Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting

Mohammad Reza Gholipour,a Cao-Thang Dinh,a François Bélandb and Trong-On Do*a

Hydrogen production via photocatalytic water splitting using sunlight has enormous potential in solving the worldwide energy and environmental crisis. The key challenge in this process is to develop efficient photocatalysts which must satisfy several criteria such as high chemical and photochemical stability, effective charge separation and strong sunlight absorption. The combination of different semiconductors to create composite materials offers a promising way to achieve efficient photocatalysts because doing so can improve the charge separation, light absorption and stability of the photocatalysts. In this review article, we summarized the most recent studies on semiconductor composites for hydrogen production under visible light irradiation. After a general introduction about the photocatalysis phenomenon, typical heterojunctions of widely studied heterogeneous semiconductors, including titanium dioxide, cadmium sulfide and graphitic carbon nitride are discussed in detail.

1. Introduction

Nowadays, fossil fuels play an important role in human life and provide for worldwide energy demands because of their low cost and availability. They are formed from prehistoric fossils over hundreds of years and are no longer available once used. Moreover, the combustion of these fossil fuels produces large quantities of air pollution gases such as nitrogen oxides, sulfur oxides and carbon oxides annually, which cause severe health problems for humans and global climate change. Finding renewable, clean and carbon-neutral alternative energy sources is thus urgently needed.

Among various available renewable energy sources, solar energy is by far the most abundant one. It is estimated that...
around 0.01% of the energy of one second of sunlight irradiation is sufficient for the annual energy consumption of human society.\textsuperscript{1,2} However, a significant challenge is to put this kind of energy into use and store it for later application. One of the promising ways is using hydrogen as an energy carrier in order to store solar energy in the form of the chemical bond between two atoms of hydrogen. This hydrogen molecule can then react with oxygen in the air to release its energy and produce water as a by-product, which is totally clean for the environment.

Water is the most plentiful supply of hydrogen that can be used to produce hydrogen via photocatalytic water splitting. Thus, hydrogen production by means of a photocatalyst, solar energy and water has noticeably attracted attention in recent decades. This technology is clean because it uses photon energy and water. Besides this, it doesn't produce any dangerous by-products or pollutants. Therefore, the photocatalysis process is expected to make a great contribution to energy and environmental challenges in the near future.

The most challenging task in photocatalytic water splitting is to develop efficient photocatalysts which are capable of absorbing sunlight to split water. In general, photocatalysis involves three processes: the excitation, bulk diffusion and surface transfer of photoinduced charge carriers. Thus, an efficient photocatalyst must satisfy several critical requirements related to its semiconducting and chemical properties, its crystalline structure and surface characteristics. However, there are always inherent deficiencies in the semiconductors, and it is very difficult to find a single component that can address all of these requirements. Thus, although many different semiconductors for water splitting have been developed in the last few decades, most of them are activated under UV light and need sacrificial reagents to produce hydrogen from water. It seems that a single-component photocatalyst, even with cocatalysts, cannot obtain a desirable quantum efficiency.

A semiconductor/semiconductor heterojunction, formed by the direct contact of two semiconductors, represents an effective architecture for overcoming the limit of single-component photocatalysts. When two semiconductors with suitable band edge positions are combined, the charge transfer between them can increase the lifetime of the charge carriers, thus promoting the photocatalytic process. In addition, when the band gap of the coupled semiconductor is small, the energy range of photo-excitation for the system is also extended. In this review paper, we summarize various nanocomposite photocatalysts which were active for hydrogen production under visible light illumination.

2. Fundamentals of photocatalytic water splitting

Fujishima and Honda were pioneers in decomposing water with light illumination.\textsuperscript{3} They discovered that TiO\textsubscript{2} and Pt can act as the anode and cathode electrodes, respectively, in a photoelectrochemical cell. This system could split water into hydrogen and oxygen under intense UV irradiation. Some years later, Bard applied the concept of this system to introduce a photocatalysis process.\textsuperscript{4} Since then, there have been enormous efforts in developing semiconductors that can decompose water into H\textsubscript{2} and O\textsubscript{2} under illumination with light.

Generally, photocatalytic water splitting with sunlight consists of three main steps: (I) a semiconductor absorbs light photons and generates excited electrons and holes; (II) these

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excited electrons and holes can migrate to the surface of the semiconductor or recombine again inside the bulk material; (III) on the surface, holes can oxidize water to O₂ (eqn (1)) and electrons can reduce protons to H₂ (eqn (2)). Fig. 1 illustrates schematically the main steps in water splitting.

\[
\text{H}_2\text{O} + 2h^+ \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ \quad (1)
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (2)
\]

The semiconductor band gap determines which wavelength of sunlight can be absorbed. A semiconductor with a wide band gap (\(E_{bg} > 3\) eV) can only absorb UV light, which approximately accounts for 5% of solar energy. In contrast, a narrow band gap semiconductor (\(E_{bg} < 3\) eV) can be activated by visible light irradiation, which constitutes 43% of the sunlight spectrum. Besides the band gap, the positions of the valence and conduction bands are also very important in photocatalytic water splitting. For H₂ evolution, the conduction-band edge should be more negative than the reduction potential of H⁺ to H₂ (\(E_{H^+/H_2} = 0\) V vs. NHE at pH = 0). On the other hand, the valence-band edge should be more positive than the oxidation potential of water (\(E_{O_2/H_2O} = 1.23\) V vs. NHE at pH = 0) in order to evolve oxygen. Therefore, the band gap of the semiconductor should be at least 1.23 eV in order to split the water. The equivalent light wavelength for this band gap energy is 1100 nm, which is in the near-infrared region of the sunlight spectrum. By considering other factors such as energy losses during different stages in the photocatalytic process, effective semiconductors should have band gaps greater than 2 eV, which is related to light with wavelength less than 620 nm.⁷⁻¹⁶ Although some semiconductors can absorb infrared light by a photon up-conversion mechanism, their applications are usually limited to the degradation of organic compounds.⁷⁻¹⁰

2.1. Overall water splitting

The decomposition of water directly into hydrogen and oxygen under sunlight irradiation is the ultimate goal of a photocatalytic hydrogen generation system. In this process, a semiconductor with proper band-edges can absorb photon energy and evolve hydrogen and oxygen simultaneously. However, this reaction is thermodynamically non-spontaneous, with a Gibbs free energy of 237 kJ mol⁻¹.¹¹

\[
2\text{H}_2\text{O} \xrightarrow{\text{photon energy}} 2\text{H}_2 + \text{O}_2 \quad (3)
\]

Some semiconductors can absorb UV light and split water directly into hydrogen and oxygen, but most of them have an energy conversion efficiency of less than 1%.¹²⁻¹⁴ Moreover, they cannot produce hydrogen and oxygen in a stoichiometric ratio because one type of charge carrier is accumulated on the surface of the photocatalyst.¹⁵ One exceptional example is a GaN–ZnO solid solution photocatalyst that can split water into hydrogen and oxygen stoichiometrically under visible light illumination with a quantum efficiency of about 6%.¹⁵ It is obvious that overall water splitting is very difficult to carry out under visible light illumination and has become one of the greatest challenges for researchers in this field.

2.2. Sacrificial reagent systems

As discussed earlier, overall water splitting is a very hard reaction to carry out, and it needs a specific kind of semiconductor with appropriate band edge positions. Nevertheless, some semiconductors can do one of the half reactions of water splitting, i.e. water reduction or oxidation, in the presence of suitable sacrificial reagents (electron donors or acceptors). In principle, sacrificial agents usually react with one type of charge carrier while the other carrier reacts with water to produce hydrogen or oxygen. Electron donors, which consume excited holes on the surface of the semiconductor, are used for the water reduction half reaction and electron acceptors (electron scavengers) are usually needed for water oxidation, as illustrated in Fig. 2. Generally, the electron donors must be more readily oxidized than water by excited holes, while the electron acceptors must be more readily reduced than water by excited electrons. The most common electron donors are methanol, ethanol, triethanolamine (TEA) and an aqueous

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Fig. 2 Schematic of the principles of water reduction or oxidation in the presence of sacrificial reagents.
solution of Na₂S–Na₂SO₃, whereas metal cations such as Ag⁺ and Fe³⁺ are usually utilized as electron acceptors.¹¹

Various mechanisms have been proposed to explain the consumption of sacrificial reagents in hydrogen production reactions.¹⁴,¹⁶ These electron donors react more easily with holes than water due to its less positive oxidation potential. This would lead to accelerated hole consumption on the surface of the photocatalyst and so the positive charge accumulation is partially prevented and, as a result, protons and photoexcited electrons can react together more easily. It should be noted that, in the case of using methanol as the electron donor, hydrogen is also produced from water as a result of methanol conversion (eqn (4)).¹⁷,¹⁸ However, by increasing the carbon chain, the contribution to H₂ production from alcohol conversions decreases substantially.¹⁸ Moreover, Guzman showed that the direct reaction of methanol with holes does not proceed to an appreciable extent in the presence of a high concentration of water.¹⁹

