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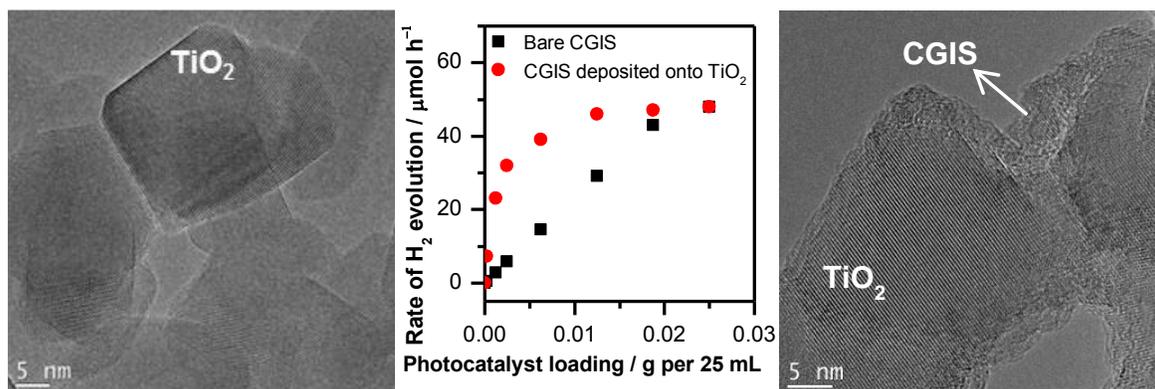
Solvent-Induced Deposition of Cu-Ga-In-S Nanocrystals onto a Titanium Dioxide Surface for Visible-Light-Driven Photocatalytic Hydrogen Production

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Graphical abstract



Highlights

- Cu-Ga-In-S (CGIS) nanocrystals with different Ga/In ratios were readily synthesized.
- A unique solvent-induced deposition method was developed for loading CGIS nanocrystals onto a TiO₂ surface.
- The CGIS/TiO₂ photocatalyst showed improved visible light activity for hydrogen production.
- The enhanced activities are explained either by the synergistic effect between CGIS and TiO₂ or by the improved dispersion and optical properties.

Abstract:

In this paper, copper-gallium-indium-sulfide (CGIS) nanocrystals with different Ga/In ratios, i.e., $\text{CuGa}_x\text{In}_{5-x}\text{S}_8$, where $x = 0, 1, 2, 3, 4$ and 5 , were synthesized and investigated for visible-light-driven hydrogen (H_2) evolution from aqueous solutions that contain sulfide/sulfite ions. The synthesized CGIS nanocrystals were characterized by diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence spectroscopy (PL). With 1.0 wt.% Ru as a co-catalyst, the H_2 evolution rate on $\text{CuGa}_2\text{In}_3\text{S}_8$ (CGIS hereafter) showed the highest activity. The CGIS nanocrystals were deposited onto a TiO_2 surface via a unique solvent-induced deposition method. The CGIS/ TiO_2 photocatalyst showed comparable activity to that obtained using bare CGIS nanocrystals when the photocatalyst amount was sufficient in the photoreactor system, suggesting that TiO_2 remains intact in terms of photocatalytic activity. The quantity of CGIS nanocrystals, however, required to achieve the rate-plateau condition at saturation was much lower in the presence of TiO_2 . The enhanced activities at low CGIS loadings observed in the presence of TiO_2 were explained by the improved dispersion of the powder suspension and optical path in the photoreactor. This TiO_2 supported photocatalyst lowers the required amount of photocatalyst, which is beneficial from an economic point of view.

Keywords: Quaternary Nanocrystals, Photocatalysis, CGIS, Hydrogen Production, Titanium Dioxide

1. Introduction

Visible light driven photocatalytic H₂ production is of great interest from both economic and environmental points of view due to its possible application for converting solar energy into carbon-free chemical fuel via water splitting or by oxidizing cheap and abundant compounds [1, 2]. For instance, a vast amount of hydrogen sulfide (H₂S) is contained in many natural gas wells, which requires a new economically viable and environmentally-friendly route to convert it [3]. Photocatalysis of H₂S splitting has tremendous benefits over the conventional Claus process because H₂ can be recovered as an advantageous product at refinery sites [4, 5]. The photocatalytic efficiency determines the area of the solar reactor, which is directly correlated with the capital cost of the photocatalytic system. Using solar energy as a sustainable energy source, visible light responsive photocatalysts are essential to make the process economically feasible.

