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Nanocomposite for Photocatalytic Hydrogen Production and Method for its Preparation

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NANOCOMPOSITE FOR PHOTOCATALYTIC HYDROGEN PRODUCTION AND METHOD FOR ITS PREPARATION

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See application file for complete search history.

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ABSTRACT

A novel M—Pd—Cr2O3 (M—Pt, Ru, Rh, Os, Au and Ag) nanocomposite cocatalysts and its preparation method. The cocatalysts loaded on Cds photocatalyst enhances the photocatalytic activities toward H2 evolution from aqueous solutions (NH4)2SO4, a regenerable electron donor, under sunlight radiation. An embodiment provides a new and facile method and system for the preparation of M—Pd—Cr2O3 nanocomposite cocatalysts at room temperature. Pd—Cr2O3 loaded Cds photocatalyst has higher hydrogen evolution activity than that of a plain Pd metal loaded Cds and its performance is comparable to that of Pt/Cds photocatalyst. Formation of a Pd—Cr2O3 composite with reduced size of nanoparticles results in an increase in the photocatalytic activity for H2 evolution.

12 Claims, 10 Drawing Sheets
Fig. 1
Fig. 2

- X-axis: Amount of chromium oxide, wt%
- Y-axis: Photon efficiency (P.E.), %

The graph shows the relationship between the amount of chromium oxide and photon efficiency.
Photocatalyst composition
- Pd/\text{Cr}_2\text{O}_3\) doped CdS (0.4 wt% Pd & 0.1 wt% \text{Cr}_2\text{O}_3)
- Pt doped CdS (0.5 wt% Pt)

$H_2$ production rate, mL/min
- Pd/\text{Cr}_2\text{O}_3\) doped CdS: 2.50 mL/min
- Pt doped CdS: 2.47 mL/min

Elapsed time, min

Fig. 3
Fig. 4
Fig. 5a
Fig. 5b

Rate of H₂ evolution (ml/min)

Pt (wt%)
1. \( \text{H}_2\text{PdCl}_4 - \text{PVP} \)

2. Colloidal \( \text{Pd} \) formed by \( \text{H}_2\text{PdCl}_4 - \text{PVP} \)

3. \( \text{H}_2\text{PdCl}_4 - \text{Cr(NO}_3)_3 - \text{PVP} \)

4. Colloidal metal formed from \( \text{H}_2\text{PdCl}_4 - \text{Cr(NO}_3)_3 - \text{PVP} \)

5. \( \text{Cr(NO}_3)_3 - \text{PVP} \) solution

6. \( \text{Cr(NO}_3)_3 - \text{PVP} \) solution with \( \text{NaBH}_4 \) added

Fig. 6
Fig. 7a

$d_{AV} = 11\text{nm}$

Fig. 7b

$d_{AV} = 37\text{nm}$
Fig. 8
NANOCOMPOSITE FOR PHOTOCATALYTIC HYDROGEN PRODUCTION AND METHOD FOR ITS PREPARATION

This application is a continuation-in-part of U.S. application Ser. No. 12/267,569 filed on Nov. 8, 2008 which claimed the benefit of priority to U.S. Provisional Application No. 60/986,820 filed on Nov. 9, 2007 and was funded in part by the National Aeronautics and Space Administration (NASA)—Glenn Research Center under contract number NAG3-2751, and claims the benefit of priority to U.S. Provisional Application No. 61/156,719 filed on Mar. 2, 2009.

FIELD OF THE INVENTION

This invention relates to hydrogen production and, in particular, to systems and methods for preparation of a Pd—Cr₂O₃ loaded CdS co-catalyst as a cocatalyst for solar photocatalytic hydrogen evolution on CdS.

BACKGROUND AND PRIOR ART

Photocatalytic water splitting has been studied extensively for converting solar energy into clean hydrogen fuel (H₂). The development of photocatalysts that can be excited by photons having sufficiently long wavelengths (e.g., greater than 400 nm) is a prerequisite to efficient solar energy conversion and storage. The solar energy conversion efficiencies of the photocatalysts developed to date for direct water splitting has been low, typically, less than 3% under visible light irradiation. However, indirect photocatalytic splitting of water is also possible using sacrificial electron donors. This method of water splitting is viable only if a closed-loop scheme (i.e. a chemical cycle) can be envisaged that allows continuous regeneration of the sacrificial agent.