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2
\]  

(4)

Semiconductors capable of decomposing water in the presence of sacrificial agents may seem to be useless. Nevertheless, these photocatalysts can not only be used in the Z-schematic system but also some of them can be used to produce H₂ using biomass-derived sacrificial reagents.²⁰,²¹

### 2.3. Electron mediator systems

The electron mediator system is also called the Z-scheme system or a dual photocatalyst system. The concept of this system is to transfer charge carriers using two different electron mediators in a solution; after participating in redox reactions, they all return to their original chemical states.²² This procedure for overall water splitting is entirely different to the two previous methods. It needs two different photocatalysts: a semiconductor providing photoexcited electrons to participate in the half-reaction for H₂ evolution and another one supplying photogenerated holes to take part in the half-reaction of water oxidation. Moreover, two semiconductors could be excited simultaneously and one half of the charge carrier will recombine in order to bring the electron mediators to their original states (Fig. 3). Some of the most common electron mediators are Fe³⁺/Fe²⁺, IO³⁻/I⁻ and Ce⁴⁺/Ce³⁺.²³

There are some review papers discussing different approaches and applications of this dual-step system, which is similar to plant photosynthesis.²⁴,²⁵ Nonetheless, this system has some drawbacks in comparison to the one-step system. For instance, Z-scheme systems are usually more complicated and need more photons to produce the same amount of hydrogen because half of the excited charges are used in order to bring the excited mediator to its ground state for further reactions.²²,²⁶

### 2.4. Activity and quantum efficiency

Photocatalytic activity depends on many factors such as the light source (Xe or Hg lamps), light intensity, reaction cell, different directions of irradiation (top, inner, or side), reaction media (water or various sacrificial agents), and the quantity of the photocatalyst. The simplest way to find the semiconductor activity is to measure the amount of evolved gases in a specific period of time and report it in µmol h⁻¹ or µmol g⁻¹ units.²³

Quantum yield (quantum efficiency) is another way to report the photocatalytic activity of a semiconductor. This is independent of the affecting factors that are mentioned above and is defined as:²⁷

\[
\text{Quantum yield (％)} = \frac{\text{Number of reacted electrons}}{\text{Number of absorbed photons}} \times 100
\]

(5)

Despite the fact that this equation can give us the accurate quantum yield, it is very hard to measure the real number of absorbed photons. In order to solve this problem, researchers have suggested using the apparent quantum yield, which is defined as follows:²³

\[
\text{Apparent quantum yield (％)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100
\]

(6)

It is obvious that the apparent quantum yield is smaller than the real quantum efficiency because of the difference between the number of absorbed photons and incident light.

Solar energy conversion efficiency is a method to calculate solar cell efficiency. It can also be used to report the photocatalytic activity of a semiconductor.

\[
\text{Solar energy conversion efficiency (％)} = \frac{\text{Output energy of H}_2 \text{ evolved}}{\text{Energy of incident solar light}} \times 100
\]

(7)

Up to now, semiconductors have had extremely low solar energy conversion values and so this indicator is seldom used.¹² It is anticipated that for industrial application of water splitting via sunlight, this efficiency should be noticeably improved.
There have been great efforts to use different types of cocatalysts including transition metals, metal oxides and noble metals for each half reaction of water splitting. The most common cocatalysts for hydrogen evolution are Pt, Rh, Au, NiO\textsuperscript{34} and RuO\textsubscript{2}\textsuperscript{34,35–39} Other types, such as a core–shell configuration of the cocatalysts, have been recently proposed to improve H\textsubscript{2} evolution in overall water splitting.\textsuperscript{33,40} Although cocatalysts are an important part of the photocatalytic system, in this review we only focus on different nanocomposites of semiconductors that are active under visible light illumination.

3. Nanocomposites for visible-light-driven photocatalytic hydrogen production

It has been proven that some semiconductor properties such as specific surface area, particle size, crystallinity, crystalline phase and morphology have considerable effect on photocatalytic activity.\textsuperscript{31} Charge recombination centers are some kind of defect (in the crystal structure or on the surface of photocatalysts) where photoexcited electrons and holes recombine together.\textsuperscript{42} Because of this phenomenon, most photocatalysts have very low efficiencies under light irradiation.\textsuperscript{43} Even in single crystals (free of defects), the charge recombination process is also possible, due to their non-directional and long-distance migration from the inside to the photocatalyst surface. It is noted that excited electrons and holes recombine together in less than 10\textsuperscript{−9} s, whereas it takes more time for absorbed species to react with these charges (10\textsuperscript{−8}–10\textsuperscript{−3} s).\textsuperscript{4} If the recombination process can be partly diminished, highly efficient photocatalysts for the water splitting reaction will be gained.

Scientists have been working on different strategies to enhance charge separation and migration. Nanotechnology has a great advantage for photocatalytic activity due to the fact that the photoexcited charges can migrate considerably shorter distances from the bulk material to the reaction sites on its surface.\textsuperscript{7} In addition, the high surface area of nanomaterials results in enhanced chemical adsorption on the surface of the nanoparticles and so the possibility of reactants reacting together is boosted noticeably. For instance, nano-sized CdS, LaFeO\textsubscript{3} and Ta\textsubscript{3}N\textsubscript{5} revealed higher photocatalytic activities for H\textsubscript{2} evolution than the bulk ones.\textsuperscript{45–47} Nevertheless, by reducing the particle size to nanoscale, surface defects and charge recombination become dominant, which compensates for the benefits of nanoparticle semiconductors.\textsuperscript{48,49} Therefore, the highest activity was not necessarily achieved with the smallest nanocrystals and so the optimal particle size is a key factor for acquiring the highest efficiency of a nano-photocatalyst.\textsuperscript{50,51} It is noteworthy that, in nanomaterials, crystallinity plays a more dominant role than having a higher surface area.\textsuperscript{7}

As seen in Fig. 5, the number of publications on nanophotocatalysts has increased significantly in the last decade,
but obviously more work needs to be done in this field in order to find suitable and efficient photocatalysts for hydrogen production.

3.1. Semiconductor heterojunction structures

Instead of using a single semiconductor, combining a semiconductor with other semiconductors, metals, and molecules would lead to the formation of a heterojunction structure between them. These heterojunctions were found to enhance the performance of various devices such as solar cells as well as photoluminescent and electro-chromic devices. In addition, the utilization of nanocomposites as photocatalysts instead of single semiconductors is another efficient and practicable approach to enhance the photocatalytic performance. In this kind of nanocomposite, excited charges migrate from one semiconductor to another semiconductor (or metal which acts as a cocatalyst). The second semiconductor should have a proper band-edge position or a higher efficiency in comparison to the first one. Furthermore, this approach can improve the device efficiency due to the fact that the reduction and oxidation reactions happen in two different components.

All heterojunctions can be categorized into three types based on their conduction and valance band positions, as illustrated in Fig. 6. In Type 1, both excited electrons and holes move from semiconductor 2 to semiconductor 1 due to their band edge positions. Usually this kind of heterojunction doesn’t improve photocatalysts because of the accumulation of both charge carriers on one semiconductor.

In the second group of heterojunctions, the conduction band of semiconductor 1 is lower than that of semiconductor 2. However, the valence band of semiconductor 1 has higher value than that of semiconductor 2. As a result, excited electrons can move from semiconductor 2 to 1, although generated holes migrate vice versa. If both semiconductors have sufficient intimate contacts, an efficient charge separation will occur during light illumination. Consequently, charge recombination is decreased and so charge carriers have a longer lifetime, which results in higher photocatalyst activity. Most of the composites discussed in this review are type 2.

Type 3 consists of semiconductors in which both the valence and conduction bands of one semiconductor are lower than the other, as can be seen in Fig. 6. This kind can be applied in the Z-scheme system with an appropriate electron mediator or some kind of bridge that attaches the two semiconductors. For instance, Wang et al. synthesized a core–shell nanocomposite of ZnO–CdS@Cd in such a way that elemental Cd acts as the charge-carrier bridge. A schematic of this nanocomposite is demonstrated in Fig. 7.
3.2. Various kinds of semiconductors

All of the semiconductors can be classified into 3 main groups based on their properties for hydrogen production: metal oxides, metal sulfides, and metal-free semiconductors.

There are different metal oxides that can be utilized as photocatalysts in a variety of reactions according to their band structures and activities. Most of them are active for hydrogen production under UV light irradiation because of their conduction band positions. Among them, titanium dioxide has attracted the most attention from scientists due to its efficiency, high stability, low cost and non-toxicity. However, it can absorb UV light, likewise other metal oxides, due to its wide band gap. Therefore, this semiconductor has a very low energy conversion from sunlight.