Binary chalcogenide nanocrystals are good candidates for visible light photocatalysts for H₂ evolution from S²⁻ containing solution. For this purpose, CdS has been widely examined [6-9]. Li and coworkers reported unprecedented quantum efficiency (QE) in the visible light region (~90% at 420 nm) [10]. The CdS photocatalyst, however, absorbs a limited portion of visible light, i.e., up to 550 nm. Knowing the required thermodynamics of H₂S splitting, i.e., 0.17 eV at standard temperature and pressure, extended visible-light utilization must be considered. The theoretical maximum rate of H₂ production per hour (at 100% QE) for the photocatalyst varies from 0.045 m³-H₂ m⁻² (absorption edge of 550 nm) to 0.114 m³-H₂ m⁻² (absorption edge of 800 nm). It is therefore challenging to reduce the bandgap while maintaining high QE, although the thermodynamic driving force for redox reactions decreases at narrower bandgaps.

In this context, Kudo and coworkers reported new approaches for bandgap engineering by preparing ternary and quaternary metal sulfide photocatalysts [11, 12]. Unlike binary chalcogenide, these nanocrystals have high flexibility for tuning the band gap without relying on toxic elements [13]. For instance, we prepared CuGa₂In₃S₈ nanocrystals that can absorb light up to 700 nm using a facile hot injection method [14]. In this paper, copper-gallium-indium-sulfide (CGIS) nanocrystals with different stoichiometry, i.e., CuGa_xIn_{5-x}S₈, where x = 0, 1, 2, 3, 4 and 5, were synthesized and investigated for visible light driven H₂ evolution from aqueous solutions that contain sulfide/sulfite ions. With 1.0 wt.% Ru as co-catalyst, the H₂ evolution rate over CuGa₂In₃S₈ had the highest activity. By depositing CGIS nanocrystals on TiO₂ via a unique

solvent-induced method, enhanced photocatalytic H₂ evolution activities were observed at low CGIS loadings. This enhancement was due to the synergistic effect between CGIS and TiO₂ or the improved dispersion and optical properties.

2. Experimental Section

2.1. Preparation of copper-gallium-indium-sulfide (CGIS) nanocrystals

The CuGa_xIn_{5-x}S₈ nanocrystals, where x = 0, 1, 2, 3, 4 and 5, were prepared by a hot-injection method, as previously reported, with modification [14]. Briefly, trace metals of copper(II) acetylacetonate, gallium(III) acetylacetonate, and indium(III) acetylacetonate with the desired ratio were dissolved in 15 mL of oleylamine (70%, Aldrich, technical grade) in a four-necked, round-bottomed flask and stirred at RT for 30 min under an Ar atmosphere. The solution was then heated to 120 °C and maintained at this temperature for 1 h to remove water. The temperature was increased to 150 °C, and 1-dodecanethiol (Sigma–Aldrich) was injected rapidly into the solution under an Ar atmosphere with continuous stirring. The temperature of the solution was maintained at 150 °C for 30 min before it was increased gradually to 285 °C over a period of 30 min. After 24 h, the mixture was cooled, and the nanocrystals were isolated by centrifugation and washed thoroughly with ethanol/hexane (50% v/v). The particles were then dried in a vacuum oven at 45 °C.

2.2. Deposition of CGIS onto the TiO₂ surface

The desired amount of CGIS was dispersed in toluene, followed by the addition of 0.5 g of TiO₂ P25 and sonication for 5 min. The resulting suspension was continuously stirred for 5 h, followed by the addition of 200 mL of ethanol. Then, the CGIS-modified TiO₂ was separated by centrifuge and washed with ethanol three times. The obtained materials were dried at 40 °C in a vacuum oven at 45 °C and were denoted as x-CGIS/TiO₂, where x is the wt% of CGIS, x = 1, 5, 10, 25, 50, and 75 wt.%.

Characterization. Diffuse reflectance spectroscopy (DRS) was performed with a JASCO (V-670) spectrophotometer equipped with a 60 mmØ integrating sphere. A USRS-99-010 labsphere was employed as a reflectance standard. The XRD patterns of the Cu–Ga–In–S nanocrystals were collected on a Bruker D8 Advance diffractometer (DMAX 2500) operating with a CuKα energy source at 40 kV and 40 mA. High-resolution transmission electron microscopy (HRTEM) was

performed at 300 kV on a TITAN G2 80-300 ST from FEI. Photoluminescence (PL) spectra were measured using a Fluoromax-4 spectrofluorometer (HORIBA Scientific). XPS analysis was performed by using an AMICUS/ESCA 3400 KRATOS instrument equipped with Mg anodes at 12 kV and 10 mA. A prominent maximum peak of C1s at 284.5 eV was taken as the reference to calibrate the XPS spectra.