Florida Solar Energy Center, a research institute of the University of the Central Florida, has proposed a class of efficient, solar driven thermochemical water splitting cycles, in which solar photonic energy is used for the production of hydrogen from an aqueous ammonium sulfite solution, while solar thermal energy is employed to produce oxygen. This unique approach of utilizing the total solar radiation spectrum may enhance the efficiency of solar to hydrogen energy conversion. Previously, a new class of solar hybrid thermo-photocatalytic water splitting cycles that utilize ammonium 45 having sufficiently long wavelengths (e.g., greater than 400 nm) is a prerequisite to efficient solar energy conversion and storage.

In a closed water splitting cycle, the overall energy conversion efficiency depends on the efficiencies of both the H₂ and O₂ production steps. The thermolytic processes represented by reactions (3) and (4) are fairly efficient due to the high reaction temperatures involved. Therefore, the energy conversion efficiency of the photocatalytic H₂ production step represented by the reaction (1) dictates the overall cycle efficiency for converting solar energy to that stored as chemical energy in hydrogen.

Although visible-light induced photocatalytic activity of CdS for H₂ production from aqueous solutions of alkali metal sulfites and sulfides has been known since the early 1980s, in most cases, Pt (alone or in combination with other metals) was used as a cocatalyst with the aim of enhancing the H₂ evolution rate. Recently, a number of composite cocatalysts with metal/oxide (core/shell) structure, such as Ni/NiO and Rh/Cr₂O₃, have been shown to impart higher catalytic activity than that of only metal or metal oxide cocatalysts.

Methods for the preparation of photocatalysts fall into two broad areas, namely: impregnation and photodeposition. In the former impregnation method, a high temperature activation process (300-500°C) is often needed. The latter photodeposition technique has been primarily used for the deposition of noble metal particles. Neither of these two methods is particularly useful in preparing composite cocatalysts containing a metal oxide.

SUMMARY OF THE INVENTION

A primary objective of the invention is to provide a reproducible method and system for the development of Pd—Cr₂O₃ nanocomposite co-catalyst. The Pd—Cr₂O₃ loaded on CdS main photocatalyst shows a higher photocatalytic activity than that of a plain Pd metal loaded catalyst.

A secondary objective of the invention is to provide a reproducible method and system for the preparation of a co-catalyst with reduction in the particle size.

A third objective of the invention is to provide methods and systems for the formation of a composite co-catalyst Pd—Cr₂O₃ for the increase in the hydrogen evolution rate.

A fourth objective of the present invention provides a Pd—Cr₂O₃ based nanocomposite as a co-catalyst that can be used to replace a more expensive Pt based co-catalyst for the photocatalytic production of hydrogen from a regenerable ammonium sulfite reagent.

A fifth objective of the present invention provides a method and system to use a polymer stabilization effect for the synthesis of cocatalyst nanoparticles. Furthermore, the technology of the present invention (the modified NaBH₄ reduction method) does not require a catalyst pre-treatment process as do conventional thermal deposition methods. A first embodiment provides a method and system for preparation of Pd—Cr₂O₃ nanocomposite particles that includes the steps of mixing H₂PdCl₄ and Cr(NO₃)₃ as a precursor solution, reducing the palladium chloride with aqueous NaBH₄ to form Pd colloidal solution, adding cadmium sulfide (CdS) powder to the Pd colloidal solution with vigorous stirring to disperse the powder and adding (NH₄)₂SO₃ solution to as prepared solution to form Pd—Cr₂O₃ nH₂O particles that are loaded on...
Cds surface forming Pd—Cr₂O₃/CdS photocatalyst. The method can also include adding and mixing polyvinylpyrrolidone (PVP) to the H₂PdCl₄ and Cr(NO₃)₃ solution prior to the reducing step to prevent the agglomeration of Pd nanoparticles formed during the reduction step.

The reacting step can include the steps of co-loading Pd and Cr₂O₃ onto the surface of CdS photocatalyst to increase the H₂ evolution rate and the adding CdS step can include the step of adding of chromium oxide in a range of on 0.05 wt% to approximately 0.1 wt% to improve the photocatalytic oxidation of aqueous ammonium sulfite for hydrogen evolution. In a preferred embodiment, the CdS content to approximately 0.5 g. Also the amount of Pd can be increased to approximately 0.4 wt% and/or Pt can be added to the Pd—Cr₂O₃/CdS photocatalyst to form a Pd—Pt—Cr₂O₃/CdS composite photocatalyst or at least one noble metal selected from a group consisting of Ru, Rh, Os, Au and Ag can be added to the Pd—Cr₂O₃ cocatalyst to form metal-Pd—Cr₂O₃ nanocomposite cocatalysts to improve the solar hydrogen evolution rates.