Contrary to metal oxides, metal sulfides usually have narrow band gaps and so they can absorb the energy of photons in the visible region. In addition, the conduction band of these semiconductors is more negative than the reduction potential of water and so they can reduce water to hydrogen. Nevertheless, these semiconductors usually consume generated holes to oxidize themselves. Thus, they are unstable during photocatalytic reactions. CdS is one of the best semiconductors with a high efficiency for hydrogen production under sunlight irradiation. Due to its instability, the metal sulfide is combined with other semiconductors with the aim of improving its stability and photocatalytic efficiency.

Besides these semiconductors, some nitrides also show photo-activity for hydrogen production in the visible range of the sunlight spectrum. Recently, graphitic carbon nitride has attracted a lot of interest because of its special properties such as its relatively narrow band gap and non-toxicity. This metal free polymer shows hydrogen production under visible light irradiation with high stability. However, its conversion efficiency is lower than that of TiO$_2$ or CdS and so further efforts need to be made in order to increase its efficiency. We will discuss different structures and compositions of these photocatalysts in detail, which shows hydrogen activity under visible light irradiation.

3.3. Titanium dioxide-based nanocomposites

Titanium dioxide typically has three crystal phases: anatase, rutile and brookite, among which anatase exhibits both high stability and high photocatalytic activity. The crystal structure of anatase and rutile are tetragonal, however brookite is orthorhombic. Various forms of TiO$_2$ have slightly different band gaps of around 3 eV, due to the variety in the crystal structures. Rutile is the thermodynamically stable form, and brookite does not usually show appreciable photocatalytic activity, but anatase is often indicated as the most active phase. The conduction band of TiO$_2$ is slightly higher than the reduction potential of water and so it can reduce protons when it is excited by light.

Some researchers synthesized nanocomposites of TiO$_2$ and some metal oxides, which are activated in the visible light region. Interestingly, some of them showed higher hydrogen production in comparison to pristine TiO$_2$ due to visible light absorption and better charge separation. For instance, Martha et al. tried to increase hydrogen production by combining doped TiO$_2$ with V$_2$O$_5$. Although N,S-doped TiO$_2$ has a very low hydrogen evolution, the combination of the doped TiO$_2$ with V$_2$O$_5$ exhibited 7 times higher hydrogen production under visible light irradiation (296.6 μmol h$^{-1}$). Xie et al. showed that a nanocomposite of TiO$_2$/BiVO$_4$ had a much longer lifetime of photoexcited charge carriers and so a higher charge separation. The main reason for this phenomenon is related to high movements of photoexcited electrons from BiVO$_4$ to TiO$_2$. Due to this reason, this photocatalyst had unexpected visible light activity for water splitting in contrast to BiVO$_4$, which was almost inactive in this region. They reported that TiO$_2$/BiVO$_4$ with a molar ratio of 5%, could evolve 2.2 mol h$^{-1}$ hydrogen, which was much higher than mixing with reduced graphene oxide nanosheets (0.75 mol h$^{-1}$) under similar conditions. Another group deposited Fe–TiO$_2$ nanoparticles (FTO) on the surface of CaIn$_2$O$_4$ nanorods (CIO). This nanocomposite revealed hydrogen production in the presence of KI as a sacrificial agent and Pt as a cocatalyst. The contact of these two nanoparticles facilitated charge separation and led to greater hydrogen evolution. This nanocomposite exhibited H$_2$ production at a rate of 280 μmol h$^{-1}$ g$^{-1}$, which was 12.3 and 2.2 times higher than CaIn$_2$O$_4$ and Fe–TiO$_2$, respectively. Due to the synthesis method (physical mixing of FTO and CIO), there is no control to give a uniform dispersion of FTO on CIO. In addition, the cocatalyst should be deposited on FTO in order to be more effective for hydrogen production. It seems that by applying some coating methods, the activity of this nanocomposite can improve, to even more than 280 μmol h$^{-1}$ g$^{-1}$.

It is worth mentioning that iron oxide is capable of use in metal organic frameworks (MOFs) in diverse morphologies with titanium oxide. For instance, Lin’s group created a nanocomposite of mixed metal oxides (Fe$_2$O$_3$ and TiO$_2$) via MOF templates. They used a MIL-101 MOF (Fe source) to deposit amorphous TiO$_2$ and after deposition they calcined the mixture in order to acquire the Fe$_2$O$_3$/TiO$_2$ nanocomposite. As a result, crystalline octahedral nano-shells were obtained which could produce hydrogen under visible light irradiation. Although TiO$_2$ is only active under UV light and Fe$_2$O$_3$ has a more positive conduction band than the reduction potential of H$_2$, this novel nanocomposite with the help of Pt metal as a cocatalyst produced 30.0 μmol g$^{-1}$ of hydrogen in 48 hours in the presence of TEA as a sacrificial agent. The reason for this weird activity is that some iron ions from MIL-101 can be doped into the TiO$_2$ crystallinity during the calcination process and the others converted into Fe$_2$O$_3$. Fe$_3$TiO$_5$ and Ti-doped Fe$_2$O$_3$ are both considered to be active photocatalysts under visible light in H$_2$ formation because of their small band gaps (Fe$_3$TiO$_5$ = 2.2 eV and Ti-doped Fe$_2$O$_3$ = 2.1 eV) and the edge of their conduction bands, which are more negative than H$^+$ reduction. Moreover, further characterizations showed that this material was stable during hydrogen evolution and no decrease in activity was observed. By introducing
this kind of hollow nanostructure, the surface area of the photocatalyst increased significantly, resulting in higher activity owing to more available active sites. Another example of this type was developed in our group. We proposed a new route to prepare a novel type of photocatalytic hollow Fe₂O₃–
TiO₂ nanostructure using the metal organic framework (MOF) structure consisting of coordinatively unsaturated metal centers (namely, MOF-UMCs) as a hard template. In this type of MOF-UMCs material, each trimeric Fe(III) center possesses terminal water molecules that can be removed by vacuum and temperature treatments to generate Lewis acid sites, to which the amine group of the titanium precursor can be grafted via the lone electron pair of the nitrogen atom for the preparation of a core/titania shell nanostructure, as illustrated in Fig. 8. The achieved hollow nanostructure of the Fe₂O₃–
TiO₂–PtOₓ photocatalyst possesses two distinct cocatalysts which are deposited separately on two sides of its hollow surface. The distance between two cocatalysts (wall thickness of the template) was 15–35 nm, which strongly facilitated charge separation and so increased photocatalytic activity. One of the cocatalysts was created from metal clusters of the MOF after calcination, located inside the hollow structure and the other was made from metal doping (PtOₓ) onto the surface of this nanocomposite. Interestingly, the visible light absorption band edge extended to 610 nm. Under visible light illumination and in the presence of lactic acid, this nanocomposite could produce 22 μmol h⁻¹ hydrogen without any reduction in its activity even after 5 cycles. The total amount of H₂ after five cycles was 110 μmol under visible light irradiation. Although this amount of hydrogen production was not so much in comparison to other photocatalysts, this approach may be used to develop other hollow structures with higher activity for hydrogen evolution in the visible light region.

In addition to metal oxides, scientists tried to mix diverse metal sulfides with titanium oxide due to their higher visible light absorption. CdS is the best metal sulfide to combine with TiO₂ because of its appropriate conduction band and higher efficiency. Due to the importance of this kind of nanocomposite, different compositions and morphologies will be discussed thoroughly in another section. Here, other metal sulfide composites with TiO₂ are explained in detail. It was reported that the single nanoparticles of In₄S₃ or Pt/TiO₂ were not active towards H₂ formation under visible light irradiation. However, the combined In₄S₃/Pt/TiO₂ nanostructure produced H₂ under visible light at the rate of 135 μmol h⁻¹ with a 1% quantum yield at λ ≥ 420 nm. In this nanocomposite, both Pt/TiO₂ and In₄S₃ nanoparticles were in close contact by the embedding of Pt/TiO₂ nanoparticles in the interstices of the In₄S₃. The optimum ratio of In₄S₃/Pt/TiO₂ was reported to be 3 : 2. Furthermore, Jang et al. synthesized a photocatalyst composite from titanium dioxide and AgGaS₂ by a solid state reaction followed by a sol–gel method. In the presence of sulfide and sulfite solution, and Pt as a cocatalyst, this composite showed a very good activity for hydrogen under visible light irradiation. Due to the conduction band structure, excited electrons can transfer from AgGaS₂ to TiO₂ and from there they can react with protons to produce hydrogen. The maximum quantum yield was 17.5% for the optimum ratio of 1 : 2 (TiO₂ : AgGaS₂) and 1% Pt.