2.3. Photocatalytic test

The photocatalytic H₂ evolution assessment of the prepared CGIS deposited onto TiO₂ photocatalysts was performed with a Pyrex top-irradiation reaction vessel connected to a glass closed-gas circulation system and a gas chromatograph (Shimadzu 5A). In a typical run, the photocatalyst powder (0.025 g) was dispersed in Na₂S/Na₂SO₃ aqueous solution (25 mL) by sonication. The suspension was poured into the photoreactor, and the desired amount of co-catalyst (i.e., Ru as RuCl₃·xH₂O (Ru 38–40%) aqueous solutions) was added. The photoreactor was then sealed and connected to the circulation system. After the photoreactor was evacuated and Ar was introduced several times, the photoreactor was irradiated using a 300 W Xe arc lamp adapted with a wide band-pass filter (MAX-303, Asahi Spectra, 385-740 nm) or narrow band-pass filters. The photon distribution of the band-pass filters was measured using a spectroradiometer (EKO, LS-100) and is presented in Figure S1. The apparent quantum efficiency (AQE) under white and monochromatic light was calculated as the rate of H₂ evolution (μmol h⁻¹) multiplied by two, divided by the incident photon flux and the illuminated area.

3. Results and Discussion

CGIS nanocrystals with different Ga/In ratios, i.e., CuGa_xIn_{5-x}S₈, where x = 0, 1, 2, 3, 4 and 5, were synthesized and investigated for photocatalytic H₂ production. Figure 1 displays the diffuse reflectance spectra of the prepared CGIS nanocrystals with different compositions. The spectra are consistent with the observed color change of the isolated powders with increasing gallium content, going from black for CuIn₅S₈ to yellow for CuGa₅S₈. Direct determination of the bandgap from the absorbance onset indicates that CuIn₅S₈, where x = 0, and CuGa₅S₈, where x = 5, exhibit bandgap values of 1.4 and 2.4 eV, respectively, consistent with the reported bandgap

values for stoichiometric CuInS_2 and CuGaS_2 , respectively [15, 16]. By controlling the gallium content in the CGIS nanocrystals, the bandgap of the prepared materials can be tuned, as shown in Figure 1. From the XRD patterns presented in Figure 2, $\text{CuGa}_x\text{In}_{5-x}\text{S}_8$ nanocrystals where $x = 1$ and 2 , exhibit four prominent peaks at $2\theta = 21.5, 27.5, 47.6,$ and 56.2 . These peaks are in good agreement with the structure for the $\text{AgGa}_2\text{In}_3\text{S}_8$ reference pattern (PDF 01-070-8366), indicating that they have a layered structure with hexagonal crystal packing [17]. For $\text{CuGa}_x\text{In}_{5-x}\text{S}_8$ nanocrystals, where $x = 3$, major diffraction peaks for CGIS nanocrystals are observed at 2θ values of $28.9, 56.5,$ and 47.8 , indicating the formation of CGIS nanocrystals with zincblende structure [18], whereas at higher gallium content, i.e., where $x = 4$ and 5 , the XRD patterns of the CGIS nanocrystals showed major diffraction peaks at 2θ values of $27.6, 29.2, 31.2, 40.4, 48.8, 52.6,$ and 57.8 , with peak positions well-matched with the powder diffraction data reported for the wurtzite structure [19, 20].

Please insert Figures 1 and 2 here

To investigate the correlation between light harvesting competency and photocatalytic activity, the rates and AQE of photocatalytic H_2 evolution over 1.0 wt.% Ru-loaded CGIS nanocrystals were measured under visible light illumination and are presented in Table 1. The CGIS nanocrystals with $\text{CuGa}_2\text{In}_3\text{S}_8$ stoichiometry showed the highest activity; however, these nanocrystals absorb a comparable or even lesser amount of photons than CGIS nanocrystals, with $x = 0, 1, 3, 4,$ and 5 , as can be concluded from the diffuse reflectance spectra presented in Figure 1, assuming that the nanocrystals scatter light with the same ratio. By comparing the photocatalytic activities and the corresponding structures, it can be concluded that the CGIS with layered structure exhibits the highest activity. Many photocatalysts with a layered structured have been reported, and this anisotropic crystal structure and associated distinctive charge mobility for electron and hole along with different crystal orientation had positive effects on effective charge separation and resultant photocatalytic activity [11]. The interlayer space is even proposed to act as an active sites for the photocatalytic process [11].