Another facile method for production of Pd metal colloid particles includes mixing H₂PdCl₄ and Cr(NO₃)₃ solution as a precursor, adding PVP to the precursor solution, mixing thoroughly and reducing the precursor solution with aqueous NaBH₄ solution to form a Pd colloidal solution. Cadmium sulfide (CdS) powder can be added to the resulting solution while stirring to disperse CdS powder. In this method, the reducing step can include adding 1.0 M (NH₄)₂SO₃ solution to as prepared solution to form Pd—Cr₂O₃/nH₂O particles that are loaded on CdS surface forming Pd—Cr₂O₃/CdS photocatalyst. An alternative method to prepare a Cr₂O₃ modified Pd metal colloid as a cocatalyst to produce hydrogen from aqueous ammonium sulfite solutions as electron donors including providing solutions of H₂PdCl₄ and Cr(NO₃)₃, adding PVP to the mixture of H₂PdCl₄ and Cr(NO₃)₃ to prevent aggregation of Pd nanoparticles, reducing the solution of H₂PdCl₄ and Cr(NO₃)₃, with NaBH₄ solution to produce nanosized Pd colloidal solution, adding CdS powder to the Pd colloidal solution while stirring vigorously and adding the resulting solution to an aqueous solution of (NH₄)₂SO₃ to produce Pd—Cr₂O₃/CdS photocatalyst for hydrogen production from (NH₄)₂SO₃ photoolyte.

Yet another method and system for preparing a catalyst for hydrogen production includes the steps of providing palladium chloride (PdCl₂) as a precursor, reducing the precursor with sodium borohydride (NaBH₄) for the preparation of nanosized palladium metal colloid and adding aqueous Cr(NH₃)₃ solution into the Pd colloid, adding CdS semiconductor powder to the mixture of Pd colloid and Cr(NH₃)₃ solution, adding aqueous (NH₄)₂SO₃ solution to as prepared solution to form Pd—Cr₂O₃/nH₂O particles that are loaded on CdS surface forming Pd—Cr₂O₃/CdS photocatalyst and immobilize Pd—Cr₂O₃ nanoparticles onto the surface of CdS main photocatalyst forming co-catalyst loaded CdS photocatalyst, wherein the activity of Pd/CdS is significantly enhanced by addition of Cr₂O₃ nanocomposites.

A second embodiment provides a nano composite cocatalyst for solar hydrogen production that is Pd—Cr₂O₃ loaded CdS co-catalyst for solar hydrogen production. At least one noble metal selected from a group consisting of Pt, Ru, Rh, Os, Au and Ag can be added to the Pd—Cr₂O₃ cocatalyst to form metal—Pd—Cr₂O₃ nanocomposite cocatalysts.

Further objects and advantages of this invention will be apparent from the following detailed description of preferred embodiments which are illustrated schematically in the accompanying drawings.
Further discussion), for simplicity, hereafter, it will be referred as CrO₂. In order to prevent agglomeration of nanoparticles formed during the reduction of H₂PtCl₆ in the presence of Cr(NO₃)₃ solution, a small amount of polyvinylpyrrolidone (PVP) was added to the solution and mixed thoroughly. This was followed by addition of 0.5 g of cadmium sulfide (CdS) powder to the solution while stirring vigorously, forming Pd–CrO₂ cocatalyst loaded CdS photocatalyst (Pd–CrO₂)/CdS. The photocatalyst was then mixed with 285 ml of 1.0 M aqueous (NH₄)₂SO₄ solution that was used as the photolyte for photocatalytic hydrogen production. During the reaction, the change in pH of the photolyte was less than 0.1.

Fig. 1 is a graph showing the effect of Pd–CrO₂ loading on the rate of H₂ evolution from an aqueous 1.0 M ammonium sulfite solution. Note that the photocatalytic activity of pure CdS for hydrogen evolution was low—i.e. 0.46 ml/min. Furthermore, the CdS loaded with 0.1 wt % CrO₂ showed negligible activity for H₂ production (0.38 ml/min). When 0.4 wt % Pd was loaded on CdS, the H₂ evolution rate increased to 1.64 ml/min. Interestingly, when CdS was co-loaded with 0.4 wt % Pd and 0.05 wt % chromium oxide as (Pd–CrO₂)/CdS, the hydrogen evolution rate increased significantly (2.29 ml/min) corresponding to a photon energy conversion efficiency (P. E.) of about 18.3%. The efficiencies in this application were calculated using the spectrum ranging from 300 to 520 nm, which is different from that calculated based on the single light irradiation (420 nm). The efficiency defined in this manner is based on the practical application and can be used for solar energy conversion calculation directly.

