolved H}_2 \text{molecules}}{\text{Total number of incident photons}} \times 100 \tag{2}
\]

Data availability
The data that support the findings of this study are available within the article and its Supplementary Information, and all data are available from the corresponding authors upon request.

Received: 10 May 2019; Accepted: 6 October 2019; Published online: 29 October 2019

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