It is desirable to enhance the photocatalytic activity while reducing photocatalyst loading. Thus, the deposition of the most active CGIS nanocrystals, i.e., $\text{CuGa}_2\text{In}_3\text{S}_8$, onto the TiO_2 surface was investigated. The loading was performed using a facile and simple method based on the fact that the as-prepared CGIS nanocrystals are decorated with 1-dodecanethiol and thus can be readily dispersed in nonpolar solvents, such as toluene. The dispersion of CGIS nanocrystals

in toluene followed by the addition of TiO₂ accompanied by the addition of a polar solvent, such as ethanol, induces the deposition of CGIS nanocrystals onto the surface of TiO₂, as confirmed by the TEM analysis (see Figure 3). By comparing the TEM images of bare (images a and c) and CGIS deposited on TiO₂ P25 (images b and d), the deposition of CGIS onto the TiO₂ surface can be confirmed. The existence of the CGIS nanocrystals was confirmed by the EDS analysis, as shown in Figure S2. The optical properties of the CGIS/TiO₂ photocatalysts, where the weight percentages of CGIS were 1.0, 5.0, 10, 25, 50, and 75, were also measured and are presented in Figure 4. The results indicated that the absorbance of the CGIS/TiO₂ materials in the visible light range increases with increasing the CGIS loadings, indicating the successful loading of the CGIS nanocrystals. It is worth mentioning that Ru sulfide precipitates were formed when Ru precursor was added to the Na₂S/Na₂SO₃ aqueous solution. XPS measurements confirmed the formation of RuS_x (see Figure S3). As can be seen in Figure 3, CGIS completely covers the surface of TiO₂. The Ru sulfide species was deposited on the CGIS outer surface and acted as a co-catalyst, consistent with the recent literature [21], although we failed to identify Ru species in TEM images probably due to their low contrast between Ru and CGIS material.

Please insert Figure 3 and 4 here

Figure 5 shows the time courses of the photocatalytic H₂ evolution from 0.05 mol L⁻¹ sodium sulfide/0.3 mol L⁻¹ sodium sulfite aqueous solutions employing CGIS/TiO₂ photocatalysts. The loading of the photocatalyst, including TiO₂, was kept constant at 1.0 g L⁻¹. The rate of the H₂ evolution increased with increasing the amount of CGIS deposited onto the surface of TiO₂, indicating that the CGIS material is the photoactive part. This behavior agrees well with the light absorbance characteristics presented in Figure 4. For comparison, the time courses of the photocatalytic H₂ evolution over bare TiO₂ and bare CGIS are also measured and presented in Figure 5. TiO₂ is a wide bandgap semiconductor and does not absorb visible light, thus exhibiting negligible activity, as shown in Figure 5. Because TiO₂ does not contribute to photocatalytic H₂ evolution under the current conditions, it is worth normalizing the amount of evolved H₂ per the amount of CGIS nanocrystals supported on the TiO₂ surfaces to compare the activities of bare CGIS nanocrystals and CGIS nanocrystals deposited on TiO₂. However, the amount of evolved H₂ does not linearly depend on the amount of the photocatalyst employed; thus, the normalization of the amount of evolved H₂ per the amount of used photocatalyst results in improved rate per gram of photocatalyst. To avoid overestimation, a comparison should be

performed in the range where the photocatalytic H₂ evolution rate increases with an increasing amount of photocatalyst, i.e., before saturation. To define this range, the effect of the bare CGIS photocatalyst loading on the H₂ evolution rate was investigated and is presented in Figure 6. The results showed that under the current conditions, the rate of H₂ evolution increases almost linearly as a function of photocatalyst loading up to 25 mg per 25 mL (i.e., 1.0 g L⁻¹); then, the rate levels off and remains almost constant.