Experimental results showed that increasing the CrO₂ content to 0.1 wt % further enhanced the H₂ evolution rate to 2.50 ml/min. This result indicates that by adding even small amounts of CrO₂ to the Pd particles, the P.E. for the photocatalytic oxidation of aqueous ammonium sulfite increases significantly. The optimum amount of chromium oxide loading appears to be about 0.1 wt % yielding a P.E. value of 20.0%. Increasing the chromium loading beyond 0.1 wt % resulted in a slight decrease in the P.E. values that in all likelihood was caused by a partial light blocking effect of CrO₂ particles.

It is known that noble metals (e.g. Pt, Pd, Ru, Rh, Ag, and Au) and some transition-metal oxides like NiO promote H₂ evolution from aqueous solutions of electron donors. Among noble metal promoters, Pt is known to be the most efficient. To determine the relative activity of Pd–CrO₂/CdS in comparison with Pt/CdS, cadmium sulfide particles were loaded with 0.5 wt % of Pt. The activity of Pt/CdS photocatalyst was measured under the same experimental conditions as those for the Pd–CrO₂/CdS photocatalyst. The results showed that CdS loaded with Pd–CrO₂ co-catalyst performed on a par with the Pt loaded CdS as shown in Fig. 2.

The experimental activities of the co-inventors leading to the novel co-catalyst and the preparation technique are discussed in the following paragraphs.

The materials and instruments used by the co-inventors during the experimental process included palladium chloride (PdCl₂, 99.99% purity), chromium nitrate (Cr(NO₃)₃, 99% purity) and ammonia sulfite ((NH₄)₂SO₄, 92% purity) were obtained from Sigma-Aldrich. Cadmium sulfide (CdS, 99.99% purity) was provided by Alfa Aesar. Sodium borohydride (NaBH₄, 98%) and polyvinylpyrrolidone (PVP, K30, [MW]avg=40,000) were acquired from Acros Organics and Fluka, respectively. All chemicals were used as received without further purification. High resolution transmission electron microscopy (HRTEM) analyses of the catalysts were carried out on a Philips EM 420 transmission electron microscope operated at 300 kV. UV-visible absorption spectra were recorded on a Shimadzu UV-2401 PC UV—Vis Recording Spectrophotometer.

Experimentally, in a typical synthesis, a CrO₂ modified Pd metal colloid was prepared by reducing a 1.5 ml aqueous solution of 1.25x10⁻⁵ M H₂PtCl₆ and 0.64x10⁻⁷ M Cr(NO₃)₃ with a few drops of NaBH₄ solution. Prior to the reduction a small amount of PVP was added to the mixture of H₂PtCl₆ and Cr(NO₃)₃ solution to prevent aggregation of Pd nanoparticles. The resulting solution contained nanosized Pd particles mixed with hydrous chromium oxide or chromic hydroxide (CrO₂–NH₄O). Approximately 0.5 g of CdS powder was added to the dark-brown Pd colloidal solution while stirring vigorously. This solution was then added to a 285 ml aqueous solution of 1.0 M (NH₄)₂SO₄ (total volume: 300 ml) and used as photolyte for hydrogen production. For the sake of comparison, a second batch of photolyte containing Pt-loaded CdS, (0.5 wt % Pt) photocatalyst was also prepared by similar method, using H₂PtCl₆ as a precursor solution.

Photocatalytic reactions were carried out in a photoreactor fitted with a quartz window (15 cm in diameter). 0.5 g of CdS powder, loaded with co-catalysts, was dispersed in approximately 300 ml aqueous solution of 1.0 M (NH₄)₂SO₄. A peristaltic pump was used to circulate the photolyte between a three-neck flask and the photoreactor. No stirring was used inside the photoreactor. A 1000 W diversion beam solar simulator (Newport/Oriel Corp.) equipped with an air mass (AM) 1.5 global filter served as the radiation source. Prior to the photocatalytic reaction, the (NH₄)₂SO₄ solution was purged with argon gas for one hour to remove all dissolved oxygen gas. The H₂ gas produced in the photoreactor was collected in a graduated cylinder by a water displacement method. In order to calculate photon efficiency of the process co-inventors used a calibrated OSM photo-spectrometer (OMS-100-UV/Vis, Newport/Oriel Corp.) equipped with a Sony CCD sensor for measuring the irradiance.

As to the efficiencies of photocatalytic hydrogen production, the definition of efficiency used in this description is different from that reported by other groups. The photon conversion efficiency (P.E.) of the photocatalyst toward H₂ production is defined as: P.E. = N_H2/N_P, Where, N_H2 and N_P refer to the number of photons utilized in generating hydrogen and total number of incident photons arriving on the photocatalyst surface, respectively. The absorption band of CdS extends from 300 nm to 520 nm. Therefore, N_H2 shown above is determined by integrating the photon flux within the wavelength band 300-520 nm.