Some researchers synthesized nanocomposites of TiO₂ with different carbon-based materials such as carbon-coated metal, carbon quantum dots, carbon nanotubes and graphene. For example, Peng’s group synthesized a novel nanocomposite of carbon coated Ni (denoted as Ni@C) and TiO₂. This nanocomposite consists of nanorods 10 nm in diameter and 40–100 nm in length. By using triethanolamine as a sacrificial reagent, this nanostructure could produce hydrogen under visible light irradiation. The highest activity was obtained when 5% of Ni was used in this nanocomposite (300 μmol h⁻¹). Furthermore, the apparent quantum yields are 12% and 7% for λ > 420 and λ > 520 nm, respectively. These yields were much higher than the same for neat Ni@C without TiO₂. Table 1 shows some nanocomposites of titanium dioxide as well as their activity under visible light irradiation.

3.4. CdS-based nanocomposites

CdS is one of the best semiconductors for photocatalytic hydrogen production because of its narrow band gap and conduction band edge position. In other words, it can absorb visible light with long wavelength and also it can reduce protons to hydrogen. However, this photocatalyst has two main disadvantages which are: (1) due to its small band gap, the recombination process of photoexcited electrons and holes is very easy and (2) this semiconductor is unstable under light irradiation and it is effortlessly corroded by excited holes. For these reasons, CdS needs to be combined with other semiconductors in order to overcome its drawbacks.

Due to the high visible light absorption of CdS (2.42 eV), scientists tried to enhance the photocatalytic efficiency of CdS by modifying the nanostructures of this semiconductor. The nanostructure of CdS provided more active sites for the water splitting reaction and so increased its photocatalytic activity. Another technique is preparing CdS in nano-porous structures that can raise the quantum yield up to 60% in the presence of Na₂SO₃ and Na₂S as sacrificial agents (λ ≥ 420 nm). The
main reasons for this development in quantum yield are effective charge separation, fast movement of charge carriers, and quick chemical reaction at the interface of the CdS nanostructure. Combining CdS nanoparticles with another semiconductor is another way to enhance its photocatalytic efficiency.88

Although metal oxides usually possess wide band gaps and cannot absorb long wavelengths of the sunlight spectrum, they are very stable during photocatalytic processes. Therefore, some studies were done in order to mix these semiconductors together and more efficient photocatalysts were obtained.55,89–99 For instance, Wang and co-workers prepared core–shell nanostructures from ZnO and CdS.89 This nanocomposite was able to split water to produce $H_2$ with sacrificial reagents. Interestingly, loading of a RuO$_2$ cocatalyst showed greater activity than Pt metal. In addition, the ratio of ZnO to CdS strongly affected its photocatalytic efficiency and it dropped slightly by raising the CdS molar ratio. The highest $H_2$ evolution is 2.96 mmol h$^{-1}$ g$^{-1}$ for $x = 0.2$, which is 34.4 times and 7.8 times higher than that of ZnO nanorods (prepared by the hydrothermal route) and CdS (prepared by the solid state route), respectively. As mentioned before, RuO$_2$ has a great impact on the photocatalytic activity, resulting in a sudden increase by around 200%. This nanocomposite could constantly produce $H_2$ for more than 30 h. Hou et al. synthesized a nanocomposite of CdS (2.45 eV) and TaON (2.5 eV) in a core–shell structure.91 They deposited TaON on the core of CdS and used Pt as a cocatalyst. Due to the band edge positions of these semiconductors, electrons migrate from CdS to TaON and holes can move from TaON to CdS. Although hydrogen evolution rates for pure CdS and TaON were 13.5 and 9 µmol h$^{-1}$, respectively, this nanocomposite could evolve 306 µmol h$^{-1}$ hydrogen using a sacrificial reagent. Moreover, combining this nanostructure with 1 wt% graphene oxide led to the production of more than two times more hydrogen than the previous one with a 31% quantum yield under visible light irradiation. Nonetheless, they didn’t examine the stability of this nanocomposite for multiple cycles in a longer runtime. One of the purposes of combining CdS with other materials is to enhance its stability during the reaction time. Usually the photocatalyst should be run for multiple cycles of hydrogen production in order to observe its stability under light illumination.

In addition to binary metal oxides, some researchers made nanocomposites of CdS and ternary metal oxides.100–103,110,111 In these nanostructures, generated holes can transfer from CdS to TaON and holes can move from TaON to CdS. Although hydrogen evolution rates for pure CdS and TaON were 13.5 and 9 µmol h$^{-1}$, respectively, this nanocomposite could evolve 306 µmol h$^{-1}$ hydrogen using a sacrificial reagent. Moreover, combining this nanostructure with 1 wt% graphene oxide led to the production of more than two times more hydrogen than the previous one with a 31% quantum yield under visible light irradiation. Nonetheless, they didn’t examine the stability of this nanocomposite for multiple cycles in a longer runtime. One of the purposes of combining CdS with other materials is to enhance its stability during the reaction time. Usually the photocatalyst should be run for multiple cycles of hydrogen production in order to observe its stability under light illumination.

### Table 1 Different nanocomposites of TiO$_2$ active for hydrogen production ($\lambda > 420$ nm)

<table>
<thead>
<tr>
<th>Semiconductor 1</th>
<th>Semiconductor 2</th>
<th>Cocatalyst</th>
<th>Sacrificial reagent</th>
<th>Light source</th>
<th>Hydrogen production ($\mu$mol h$^{-1}$ g$^{-1}$)</th>
<th>Quantum yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Carbon-coated Ni (Ni@C)</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>2000</td>
<td>12 at $\lambda = 420$ nm</td>
<td>12 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>TiO$_2$ nanosheets</td>
<td>Graphene</td>
<td>Pt</td>
<td>Methanol</td>
<td>350 W Xe, $\lambda \geq 420$ nm</td>
<td>736</td>
<td>420 nm</td>
<td>736</td>
</tr>
<tr>
<td>TiO$_2$ mesocrystals</td>
<td>Au nanoparticles</td>
<td>Pt</td>
<td>Propanol</td>
<td>Xe light, $\lambda &gt; 460$ nm</td>
<td>0.5</td>
<td>No data</td>
<td>0.5</td>
</tr>
<tr>
<td>TiO$_2$ MOF MIL-101</td>
<td>Pt</td>
<td>Lactic acid</td>
<td>450 W Xe, $\lambda \geq 420$ nm</td>
<td>1250</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>TiO$_2$ MOF MIL-88</td>
<td>PtO$_2$</td>
<td>Lactic acid</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>1100</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Mesoporous TiO$_2$</td>
<td>WS$_2$</td>
<td>Pt</td>
<td>Na$_2$S</td>
<td>350 W Xe, $\lambda &gt; 430$ nm</td>
<td>10</td>
<td>No data</td>
<td>10</td>
</tr>
<tr>
<td>AgIn$_2$S$_4$</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$S$_4$</td>
<td>450 W Hg, $\lambda &gt; 450$ nm</td>
<td>4200</td>
<td>17.5 at $\lambda = 420$ nm</td>
<td>17.5 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CaIn$_2$O$_4$</td>
<td>Fe–TiO$_2$</td>
<td>Pt</td>
<td>KI</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>280</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Graphene</td>
<td>Au–TiO$_2$</td>
<td>—</td>
<td>Methanol</td>
<td>3W LED, $\lambda = 420$ nm</td>
<td>296</td>
<td>4.1 at $\lambda = 420$ nm</td>
<td>4.1 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>TiO$_2$</td>
<td>—</td>
<td>Na$_2$S–Na$_2$S$_4$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>7253</td>
<td>0.94 at $\lambda = 447$ nm</td>
<td>0.94 at $\lambda = 447$ nm</td>
</tr>
</tbody>
</table>
Furthermore, CdS can be combined with other metal sulfides in various morphologies such as nanocrystals,\textsuperscript{104} nanowires\textsuperscript{105} and nano-layers\textsuperscript{106} in order to enhance its efficiency. Among all metal sulfides, ZnS attracts more attention due to its strong ability to form a solid solution with CdS which results in higher charge separation and greater quantum efficiency.\textsuperscript{107–114} For example, a solid solution of (Zn\textsubscript{0.95}Cu\textsubscript{0.05})\textsubscript{1−x}Cd\textsubscript{x}S was examined with various ratios of Cd for H\textsubscript{2} production under visible light and in the presence of SO\textsubscript{2} and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}.\textsuperscript{107} This solid solution consisted of nanocrystals of about 2−5 nm and had a band gap of 2.0 eV. This nanostructure showed 508 \(\mu\)mol h\textsuperscript{−1} hydrogen without any cocatalyst and possessed a quantum yield of 15.7\% under visible light when \(x\) was equal to 0.33. However, by depositing 0.75\% Pt, its activity was enhanced significantly and the hydrogen production and quantum yield reached 1.09 mmol h\textsuperscript{−1} and 31.8\%, respectively. Moreover, this nanocomposite was stable after three 12 h cycles. Zhang et al. synthesized a nanocrystal of a ZnS–CdS solid solution that was involved in H\textsubscript{2} evolution at 420 nm.\textsuperscript{109} They used MoS\textsubscript{2} as a cocatalyst and reported that with 0.2 wt\% of this cocatalyst, the hydrogen formation was 36 times higher than for CdS with noble metals as cocatalysts.\textsuperscript{115,116} Moreover, Liu et al. showed that nano-twin structures of the Cd\textsubscript{1−x}Zn\textsubscript{x}S solid solution could produce hydrogen from water without noble metals. Its apparent quantum yield was reported to be 43\% at 425 nm in the presence of sacrificial reagents.\textsuperscript{110} Another type of nanocomposite of ZnS and CdS is the physical mixture of their nanoparticles without making a solid solution phase. Shen et al. improved the nanocrystals of ZnS/CdS (5−10 nm) with In\textsubscript{2}S\textsubscript{3} without any surfactant or supports at room temperature and normal pressure.\textsuperscript{104} These microspheres could produce hydrogen from an aqueous solution of sulfide and sulfite ions with no cocatalysts and it was reported that the quantum yield reached 40.9\% at \(\lambda \geq 420\) nm. The optimum ratio of CdS:ZnS is 75\%, which can produce 8.1 mmol h\textsuperscript{−1} g\textsuperscript{−1} hydrogen. Despite the fact that this nanocomposite showed a very high efficiency for hydrogen evolution, no further experiments were done to examine its stability during hydrogen generation, which should be considered in further studies.