Please insert Figure 5 and 6 here

The rates of H₂ evolution over CGIS/TiO₂ photocatalysts were plotted against the amount of CGIS supported on TiO₂ and are presented in Figure 6. Figure 6 shows that the amount of the CGIS to reach the plateau of H₂ evolution rate is reduced to half when using TiO₂ as a support; the rate of H₂ evolution is comparable to that observed over bare CGIS when the amount is doubled. The enhancement is more substantial at lower CGIS loadings on TiO₂. The enhanced photocatalytic activity observed when using CGIS/TiO₂ photocatalysts compared bare CGIS nanocrystals can be explained by the enhanced electron transfer between CGIS and TiO₂, the improved dispersion of the photocatalyst powder in the solution and the improved optical properties in the presence of TiO₂. From a thermodynamic point of view, the conduction band edge of TiO₂ is positioned at -0.2 V vs. RHE [22], whereas the conduction band edge of CGIS is positioned at -0.6 vs. RHE at pH 12 [14]. Thus, the conduction band edge of CGIS is approximately 0.4 eV more negative than that of TiO₂, indicating potential electron transfer from CGIS to TiO₂ without back electron transfer, which may lead to better charge carrier separation and thus to an increase in photocatalytic activity, as is commonly encountered in the case of anatase/rutile mixtures [23-25] and CdS-loaded TiO₂ [26, 27]. However, it is reasonable to consider that, in our experiment, the improved charge separation is unlikely the reason for this finding because the rate at the plateau in terms of photocatalyst amount (saturation) gave similar values for bare and supported CGIS photocatalysts. Therefore, electron transfer is not the cause of this rate enhancement. As expected, the photoluminescence (PL) spectra of bare CGIS and CGIS/TiO₂ show negligible differences (see Figure S4). The TiO₂ nanoparticles scatter light, which influences the total path of the visible light in the photoreactor. To further rationalize the benefit of the deposition of CGIS nanocrystals onto the TiO₂ surface using the solvent-induced deposition method, the CGIS nanocrystals were tested together with TiO₂ by physical mixing. The photocatalytic H₂ evolution measurements indicated that the rate of photocatalytic H₂

evolution using CGIS-TiO₂ photocatalyst via physical mixing was not significantly improved (see Figure S5), excluding a strong contribution of light management in the photoreactor in the presence of TiO₂. Therefore, the dispersion of CGIS in toluene followed by the addition of ethanol creates a better dispersion of the CGIS nanocrystals onto the TiO₂ particles, as evident from the TEM images (Figure 4). For comparison, the CGIS was supported on SiO₂ nanoparticles (~20 nm spherical powder) by the solvent-induced deposition method. No prominent improvement was achieved with SiO₂, compared with TiO₂ (see Figure S5), which may suggest that the synergistic effect between CGIS nanocrystals closely located on TiO₂ contributes to the improved photocatalytic H₂ evolution activity. This may be a specific interaction between CGIS and TiO₂, but further examination to determine the exact cause is required. The AQE of H₂ evolution over 50 wt.% CGIS loaded TiO₂ was measured under semi-monochromatic irradiation using band-pass filters and is presented in Figure 7. For comparison, the diffuse reflectance spectrum of bare CGIS is also shown in Figure 7. The onset of the action spectrum is in good agreement with the diffuse reflectance spectrum, which indicates that photocatalytic H₂ evolution proceeds through the excitation of the CGIS nanocrystal band gap.

Conclusions

In conclusion, copper-gallium-indium-sulfide (CGIS) nanocrystals with different Ga/In ratios were synthesized and investigated for visible-light-driven H₂ evolution from aqueous solutions that contain sulfide/sulfite ions. The Cu₂Ga₂In₃S₈ showed the highest activity among the different prepared CGIS nanocrystals. A unique, solvent-induced deposition method for depositing CGIS nanocrystals onto a TiO₂ surface was developed. The as-prepared CGIS nanocrystals are decorated with 1-dodecanethiol and can be readily dispersed in nonpolar solvents, such as toluene. The dispersion of CGIS and TiO₂ in toluene followed by the addition of polar solvent, such as ethanol, induces the deposition of CGIS onto the surface of TiO₂. The CGIS nanocrystals supported on TiO₂ showed an enhanced rate based on the photocatalyst amount when utilizing a small quantity of the CGIS materials photocatalyst. This enhancement is explained by the improved dispersion and optical properties of the photocatalyst materials in the photoreactor. For large scale application, it is desirable from the economic point of view to achieve H₂ evolution rates with reduced photocatalyst amounts.