The efficiency calculation for the present invention is closer to the solar radiation spectrum. The method of efficiency calculation based on integration over a wide range of wavelengths is an innovation that has not been previously employed and is the primary reason for the lower reported efficiencies of the present catalysts. To make a comparison, the quantum efficiency of hydrogen evolution at the 420 nm light over the present catalysts, Pd–CrO₂/CdS was calculated to be approximately 55.6% on the assumption that the light was irradiated at 420 nm. In contrast, the quantum efficiency from 300 to 520 nm is calculated to be about 20%. However, it should be pointed out that the efficiency calculation for the present invention is based on the practical application and is a real datum that can be used for solar energy conversion calculation directly.

Fig. 2 is a graph showing the effect of chromium oxide loading percentage on the activity of Pd–CrO₂/CdS photocatalyst performance with 300 ml of 1.0 M (NH₄)₂SO₄. It is noted that the photon efficiency (P.E.) of the photocatalyst using 0.4 wt % Pd loaded on 0.5 g of CdS was approximately

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The average particle size of the PVP-stabilized Pd nano-particles was approximately 4.1 nm and approximately 3.7 nm for the colloidal particles obtained from H₂PdCl₄-PVP solution and H₂PdCl₄-Cr(NO₃)₃—PVP solution, respectively. The differences in the average particle size and distribution for these two solutions implies that colloidal Pd formation is affected by the addition of Cr(NO₃)₃, which is in agreement with the UV-visible spectrometric measurements. The reduction in the size of Pd particles appears to be one of the reasons for the improved activity of Pd—Cr₂O₃/Cds photocatalyst that is affected by the size of the deposited cocatalyst particles. High Resolution TEM (HRTEM) images showed that Pd colloids exhibit clear crystal features involving single crystal, simple twin and multiple twin icosahedron or decahedron structures.

In the series of experiments previously described, the cocatalyst preparation procedure was modified such that Cr(NO₃)₃ was not preliminarily converted to chromium oxide, i.e., Cr(NO₃)₃ solution was directly added to the colloidal Pd solution followed by addition of CdS powder to the resulting mixture. Finally, the prepared solution was mixed with aqueous (NH₄)₂S₉O₃ solution and used as the photolyte in the photocatalytic H₂ production experiment. Thus, unlike previous Pd—Cr₂O₃ cocatalyst preparation for experiments, preparation leading to the present invention the Cr(NO₃)₃ was mixed with colloidal Pd solution without PVP addition and without co-reduction by NaBH₄. The addition of Cr(NO₃)₃ is unlikely to affect the particle size distribution and/or light absorbance characteristics of already formed colloidal Pd solution. But this method of photocatalyst preparation yielded a photocatalyst that showed relatively high activity generating 2.27 ml/min of hydrogen from (NH₄)₂S₉O₃—more than 1.64 ml/min H₂ obtained from the plain Pd/CdS (catalyst prepared from colloidal A) and slightly lower than 2.5 ml/min H₂ obtained from the Pd—Cr₂O₃/Cds (catalyst prepared using colloidal solution B). FIG. 4 shows that Pd/CdS with Cr(NO₃)₃ added shows much higher activity than that of Pd/CdS, although the activity is slightly lower than that of the Pd—Cr₂O₃/Cds prepared from H₂PdCl₄—Cr(NO₃)₃—PVP solution. The following data on Cr(III) ion —water equilibria may shed light on the nature of this experimental result:

\[
\text{Cr}^{3+} + \text{H}_2 \text{O} \rightarrow \text{Cr(OH)}^{2+} + \text{H}^+ \quad \text{pH}=4.0
\]

\[
\text{Cr(OH)}^{2+} + \text{H}_2 \text{O} \rightarrow \text{Cr(OH)}_2^{+} + \text{H}^+ \quad \text{pH}=5.7
\]

\[
\text{Cr(OH)}_2^{+} + \text{H}_2 \text{O} \rightarrow \text{Cr(OH)}_3^{+} + \text{H}^+ \quad \text{pH}=5.7
\]

Cr(NO₃)₃ exists as Cr³⁺ cations in the colloidal Pd solution at pH values lower than 2. Increasing the pH of the solution by adding aqueous (NH₄)₂S₉O₃ results in Cr⁴⁺ hydrolysis forming initially [Cr(OH)]⁴⁺, and then Cr(OH)₃ (or Cr₂O₃·3H₂O) precipitate at pH~8.3. The pH of 1.0 M (NH₄)₂S₉O₃ aqueous solution is in the range of 7.9 to 8.3 at room temperature and, at this pH range, Cr(NO₃)₃ will precipitate completely as Cr(OH)₃ onto and coat the Pd and CdS particles.