In addition to a solid solution, CdS can mix with other metal sulfides in order to increase hydrogen production under visible light irradiation.\textsuperscript{105,117–119} For instance, TiS\textsubscript{2} and TaS\textsubscript{2} are both semiconductors with small band gaps less than 1 eV. A nano-layer combination of one of these two semiconductors with nanoparticles of CdS resulted in highly efficient photocatalysts for H\textsubscript{2} evolution from an aqueous solution of benzyl alcohol.\textsuperscript{106} The nanocomposite of TiS\textsubscript{2} and CdS could generate 1000 \(\mu\)mol h\textsuperscript{−1} g\textsuperscript{−1} hydrogen, whereas the other one (TaS\textsubscript{2} and CdS) showed 2.3 times higher hydrogen evolution (2320 \(\mu\)mol h\textsuperscript{−1} g\textsuperscript{−1}) under visible light irradiation. The reason for this phenomenon was explained by the metallic nature of few-layer TaS\textsubscript{2}. In another study, Zhang et al. deposited NiS nanoparticles onto the CdS surface with the help of the hydrothermal route.\textsuperscript{117} They reported that the nanocomposite with 1.2\% of NiS had the highest activity and quantum yield. Its quantum efficiency under visible light irradiation (\(\lambda > 420\) nm) was 51.3\%, which was the highest photocatalyst activity without a noble metal cocatalyst. In addition, its H\textsubscript{2} evolution rate was 2.18 mmol h\textsuperscript{−1}, which was 35 times higher than that of CdS alone. Hou et al. decorated CdLa\textsubscript{2}S\textsubscript{4} microspheres with CdS nanocrystals by a hydrothermal procedure in order to enhance hydrogen generation.\textsuperscript{114} Due to the intimate contact of these nanoparticles and also the high dispersion of CdS nanocrystals, this nanocomposite exhibited a significant quantum yield of 54\% under the visible light region corresponding to 2250 \(\mu\)mol h\textsuperscript{−1} g\textsuperscript{−1}, which was 9 times higher than for the pristine CdLa\textsubscript{2}S\textsubscript{4}.

Carbon nanotubes are one of the most famous building blocks for synthesizing nanostructures that can be combined with diverse semiconductors, particularly CdS, in order to enhance the charge separation step, as demonstrated in Fig. 9.\textsuperscript{120–125} Furthermore, graphene nanosheets have some special properties such as high surface area, high charge carrier mobility (due to their two-dimensional sp\textsuperscript{2}-hybridization), and good mechanical stability.\textsuperscript{126} The intimate contact between CdS and graphene can enhance the migration of photoexcited electrons and can surpass the recombination process more efficiently. In principle, photoexcited electrons move from the conduction band of the CdS to graphene and in accordance with the great mobility of electrons on the graphene sheets, the recombination process is partially prevented.\textsuperscript{123,125,127–133} For instance, Li et al. synthesized CdS nanoparticles of about 3 nm diameter in an autoclave and they dispersed them completely onto graphene nanosheets.\textsuperscript{133} This nanocomposite, which had 1 wt\% graphene and 0.5 wt\% Pt, showed 1.12 mmol h\textsuperscript{−1} hydrogen evolution from a solution of lactic acid. This rate of hydrogen production was around 5 times higher than for pristine CdS and the apparent quantum efficiency was reported to be 22.5\% at \(\lambda \geq 420\) nm.

There have been different methods to synthesize graphene-based photocatalysts, but the simplest and most direct technique is to mix graphene with target semiconductors.\textsuperscript{134–136}
The other popular method to provide nanocomposites of various semiconductors with graphene is an in situ growth method in which graphene oxide (GO) or reduced graphene oxide (RGO) is chosen as the starting material. Nanocrystals of CdS or other semiconductors can grow on the surface of graphene nanosheets via oxygen-containing functional groups which act as nucleation sites. The structure and electrical properties of RGO as well as the location of the conduction band of CdS and RGO lead the transfer of photoexcited electrons from CdS to RGO and from there they can reduce hydrogen atoms (Fig. 10).

Table 2 summarizes the hydrogen production of different nanocomposites of CdS under visible light irradiation with their quantum yields.

### 3.5. CdS and TiO2 nanostructures

TiO2 and CdS are the most studied semiconductors in recent decades due to their photocatalytic properties and benefits. However, each of them has some drawbacks that limit their applications for hydrogen production from sunlight. For example, TiO2 has a wide band gap inapplicable for visible light absorption and CdS is unstable during photocatalytic reactions. The combination of these semiconductors at the nanoscale leads to more efficient photocatalysts that can generate hydrogen under visible light irradiation with high stability. Under visible light illumination, CdS can absorb photons and produce holes and electrons. Although TiO2 cannot absorb visible light, due to its wide band gap, excited electrons can move from CdS to TiO2. This leads to better charge separation, and results in a higher quantum yield. It should be noted that the excited holes remain in the valence band of CdS and from there they can oxidize any sacrificial agents.

Various nanocomposites with different morphologies can be created from CdS and TiO2, as shown in Table 3. Some important morphologies will be discussed here, which result in higher light absorption and higher hydrogen evolution in the visible light region.

Generally, two different morphologies for mixing CdS nanoparticles and titanate nanotubes have been proposed in order to improve photocatalytic activity, as illustrated in Fig. 11. Cds/titanate nanotubes (CdS/TNTs) were reported to have a higher increase in photocatalytic activity in comparison to traditional nanocomposite-Cds@TNTs. The CdS/TNT nanostructures lead to a proper dispersion of CdS as well as intimate multipoint contacts between two nanocrystals. It is clear that the ratio of Cd : Ti plays an important role in photocatalyst activity. The optimum value of this proportion was 0.05, which corresponds to 6 wt% of CdS in the photocatalysts. With the optimum cocatalyst quantity of Pt (2.0 wt%), the CdS/TNTs could generate 353.4 μmol h⁻¹ hydrogen with a 25.5% quantum yield under visible light. Nevertheless, the quantum yield of traditional CdS@TNTs could hardly reach 2.7% and as mentioned before, changing the structure of the nanoparticles can have major impacts on their activity. It is noteworthy that this nanocomposite was stable for hydrogen production during six 120 h cycles. Therefore, this nanocomposite noticeably improved the stability of the photocatalyst during hydrogen evolution.

Many researchers have investigated the deposition of CdS nanoparticles inside different nanostructures of titane, such as tubular and nanotubes, with the aim of obtaining highly efficient nanocomposites. Li et al. homogeneously deposited Cds nanoparticles inside TiO2 nanotubes. They examined its photocatalytic water splitting with electron donors containing S²⁻ and SO₃⁻ at a wavelength of 420 nm. They attained a 43.4% quantum yield for H₂ evolution. This is due to the quantum size effect of CdS nanoparticles as well as synergetic effects between two nanocomposites. This also means that the potential energy at the interface of CdS and TiO2 would help electrons to transfer from CdS to TiO2 more easily and consequently enhanced the photocatalytic activity.