Acknowledgments

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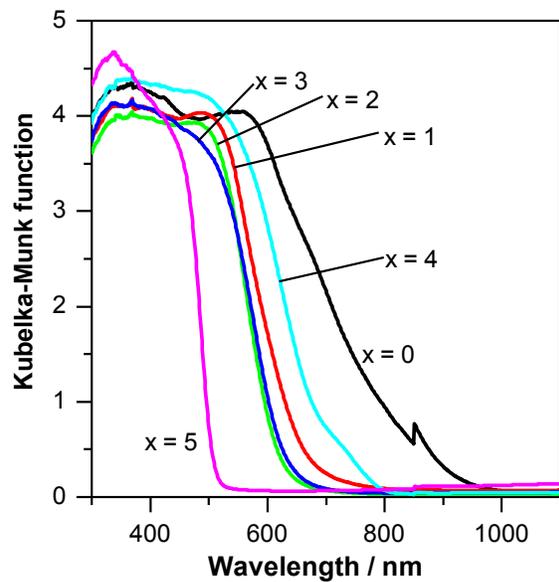


Figure 1. Diffuse reflectance spectra of $\text{CuGa}_x\text{In}_{5-x}\text{S}_8$ nanocrystals, where $x = 0, 1, 2, 3, 4,$ and 5 .

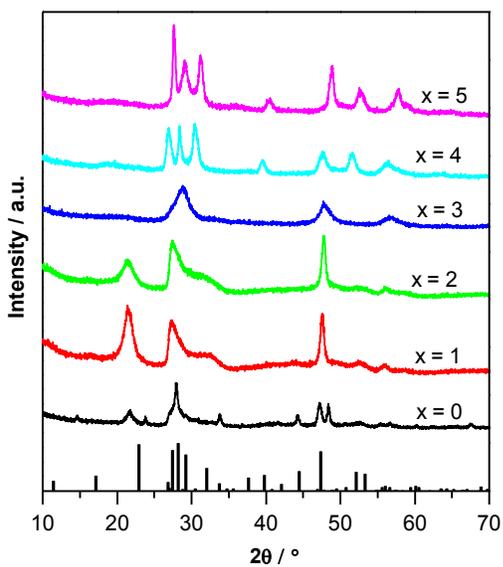


Figure 2. XRD patterns of $\text{CuGa}_x\text{In}_{5-x}\text{S}_8$ nanocrystals, where $x = 0, 1, 2, 3, 4,$ and 5 .

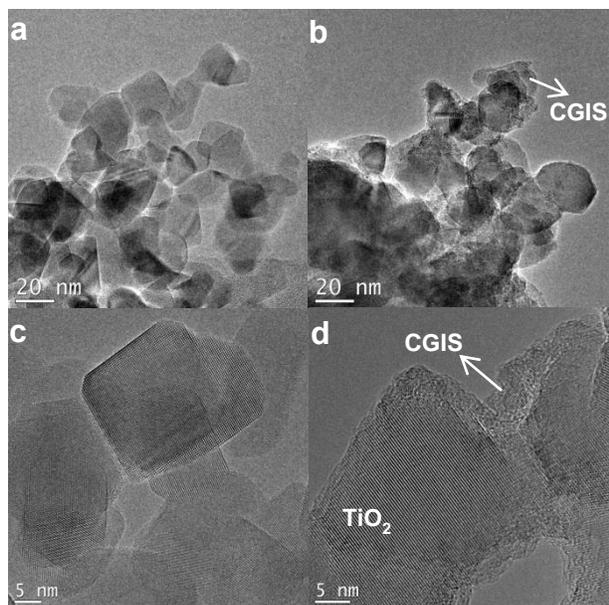


Figure 3. TEM images of bare TiO₂ p25 (a, c) and CuGa₂In₅S₈ deposited onto TiO₂P25 (b, d) at low and high magnifications.

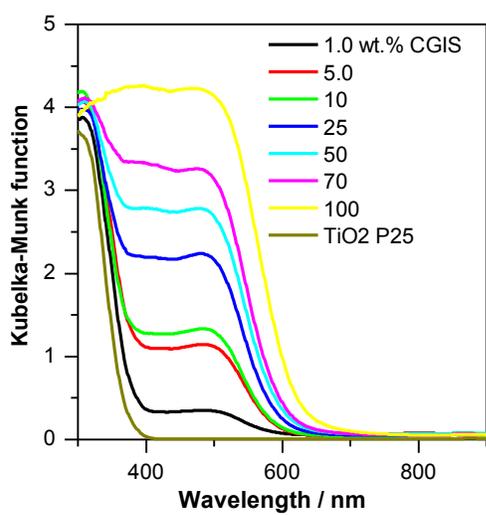


Figure 4. Diffuse reflectance spectra of CuGa₂In₃S₈ nanocrystals deposited onto TiO₂.