It was shown that almost 100% of the metal hydroxides can be deposited onto the surfaces of zeolites and their internal surfaces within the pore walls. Due to the residual positive charge of the Cr(OH)₃ particles they could potentially impart a charge to Pd nanoparticles as they form, thus preventing them from further aggregation to larger particles. This may explain why the deposition of Cr₂O₃·3H₂O onto Pd yields Pd—Cr₂O₃/Cds photocatalyst having enhanced hydrogen evolution activity. The lower activity of the photocatalyst prepared directly from Cr(NO₃)₃ compared to that of Pd—Cr₂O₃/Cds formed by pre-hydrolysis of Cr(NO₃)₃ implies that the photocatalyst activity is affected by the method employed in its preparation. Indeed, in the former...
case, Cr$_2$O$_3$ is deposited on the surface of Pd particles after they are already formed (i.e., the presence of Cr$_2$O$_3$ has no effect on the size of Pd particles). This experimental fact supports the co-inventors hypothesis that simultaneous formation of Pd and Cr$_2$O$_3$ nanocomposite particles during the reduction of Pd precursor and hydrolysis of Cr$_2$O$_3$ precursor by NaBH$_4$ yields much smaller particles than those prepared by consecutive synthesis of Pd and Cr$_2$O$_3$ particles.

New noble metal-Cr$_2$O$_3$ nano-composite cocatalysts can also be prepared using the above-described method. During experiments, the co-inventors prepared Pt—Pd—Ru—Rh—Ag—Au—Cr$_2$O$_3$ single and bi-metal nanocomposite cocatalysts that showed excellent H$_2$ production activities. FIG. 5a is a graph showing the effect of platinum loading on the photocatalytic activity of Pd—Cr$_2$O$_3$/CdS photocatalysts for H$_2$ evolution from aqueous ammonia sulfite solution and FIG. 5b is a histogram showing the rate of H$_2$ evolution as a function of Pt loading percentage. As shown in FIGS. 5a and 5b, addition of Pt further promotes the activity of Pd—Cr$_2$O$_3$/CdS for hydrogen evolution. Moreover, these cocatalysts and the methods for their synthesis can be combined with other bandgap photocatalysts, such as TiO$_2$ or solid solution based metal sulfide photocatalysts, for H$_2$ production or environmental remediation applications.

In summary, the present invention provides a facile method for preparation of novel efficient photocatalysts based on CdS supported Pd—Cr$_2$O$_3$ and Pd—Cr$_2$O$_3$—Pt nanocomposite cocatalysts for solar hydrogen production using (NH$_4$)$_2$SO$_4$ as a regenerative electron donor. The Pd—Cr$_2$O$_3$ loaded CdS photocatalyst shows a much higher hydrogen evolution rate than that of a plain Pd metal loaded CdS, having a photocatalytic activity that is comparable to that of the Pt/CdS photocatalyst. The observed enhancement in the photocatalytic activity of Pd—Cr$_2$O$_3$/CdS toward hydrogen evolution from ammonium sulfite is attributed to the formation of a catalytically active and relatively stable Pd—Cr$_2$O$_3$ nanocomposite cocatalyst on the surface of CdS particles with reduced particle size compared to plain Pd cocatalyst. In the experiments leading to the present invention, the feasibility of (NH$_4$)$_2$SO$_4$ regeneration from (NH$_4$)$_2$SO$_4$ by means of a series of thermochemical reactions is shown, which collectively allow water splitting via a closed loop, hybrid solar photo-thermochemical cycle.

As to the efficiencies of photocatalytic hydrogen production, the apparent differences between the experimental results in the present patent application and other literature results from three major factors: basic definitions, photocatalysis systems and photoreactor configurations.

Firstly, the quantum efficiency defined by other groups is calculated based on a single light irradiation at 420 nm. Referring to FIG. 8, the efficiency defined in this application is calculated using the spectrum ranging from 300 to 520 nm, which covers the entire absorption of the CdS main photocatalyst. The total number of photons ($N_p$) from 300 to 520 nm are calculated based on the following function:

$$N_p = \frac{t \times s \times I \times \Delta \lambda}{h c \lambda}$$

$$N_p = \int_{300}^{520} \frac{I \times \Delta \lambda \times s}{h c \lambda}$$

Where $t$, $s$, $I$, $h$, $\lambda$, and $c$ are radiation time (second), irradiated light area (photoreactor window area in cm$^2$), Avogadro’s number, Plank’s constant, light speed, light intensity (μW·cm$^{-2}$·nm$^{-1}$) at specific wavelength, and wavelength, respectively.