CdS nanoparticles can also be deposited on nanosheets of titanate, which leads to increased quantum yield of the nanocomposite. The powerful interaction between the titanate 2D nanostructures and CdS helped to create visible light absorption photocatalysts with high stability towards the photocorrosion of CdS. Our group synthesized ultrathin titanate nanodisks (TNDs) by the solvothermal method. After that, we grew both CdS nanoparticles as a visible light semiconductor and Ni nanoparticles as a cocatalyst on the surface of TNDs for hydrogen evolution. This nanocomposite was able to efficiently separate photoexcited charges and as a result it showed a very high activity for water splitting under visible light irradiation. The concept of depositing a cocatalyst on the other surface (here, on TNDs), would help to enhance the photocatalytic activity by increasing charge separation and preventing recombination phenomena. As can be seen in Fig. 12 (a), an excited electron can easily transfer from CdS to the TNDs and from there to the Ni cocatalyst. With an optimum ratio of CdS : TNDs and Ni loading, this nanocomposite can generate H₂ from a water–methanol solution under visible light irradiation. The hydrogen evolution rate was...
<table>
<thead>
<tr>
<th>Semiconductor 1</th>
<th>Semiconductor 2</th>
<th>Cocatalyst reagent</th>
<th>Light source</th>
<th>Hydrogen production ($\mu$mol h$^{-1}$ g$^{-1}$)</th>
<th>Quantum yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>SrS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda &gt; 400$ nm</td>
<td>246</td>
<td>10 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS</td>
<td>ZnCu</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Halogen, $\lambda \geq 420$ nm</td>
<td>1693</td>
<td>15.7 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS</td>
<td>CuIn</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>3633</td>
<td>31.8 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS nanorods</td>
<td>ZnO</td>
<td>Pt</td>
<td>2-Propanol</td>
<td>300 W Xe</td>
<td>2960</td>
<td>2.14 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS nanorods</td>
<td>CdSe</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe</td>
<td>200</td>
<td>26.5 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS</td>
<td>Ni/NiO/KNbO$_3$</td>
<td>—</td>
<td>Isopropanol</td>
<td>500 W Hg–Xe, $\lambda &gt; 400$ nm</td>
<td>203.5</td>
<td>8.8 at $\lambda &gt; 400$ nm</td>
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<tr>
<td>CdS</td>
<td>Ni/NiO/KNbO$_3$</td>
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<td>Isopropanol</td>
<td>500 W Hg–Xe, $\lambda &gt; 400$ nm</td>
<td>150</td>
<td>4.4 at $\lambda &gt; 400$ nm</td>
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<tr>
<td>CdS</td>
<td>LaMnO$_3$</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>595</td>
<td>No data</td>
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<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$S</td>
<td>ZnO</td>
<td>Pt</td>
<td>Benzy alcohol</td>
<td>450 W Xe</td>
<td>36 500</td>
<td>50.4 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>CdS nanorods</td>
<td>NiS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>1131</td>
<td>6.1 at $\lambda = 420$ nm</td>
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<tr>
<td>Cd$<em>{0.7}$Zn$</em>{0.3}$S</td>
<td>Multi-walled carbon nanotubes</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>1563.2</td>
<td>7.9 at $\lambda = 420$ nm</td>
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<tr>
<td>CdS</td>
<td>CeO$_2$</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
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<td>223</td>
<td>No data</td>
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<tr>
<td>CdS</td>
<td>Multi-walled carbon nanotubes</td>
<td>Pt</td>
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<tr>
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<td>MWCNTs</td>
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<td>4977</td>
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<tr>
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<td>ZnS</td>
<td>Ru</td>
<td>Formic acid</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>6000</td>
<td>20 at $\lambda = 420$ nm</td>
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<tr>
<td>In$_2$S$_3$</td>
<td>CdS–ZnS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
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<td>8100</td>
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<td>CdLa$_5$S$_4$ microspheres</td>
<td>CdS nanocrystals</td>
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<td>2250</td>
<td>54 at $\lambda = 420$ nm</td>
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<tr>
<td>ZnS</td>
<td>CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
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<td>46</td>
<td>15 at $\lambda = 420$ nm</td>
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<tr>
<td>TaON</td>
<td>CdS</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>1530</td>
<td>No data</td>
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<tr>
<td>Graphene oxide</td>
<td>CdS@/TaON</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3165</td>
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<tr>
<td>ZnO</td>
<td>CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>500 W Xe, $\lambda \geq 420$ nm</td>
<td>831</td>
<td>3 at $\lambda = 420$ nm</td>
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<tr>
<td>CdO$_2$W$_4$</td>
<td>CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>500 W Xe</td>
<td>90.25</td>
<td>9.8 at $\lambda = 420$ nm</td>
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<td>Reduced graphene oxide</td>
<td>CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>350 W Xe, $\lambda \geq 420$ nm</td>
<td>2310</td>
<td>No data</td>
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<td>Nanosized MoS$_2$/graphene hybrid</td>
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<td>MoS$_2$</td>
<td>Lactic acid</td>
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<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
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<td>No data</td>
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<td>Vermiculite</td>
<td>CdS quantum dots</td>
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<td>SiC</td>
<td>CdS particles</td>
<td>Pt</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>555</td>
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<td>Framework of structured WO$_3$</td>
<td>Orderedly depositing Au and CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>1730</td>
<td>No data</td>
</tr>
<tr>
<td>ZSM-5 type metallosilicates</td>
<td>CdS nanoparticles</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>500 W Osram, $\lambda \geq 420$ nm</td>
<td>11 000</td>
<td>65.62 at $\lambda = 420$ nm</td>
</tr>
<tr>
<td>γ-TaON hollow spheres</td>
<td>CdS nanoparticles</td>
<td>MoS$_2$</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>300 W Xe, $\lambda \geq 420$ nm</td>
<td>3142.5</td>
<td>No data</td>
</tr>
<tr>
<td>ZnO core/shell nanofibers</td>
<td>CdS</td>
<td>—</td>
<td>Na$_2$S–Na$_2$SO$_3$</td>
<td>500 W Xe, $\lambda \geq 420$ nm</td>
<td>354</td>
<td>No data</td>
</tr>
</tbody>
</table>
Sulfite ions. The optimum ratio of TiO2 : CdS in this nano-
hydrogen production from an aqueous solution of sulfide and
hydrogen production. For instance, Jang
most of them, a cocatalyst had to be utilized in order to show
TiO2 nanoparticles on CdS nanostructures.161,162,182

Table 2 (Contd.)

<table>
<thead>
<tr>
<th>Semiconductor 1</th>
<th>Semiconductor 2</th>
<th>Cocatalyst</th>
<th>Sacrificial reagent</th>
<th>Light source</th>
<th>Hydrogen production (µmol h⁻¹ g⁻¹)</th>
<th>Quantum yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnIn₂S₄ heterostructures coupled with graphene</td>
<td>CdS quantum dots</td>
<td>Pt</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>27 000</td>
<td>56 at λ = 420 nm</td>
<td>132</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Zn₇Cd₁₋₉S</td>
<td>—</td>
<td>Na₂S–Na₂SO₃</td>
<td>500 W Xe</td>
<td>6030</td>
<td>No data</td>
<td>123</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>CdS</td>
<td>NiS</td>
<td>Na₂S–Na₂SO₃</td>
<td>350 W Xe, λ ≥ 420 nm</td>
<td>12 130</td>
<td>No data</td>
<td>124</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>Cu₀.₀₂In₀.₄₇ZnS₁₄₋₄₇</td>
<td>Pt</td>
<td>Na₂S–Na₂SO₃</td>
<td>800 W Xe–Hg, λ ≥ 420 nm</td>
<td>3800</td>
<td>No data</td>
<td>140</td>
</tr>
<tr>
<td>Ti-MCM-48 mesoporous</td>
<td>CdS</td>
<td>RuO₂</td>
<td>Ethanol</td>
<td>300 W Xe, λ &gt; 400 nm</td>
<td>2730</td>
<td>36.3 at λ = 400 nm</td>
<td>156</td>
</tr>
<tr>
<td>MoO₃</td>
<td>CdS</td>
<td>—</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>5250</td>
<td>28.86 at λ = 420 nm</td>
<td>98</td>
</tr>
<tr>
<td>Cubic MCM-48 mesoporous</td>
<td>CdS</td>
<td>Pt</td>
<td>Ethanol</td>
<td>300 W Xe, λ &gt; 400 nm</td>
<td>1810</td>
<td>16.6 at λ = 400 nm</td>
<td>157</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>CdS</td>
<td>—</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>4200</td>
<td>10.4 at λ = 420 nm</td>
<td>139</td>
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<tr>
<td>Ga₂O₃</td>
<td>CdS quantum dots</td>
<td>Pt</td>
<td>Lactic acid</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>9052</td>
<td>43.6 at λ = 420 nm</td>
<td>99</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>CdS</td>
<td>—</td>
<td>Benzyl alcohol</td>
<td>450 W Xe, λ &gt; 400 nm</td>
<td>9382</td>
<td>45.3 at λ = 460 nm</td>
<td>106</td>
</tr>
<tr>
<td>TiS₂</td>
<td>—</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>5731</td>
<td>47.1 No data</td>
<td>158</td>
</tr>
<tr>
<td>TaS₂</td>
<td>—</td>
<td>—</td>
<td>Triethanolamine</td>
<td>3410</td>
<td>47.1</td>
<td>No data</td>
<td>158</td>
</tr>
<tr>
<td>TaS₂</td>
<td>—</td>
<td>—</td>
<td>Triethanolamine</td>
<td>3410</td>
<td>47.1</td>
<td>No data</td>
<td>158</td>
</tr>
<tr>
<td>MCM-41</td>
<td>CdS</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>4730</td>
<td>19.7 at λ = 420 nm</td>
<td>159</td>
</tr>
<tr>
<td>AgGaS₂</td>
<td>CdS</td>
<td>Pt</td>
<td>Na₂S–Na₂SO₃</td>
<td>450 W Hg, λ ≥ 420 nm</td>
<td>4731</td>
<td>No data</td>
<td>138</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>CdS</td>
<td>Ni(OH)₂</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>4731</td>
<td>No data</td>
<td>138</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>CdS</td>
<td>—</td>
<td>Na₂S–Na₂SO₃</td>
<td>3410</td>
<td>4.8 at λ = 420 nm</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>CdS clusters</td>
<td>Pt</td>
<td>Lactic acid</td>
<td>350 W Xe, λ ≥ 420 nm</td>
<td>5600</td>
<td>22.5 at λ = 420 nm</td>
<td>133</td>
</tr>
<tr>
<td>N-graphene</td>
<td>CdS</td>
<td>—</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>1050</td>
<td>No data</td>
<td>130</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>CdS quantum dots</td>
<td>Pt</td>
<td>Methanol</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>348</td>
<td>No data</td>
<td>160</td>
</tr>
</tbody>
</table>