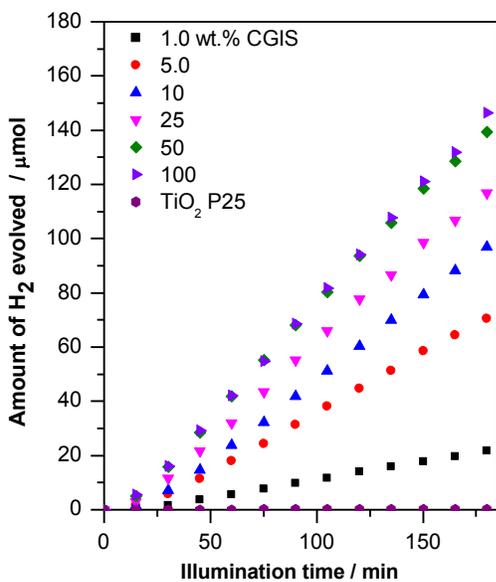


Figure 5. Time-course of the photocatalytic H₂ evolution over 1.0 wt.% Ru-loaded CuGa₂In₃S₈ nanocrystals deposited onto TiO₂. For comparison, bare TiO₂ and bare CGIS are also presented.

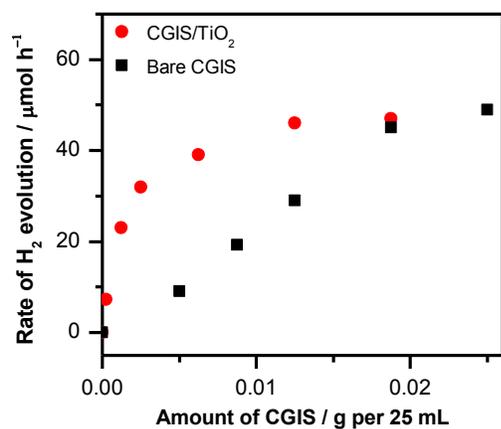


Figure 6. Effect of the amount of CGIS nanocrystals on the rate of H₂ evolution (■) bare and (●) deposited onto the TiO₂ surface.

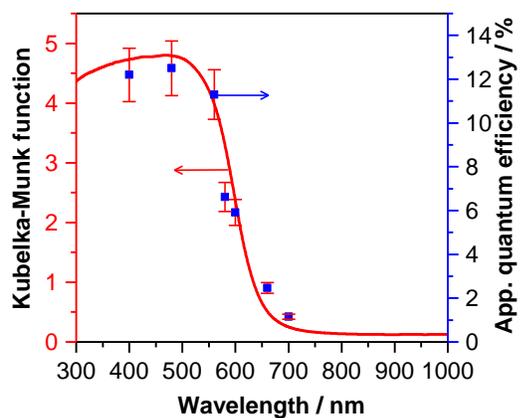


Figure 7. Action spectrum of H₂ evolution over 50 wt.% CGIS nanocrystals-loaded TiO₂. Conditions: Na₂S (0.05 mol L⁻¹)/Na₂SO₃ (0.3 mol L⁻¹) aqueous solution, 1.0 wt.% Ru co-catalyst. The diffuse reflectance spectrum of CGIS nanocrystals is included for comparison.

Table 1. Rates (R_{H_2}) and AQE of photocatalytic H₂ evolution from 0.05 mol L⁻¹ sodium sulfide/0.3 mol L⁻¹ sodium sulfite aqueous solutions over 1.0 wt.-%-loaded CuGa_xIn_{5-x}S₈ photocatalysts under white light irradiation (photon flux = 1.19×10³ μmol cm⁻² h⁻¹).

x in CuGa _x In _{5-x} S ₈	R_{H_2} (μmol h ⁻¹)	AQE (%)
0	2.3	0.38
1	19.8	3.32
2	50.6	8.48
2.5	22.8	3.82
3	16.7	2.80
4	28.5	4.78
4.5	10.5	1.76
5	3.2	0.54