As shown in the formula above, the efficiency calculation is based on the solar radiation spectrum and is more realistic in terms of solar energy utilization than the prior art methods. As reported, the quantum efficiency of a photocatalytic reaction as a function of radiation wavelength is similar to that of the UV-vis absorption spectrum of the photocatalyst, meaning that the longer wavelength radiation results in lower efficiency. The efficiency calculation includes longer wavelength radiation, therefore, photocatalyst efficiencies calculated using our method are expected to be lower than those calculated using only 420 nm wavelength. For example, photocatalyst efficiency calculated based on wavelength ranging from 420 nm to 520 nm show much lower efficiencies for hydrogen production over CdS. However, it also include wavelengths from 300 nm to 420 nm photons (0.0019 mol photons irradiated in one hour), but compared to the number of photons from 420 nm to 520 nm (0.0087 mmol/hour), the shorter wavelength photons are about 21.8%.

In order to have a better understanding of the efficiency calculations based on the two definitions, the total number of photons is calculated based on a given photon energy and then calculate efficiencies based on 420 nm and on 300 to 520 nm. It was found that the quantum efficiency of hydrogen evolution based on 420 nm radiation over the present catalysts Pd—Cr$_2$O$_3$/CdS is 55.6%. In contrast, the efficiency based on 300 to 520 nm is only about 20%, over 2.5 times lower than that using the method of the present invention. The efficiencies described are based on the solar spectrum and can be directly used for solar energy conversion calculations.

The efficiency of a photocatalyst is associated with a photoreactor system. For example, hydrogen production via photo-oxidation of an aqueous sulfide (S$^{2-}$) is far more efficient than that of a sulfite solution based photoreaction over CdS based photocatalysts. On the other hand, although the highest reported quantum efficiency for hydrogen evolution from a sulfite solution reached 90% twenty years ago, the highest quantum efficiency for hydrogen evolution from an aqueous sulfite solution is only 35% at 436 nm. As mentioned previously, the method of the present invention achieves 55.6% of quantum efficiency, based on radiation at 420 nm, for hydrogen evolution over Pd—Cr$_2$O$_3$/CdS photocatalysts via photo-oxidation of aqueous ammonium sulfite solutions. This is the highest reported quantum efficiency resulting from an aqueous sulfite solution.

The other important issue related to the efficiency calculation is that the co-inventors used absorbed photons ($N_{p,a}$) for efficiency calculation. In this case, photon energy losses ($N_{p,n}$), such as light scattering, reflection and light absorption by the reactor walls, were neglected. This is a theoretical ideal condition. The co-inventors used photon energy passing through a photoreactor window as total photon energy received for the calculation. This total energy ($N_{p,r}$) takes into account all the light energy losses, and the efficiency calculated based on this method must definitely be lower than the ideal condition. The method is more realistic and can be used for process designs and cost estimations for solar water splitting.
The present invention provides a novel Pd—Cr₂O₃ co-catalyst with high efficiency, comparable to a Pt based co-catalyst, and a novel technique for the preparation of a nanosized non-platinum based composite using a simple, fast, and effective method. It has been shown that the novel method of the present invention can also be used to prepare other noble metal based catalysts. It has to be pointed out that although NaBH₄ reduction technology for preparation of Pt and Pd nanoparticles has previously been reported, the methods of the present invention is the first to modify the previously known method and apply the method of the present invention to the preparation of Pt and Pd based metals and alloys as co-catalysts for water splitting.

Prior art polymer stabilized technology can be used to synthesize nanosized metal particles. However, when the particles are small and stabilized in colloidal form, they are very difficult to deposit onto a main photocatalyst in the formation of an effective photocatalyst. The present invention provides a method wherein the solution’s pH has a significant effect on the stability of the nanosized metal or alloy particles. The experimental results have shown that metal particles and Cr₂O₃ can be loaded to CdS powder photocatalyst by increasing the pH of the reduced colloidal solution from approximately 2.0 to approximately 8.5. The UV-vis spectral analyses indicated that the particle loading efficiency (from colloidal particles to particles absorbed onto CdS surface) could reach up to 100%. Thus, the present invention provides a method that overcomes the polymer stabilization effect. Furthermore, the technology of the present invention (the modified NaBH₄ reduction method) does not require a catalyst pre-treatment process as do conventional thermal deposition methods.