15.326 mmol g⁻¹ h⁻¹ over 15 h of reaction, which results in
having a 24% quantum yield at λ ≥ 420 nm. It is noteworthy
that this approach of mixing a semiconductor with TNDs can
also be used for other efficient visible light active semicon-
ductors. The intimate contact between TNDs and CdS plays a
crucial role in this kind of nanostructure. In other words,
physical mixing of these semiconductors cannot result in high
photocatalytic activity. By growing CdS as well as selectively
depositing Ni clusters on the surface of the TNDs by means of
an ion exchange method, we were certain that the nanoparti-
cles had intimate contact and so charge carriers can easily
transfer between the semiconductors, as shown in Fig.
12(b).176 In another technique, researchers tried to deposit
TiO₂ nanoparticles on CdS nanostructures.161,162,182–184,186 In
most of them, a cocatalyst had to be utilized in order to show
hydrogen production. For instance, Jang et al. made a nano-
composite of CdS nanowires (NWs) with a high crystallinity,
which had TiO₂ nanocrystals on their surfaces, as shown in
Fig. 13.183 Under visible light, this nanostructure displayed
hydrogen production from an aqueous solution of sulfide and
sulfite ions. The optimum ratio of TiO₂ : CdS in this nano-
structure would be 0.2, which led to the highest activity under
visible light irradiation. The possible role of TiO₂ NPs is to
provide sites for collecting the photoelectrons generated from
the CdS NWs, thereby enabling an efficient electron–hole sep-
Arating as depicted in Fig. 13.

Preparing a nanocomposite is a very delicate process and
each step should be considered precisely, even though the
nanostructure and crystallinity may change by the order of
adding precursors. Park et al. showed that reversing the chemi-
cal precipitation order of CdS on TiO₂ nanoparticles caused
different H₂ evolution rates under the same conditions.177
They prepared CdS₉ by adding Cd²⁺ in an aqueous solution
containing S²⁻ and Pt-loaded TiO₂. Another nanocomposite
with an equal molar ratio was prepared by adding sulfide
drops into the solution of Cd²⁺ and Pt–TiO₂ (Cd₉S). Surpris-
ingly, CdS₉ showed 10 times higher hydrogen evolution than
Cd₀.₄₇S under visible light irradiation (Fig. 14).

Khattamian et al. prepared a metallosilicate-based (ferrilisi-
cate and aluminosilicate) nanocomposite of CdS/TiO₂ via a
hydrothermal method.178 Utilizing a metallosilicate support
has many advantages such as offering high surface area and
providing a homogeneous dispersion of CdS nanoparticles.
Moreover, this support both prevents agglomeration of the
semiconductor and facilitates electron transfer and separation. It is noteworthy to consider that in applying ferrisilicate, the presence of partially occupied d orbitals of Fe$^{3+}$, which can interact with TiO$_2$ orbitals, enhances the photocatalytic activity, while applying aluminosilicate as a support didn’t improve its activity compared to the unsupported composite.

In the case of the CdS phase, the hexagonal structure showed around a sixfold higher photocatalytic activity than the cubic one.
Vu et al. provided a nanocomposite of TiO₂ nanorods and CdS nanoparticles with Ni clusters in order to enhance charge separation and photocatalytic activity.¹⁶⁸ A dominant feature of this nanorod-based material is that nanoparticles of second semiconductors could be dispersed uniformly on the nanorod surface. Ni nanoparticles acting as cocatalysts were selectively deposited on the surfaces of these nanorods. This configuration can improve the efficiency of electron transfer from the sensitized CdS nanoparticles to TiO₂ and then to Ni clusters, as depicted in Fig. 15. The H₂ production rate was 33.36 μmol h⁻¹ g⁻¹ under visible light in the presence of a sacrificial reagent, which was about 44 times higher than for the neat Ni–CdS system.

A new ternary nanostructure of three different nanoparticles was synthesized in order to enhance H₂ production under visible light irradiation.¹⁸⁶ Firstly, they synthesized nanoparticles of Au with an average size of 40 nm. After this step, they grew TiO₂ nanocrystals as a shell structure on the Au nanoparticles via a hydrothermal method according to previous research.¹⁸⁷ They then deposited CdS nanoparticles onto the surface of Au@TiO₂ core–shell nanostructures. This ternary nanocomposite showed considerably high activity for H₂ evolution compared to both binary nanostructures (CdS–TiO₂ or Au@TiO₂). This ternary design builds up a transfer path for the photoexcited electrons from CdS to the core Au particles via the TiO₂ nanocrystal bridge and thus effectively suppresses the electron–hole recombination on the CdS photocatalyst. However, this nanocomposite is very complicated to obtain and needs precise conditions for each step of the synthesis, which is one of its drawbacks in comparison with other binary nanocomposites for hydrogen production.

3.6. g-C₃N₄-based nanocomposites

Graphitic carbon nitride (g-C₃N₄) is a metal-free semiconductor that consists of s-triazine or tri-s-triazine units. These units are connected in a two-dimensional graphite-like framework by amino groups in each layer and weak van der Waals forces between layers.¹⁸⁸ As a result, this polymeric semiconductor shows very high thermal and chemical stability. In 2009, Wang et al. synthesized g-C₃N₄ from cyanamide by pyrolysis at high temperature (400–600 °C).¹⁸⁹ The obtained semiconductor could not only produce hydrogen under visible light irradiation from an aqueous solution of triethanolamine (TEA), but it also gave a steady hydrogen production rate over 75 h. Since then, other researchers tried to synthesize g-C₃N₄ from other nitrogen-rich precursors such as dicyanamide, urea and melamine.¹⁹⁰ In addition, some other scientists combined it with other semiconductors or charge carrier mediator to boost its photocatalyst activity.¹⁹¹–¹⁹⁶ Here, we discuss various heterojunctions of g-C₃N₄ and semiconductors that could improve hydrogen production under visible light (Table 4).

Due to the structural similarity between carbon bonds in carbon-based nanostructures (nanotubes and graphene) and graphite carbon nitride, it is believed that these materials can mix together and as a result the photocatalytic efficiency will increase substantially.¹⁹⁴,¹⁹⁶ For instance, g-C₃N₄ nanosheets were mixed with graphene in order to increase the visible light photocatalytic activity for H₂ generation.¹⁹⁴ This metal-free nanocomposite could generate hydrogen from an aqueous solution of methanol under light illumination (λ > 400 nm). Using 1 wt% of graphene with Pt-loaded g-C₃N₄, the H₂ evolution rate was noticeably enhanced from 147 μmol h⁻¹ g⁻¹ to 451 μmol h⁻¹ g⁻¹. Another group tried to modify g-C₃N₄ by introducing carbon nanotubes into its structure.¹⁹⁶ Despite the fact that the new composite and pure g-C₃N₄ are very similar in their properties, the new photocatalyst possessed higher activity (around 2.5 times) than the other one. With
optimal amounts of carbon nanotubes (2 wt%), it produced 394 µmol h⁻¹ g⁻¹ hydrogen under visible light illumination because of the increased lifetime of excited electron and holes and the prevention of their recombination.

Furthermore, other semiconductors can be combined with g-C₃N₄ in order to prevent charge recombination. For example, Chai et al. generated a nanocomposite consisting of porous g-C₃N₄ with TiO₂ nanoparticles. In accordance with this nanocomposite was improved using Pt metal as a cocatalyst, it showed hydrogen evolution under visible light illumination (λ > 420 nm). The maximum hydrogen evolution (178 µmol h⁻¹) was achieved when the mass ratio of g-C₃N₄ and TiO₂ was 70 to 30. Kang et al. synthesized a composite of graphitic carbon nitride and Rh-doped SrTiO₃. Using Pt as a cocatalyst, this photocatalyst could produce hydrogen from an aqueous solution of methanol at 410 nm with a quantum yield of 5.5%. Doping Rh into the structure of SrTiO₃ provides a donor level in the band gap region of SrTiO₃: Rh. As a result, the excited holes can easily transfer from the SrTiO₃: Rh semiconductor to the carbon nitride and the excited electrons move from the conduction band of the g-C₃N₄ to the SrTiO₃: Rh. This leads to high charge separation and higher hydrogen production (2223 µmol h⁻¹ g⁻¹) in comparison to each of the semiconductors alone.

### Table 4 Different nanocomposites of graphitic carbon nitride

<table>
<thead>
<tr>
<th>Semiconductor 1</th>
<th>Semiconductor 2</th>
<th>Cocatalyst</th>
<th>Sacrificial reagent</th>
<th>Light source</th>
<th>Hydrogen production (µmol h⁻¹ g⁻¹)</th>
<th>Quantum yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered g-C₃N₄ sheets</td>
<td>Graphitized polyacrylonitrile</td>
<td>Pt</td>
<td>Triethanolamine</td>
<td>150 W Halogen, λ ≥ 420 nm</td>
<td>370</td>
<td>No data</td>
<td>203</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Nickel sulfide (NiS)</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>447.7</td>
<td>No data</td>
<td>197</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Zinc phthalocyanine</td>
<td>Pt</td>
<td>Ascorbic acid</td>
<td>350 W Xe, λ ≥ 420 nm</td>
<td>12500</td>
<td>1.85 at λ = 700 nm</td>
<td>204</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>C/N co-doped TiO₂</td>
<td>Ag</td>
<td>Methanol</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>96</td>
<td>No data</td>
<td>198</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>PEDOT</td>
<td>Pt</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>327</td>
<td>No data</td>
<td>195</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>WO₃</td>
<td>Pt</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>110</td>
<td>0.9 at λ = 420 nm</td>
<td>199</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Carbon nanotubes</td>
<td>Pt</td>
<td>Triethanolamine</td>
<td>350 W Xe, λ ≥ 420 nm</td>
<td>394</td>
<td>No data</td>
<td>196</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>ZnFe₂O₄</td>
<td>Pt</td>
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<td>300 W Xe, λ ≥ 420 nm</td>
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</tr>
<tr>
<td>g-C₃N₄</td>
<td>Ag₂S</td>
<td>—</td>
<td>Methanol</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>200</td>
<td>No data</td>
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<tr>
<td>g-C₃N₄</td>
<td>TiO₂</td>
<td>Pt</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>1780</td>
<td>No data</td>
<td>192</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Poly(3-hexylthiophene)</td>
<td>Pt</td>
<td>Na₂S–Na₂SO₃</td>
<td>300 W Hg, λ ≥ 420 nm</td>
<td>1866</td>
<td>2.9 at λ = 420 nm</td>
<td>205</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Au nanoparticles</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>8870</td>
<td>No data</td>
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<tr>
<td>C₃N₄</td>
<td>NiS</td>
<td>—</td>
<td>Triethanolamine</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>482</td>
<td>1.99 at λ = 440 nm</td>
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</tr>
<tr>
<td>Carbon nitride</td>
<td>N-doped tantalic acid</td>
<td>—</td>
<td>Methanol</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>70.6</td>
<td>4.89 at λ = 420 nm</td>
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</tr>
<tr>
<td>g-C₃N₄</td>
<td>SrTiO₃: Rh</td>
<td>Pt</td>
<td>Methanol</td>
<td>300 W Xe, λ ≥ 420 nm</td>
<td>2223</td>
<td>5.59 at λ = 420 nm</td>
<td>193</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>MWNTs</td>
<td>Pt</td>
<td>Methanol</td>
<td>350 W Xe, λ ≥ 420 nm</td>
<td>75.8</td>
<td>No data</td>
<td>202</td>
</tr>
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</table>

#### 3.7. Other nanocomposites

In spite of the above nanocomposites and nanostructures, scientists have tried to synthesize and combine other nano-scale semiconductors in order to achieve highly efficient photocatalysts for hydrogen evolution under visible light illumination. 1D and 2D nanoparticles and nanostructures such as nanowires, nanotubes, nanorods, nanobelts, nanosheets, and nanoplates, have interested researchers in the last decade for water splitting via sunlight. The combination of these kinds of nanostructures can effectively enhance charge separation and prevent the recombination process, and so increase the photocatalyst efficiency as summarized in Table 5.

Andrew Frame et al. found that CdSe nanoribbons were active in photocatalytic H₂ evolution from a S²⁻/SO₃²⁻ solution under visible light, whereas bulk CdSe was not. By linking these nanoparticles with MoS₂ nanoplates, the activity was enhanced by about four times and so their quantum yields reached 9.2% at 440 nm. Interestingly, in this nanocomposite Pt cannot be used as a cocatalyst due to sulfide poisoning of the surface sites.

Jing et al. synthesized a Cu-doped core–shell tubular nanocomposite of ZnO/ZnS. They tried to deposit Cu-doped ZnS nanoparticles on the outside of ZnO nanotubes. As a result, this nanocomposite showed higher hydrogen evolution than...
the undoped ZnO/ZnS nanocomposite. Copper ions act as the donor level to induce the visible light response of ZnS and thus excited electrons can migrate from ZnS to ZnO and from there they reduce protons. Two ferrites of calcium (CFO) and magnesium (MFO), i.e. CaFe₂O₄ and MgFe₂O₄ were used to synthesize nanocomposites for the H₂ evolution reaction.²²⁰ Due to the difference in band position of these semiconductors, photoexcited electrons transfer from CaFe₂O₄ to MgFe₂O₄, whereas the holes can move vice versa. Both CFO and MFO are active for hydrogen production under visible light irradiation when promoted with cocatalysts (Pt and RuO₂ for CFO and MFO, respectively). However, the nanocomposite of CFO and MFO produced 82.8 mmol h⁻¹ g⁻¹ with a quantum yield of 10.1% which was an order of magnitude higher than that of RuO₂/MFO or Pt/CFO.

Pradhan et al. synthesized a mesoporous nanocomposite of Fe/Al₂O₃–MCM-41 with a pore size of 50 nm. They reported that this photocatalyst with 5 wt% of Fe showed hydrogen production activity under visible light (146 µmol h⁻¹) with a quantum yield of 6.1%. The main reason for such activity is due to the properties of mesoporous materials, which are their high pore volume, narrow pore size distribution and high surface area. Furthermore, iron doping on the surface helped to absorb visible light, although the mesoporous nanocomposite by itself didn’t show any activity for λ > 400 nm.²²¹

### 4. Conclusion

Photocatalytic hydrogen production based on solar-driven water splitting is one of the best ways to use solar energy. However, industrial application of this strategy is still hindered by its currently low efficiency originating from the lack of efficient photocatalysts. Various methods have been developed to boost the photocatalyst efficiency such as metal or non-metal doping of wide band-gap semiconductors to decrease their band gap and applying cocatalysts to improve the charge...
separation and to provide active sites on the surface of the semiconductor for water splitting. Making multicomponent heterojunctions of different semiconductor nanocomposites offers an effective tool to extend sunlight absorption and also to increase charge carrier lifetimes by enhancing charge separation. Nanostructured photocatalysts can improve the efficiency by providing a large surface area and small particle size. As a result, charge carriers transfer noticeably small distances from the bulk material to its surface, which partially limits the recombination phenomenon.

Among various semiconductor heterojunctions for photocatalytic hydrogen generation, TiO$_2$ and CdS-based systems have been most studied. TiO$_2$ is one of the applicable and commercial photocatalysts that can be utilized in different photocatalysis processes. Combining nano-sized TiO$_2$ with suitable small band-gap semiconductors produces nanocomposite photocatalysts which exhibit an improvement in hydrogen production from the visible light region. CdS, on the other hand, has been widely studied for hydrogen production under visible light. Although coupling semiconductors has been shown to improve the photocatalytic efficiency of the photocatalyst, the overall efficiency for hydrogen production using sunlight is still very low. Factors such as composition, interface between the semiconductors, and morphology of each component, all of which determine the photocatalytic activity of such materials, need to be further elucidated in great detail. Furthermore, the charge transfer in multi-component photocatalysts is sensitively and greatly affected by how the hybrid is organized. Thus, the relative position of both the semiconductor and cocatalysts needs to be controlled in order to optimize the electron transfer throughout the photocatalyst. Besides this, new material design and innovative strategies for improving the charge separation and sunlight absorption of the photocatalysts are also very important for the realization of hydrogen production based on solar driven water splitting.

Notes and references

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