The efficiency of a photocatalyst also depends on the photoreactor used. In the experiments, a passive stirring reactor with a photolyte as shallow as 10 mm was used. No internal stirring mechanism was applied. The advantages of this design are (1) only a small amount of photolyte is needed, thus saving the cost of the chemicals and (2) it is applicable for design of a practical system because mixing photocatalyst particles with an electrolyte in a large photochemical reaction is an engineering issue. The present invention successfully resolves this issue by introducing a passive mixing photoreactor design as shown in FIG. 9.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:
1. A method comprising the steps of:
   mixing H₃PdCl₄ and Cr(NO₃)₃ as a precursor solution;
   reducing the palladium chloride with aqueous NaBH₄ to form Pd colloidal solution;
   adding cadmium sulfide (CdS) powder to the Pd colloidal solution with vigorous stirring to disperse the powder; and
   adding (NH₄)₂SO₃ solution to as prepared solution to form Pd—Cr₂O₃, nH₂O particles that are loaded on CdS surface forming the (Pd—Cr₂O₃, nH₂O)/CdS photocatalyst.

2. The method of claim 1 further comprising the step of:
   adding mixing polyvinylpyrrolidone (PVP) to the H₃PdCl₄ and Cr(NO₃)₃ solution prior to the reducing step to prevent the agglomeration of Pd nanoparticles formed during the reduction step.

3. The method of claim 2 wherein the adding (NH₄)₂SO₃ solution step includes the step of:
   co-loading Pd and Cr₂O₃ onto the surface of CdS photocatalyst to increase the H₂ evolution rate.

4. The method of claim 1 further comprising the step of:
   adding Pt to the (Pd—Cr₂O₃, nH₂O)/CdS photocatalyst to form a (Pt—Pd—Cr₂O₃, nH₂O)/CdS composite photocatalyst.

5. The method of claim 1 further comprising the step of:
   adding at least one noble metal selected from a group consisting of Ru, Rh, Os, Au and Ag to the Pd—Cr₂O₃ cocatalyst to form (metal-Pd—Cr₂O₃) nanocomposite cocatalysts to improve the solar hydrogen evolution rates.

6. A method for production of Pd colloidal solution comprising the steps of:
   mixing H₃PdCl₄ and Cr(NO₃)₃ solution as a precursor;
   adding PVP to the precursor solution;
   mixing thoroughly; and
   reducing the precursor solution with aqueous NaBH₄ solution to form a Pd colloidal solution.

7. The method of claim 6 further comprising the step of:
   adding cadmium sulfide (CdS) powder to the resulting solution and stirring to disperse CdS powder.

8. The method of claim 7 wherein the reducing step comprises the step of:
   adding 1.0 M (NH₄)₂SO₃ solution to as prepared solution to form Pd—Cr₂O₃, nH₂O particles that are loaded on CdS surface forming (Pd—Cr₂O₃)/CdS photocatalyst.

9. A method to prepare photococatalyst to produce hydrogen using aqueous ammonium sulfite solutions as electron donors comprising the step of:
   providing solutions of H₃PdCl₄ and Cr(NO₃)₃;
   adding PVP to the mixture of H₃PdCl₄ and Cr(NO₃)₃ to prevent aggregation of Pd nanoparticles;
   reducing the solution of H₃PdCl₄ and Cr(NO₃)₃ with NaBH₄ solution to produce monosized Pd colloidal solution;
   adding CdS powder to the Pd colloidal solution while stirring vigorously; and
   adding the resulting solution to an aqueous (NH₄)₂SO₃ solution to produce (Pd—Cr₂O₃)/CdS photocatalyst for hydrogen production from the aqueous (NH₄)₂SO₃ solution.

10. A method for preparing a (Pd—Cr₂O₃)/CdS photocatalyst for hydrogen production comprising the steps of:
    providing an aqueous palladium chloride (PdCl₂) solution as a precursor;
    adding PVP to the precursor solution;
    reducing the precursor solution with the presence of PVP with sodium borohydride (NaBH₄) for the preparation of nanosized palladium metal colloid;
    adding aqueous Cr(NO₃)₃ solution into the Pd colloid;
    adding CdS semiconductor powder to the mixture of Pd colloid and Cr(NO₃)₃ solution; and
    adding aqueous (NH₄)₂SO₃ solution to as prepared solution to form (Pd—Cr₂O₃, nH₂O) particles that are immobilized Pd—Cr₂O₃ particles on CdS surface forming the (Pd—Cr₂O₃)/CdS photocatalyst.

11. A nano composite cocatalyst for solar hydrogen production comprising:
    Pd—Cr₂O₃ loaded CdS co-catalyst.

12. The nano composite cocatalyst of claim 11 further comprising:
    at least one noble metal selected from a group consisting of Pt, Ru, Rh, Os, Au and Ag added to the Pd—Cr₂O₃ cocatalyst.

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