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Light-triggered hydrogen production from anhydrous alkaline methanol on a multi-layer device

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Abstract: Hydrogen production from methanol has attracted substantial interest because of the clean combustion of hydrogen and the convenience of methanol in storage and transportation. However, it requires high-temperature and high-pressure conditions to reform methanol with water to hydrogen with high turnover frequency (TOF, *e.g.* 10^4 moles of hydrogen per mole of Pt per hour). Here we show that hydrogen can be produced from anhydrous alkaline methanol with a remarkable TOF of 1.8×10^6 moles of hydrogen per mole of Pt per hour on a light-triggered multi-layer system under mild conditions. The performance is attributed to the use of anhydrous methanol as both the proton source and the hole scavenger in alkaline conditions. In contrast to a slurry system, we show that the proposed multi-layer system avoids particle aggregation, and it leads to the effective utilization of methanol, light and Pt active sites. This notable performance steps forward to the practical light-triggered hydrogen generation.

Hydrogen is an excellent energy reservoir because of the high gravimetric energy density and clean combustion to water¹. However, the transport and storage of hydrogen, usually in tanks, remain the difficulty in the use of hydrogen². In contrast, liquid fuels are more convenient to store and to transport and possess relatively high volumetric energy density³. Therefore, the *in situ* generation of the required hydrogen from inexpensive and stable liquid media offers a promising alternative and has attracted much attention⁴⁻⁷. The use of water as a proton source to produce hydrogen is

known as water splitting, *e.g.* via photolysis or electrolysis under moderate conditions (*e.g.* 25 °C and 1 atm)^{8,9}. While very appealing, this is a challenging reaction both from thermodynamic and kinetic standpoints due to the significant required energy input ($\text{H}_2\text{O} \rightarrow \text{H}_2 \uparrow + \frac{1}{2}\text{O}_2 \uparrow$, $\Delta G = +237 \text{ kJ/mol}$) and considerable intermediate energy barriers, respectively. Recent benchmarks in photocatalytic water splitting include the SrTiO_3 : La, Rh/Au/ BiVO_4 : Mo sheet with a solar-to-hydrogen (STH) efficiency of $\sim 1\%$ ¹⁰ and the Rh/ SrTiO_3 : Al catalyst with a quantum efficiency of almost unity at 350-360 nm¹¹. However, the turnover frequency (TOF) on active sites (*e.g.* noble metals such as platinum or rhodium) of these photocatalytic systems is low (*e.g.* 3,600 moles of hydrogen per mole Rh per hour on the SrTiO_3 :Al catalyst), indicating an unsatisfactory utilization of the active sites. Compared with water splitting, hydrogen evolution from thermal catalytic aqueous-phase reforming of methanol (APRM, $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 \uparrow + 3\text{H}_2$, $\Delta G = +9 \text{ kJ/mol}$) is less endergonic and has reached an industrial-grade TOF (1.8×10^4 moles of hydrogen per mole of Pt per hour) on Pt/a-MoC catalyst³. However, heat-driven APRM usually occurs at 190-350 °C under pressures of 20-50 atm and releases carbon dioxide^{3,7,12}. An ideal hydrogen production process should possess a high TOF under mild conditions with zero carbon emission, a combination which has not yet been reported in the literature.

Light-driven APRM systems, also known as the photocatalytic hydrogen production half-reaction, possess the potential to meet the requirements mentioned above since it can operate under room temperature and ambient conditions¹³. More importantly, the photocatalytic proton reduction to hydrogen on Pt active sites has been reported to proceed at the timescale of 10-900 μs , corresponding to a theoretical TOF of 10^6 - 10^8 moles of hydrogen per mole of Pt per hour¹⁴. Although the recent developments have improved the hydrogen evolution rates by a few orders of magnitude, such remarkable TOF has never been achieved in photocatalysis. In photocatalytic

hydrogen production, water is generally considered to be the proton source, while methanol is commonly used as a hole scavenger to promote the reduction of protons by electrons (Scheme 1a). Hydrogen production only from methanol under light offers a potential alternative solution if a high TOF can be reached. One favorable reaction to release hydrogen is the reforming of methanol with alkali: $\text{CH}_3\text{OH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + 3\text{H}_2 \uparrow$, $\Delta G = -123 \text{ kJ/mol}$, $\Delta H = -38.5 \text{ kJ/mol}$). The reaction is exothermic (*cf.* Scheme 1b), in contrast to an endothermic reaction in aqueous methanol solutions. In effect, the role of light is only kinetic to help overcome the energy barrier, and the reaction can proceed without the harsh high-temperature and high-pressure conditions.

Scheme 1. Photocatalytic hydrogen production from (a) methanol aqueous solution and (b) water-free alkaline methanol.

A slurry system, where catalysts disperse in a liquid medium, is the most commonly used system in photocatalysis¹⁵⁻¹⁸. However, a slurry system is difficult to scale-up, because it is constrained by the need for extra energy input for agitation to avoid the precipitation of the catalysts. It also suffers from the particle aggregation, non-uniform distribution of the catalyst and light-scattering

losses¹⁹. Therefore, a non-slurry design might offer a more practical approach with controllable management of light and catalysts and a high TOF over active sites.

Herein, we report that hydrogen could be released from anhydrous alkaline methanol with TOF up to 1.8×10^6 moles of hydrogen per hour per mole of Pt and a hydrogen evolution rate of 1 $\mu\text{mol/s}$ under the light on a multi-layer system. Such TOF is two orders of magnitude higher than that in thermal catalytic APRM. This unprecedented activity is due to the anhydrous alkaline methanol reaction and the multi-layer architecture of transparent membrane coated with photocatalysts, which avoids particle aggregation and tunes the light propagation without the need for agitation. Moreover, the system has zero carbon emission to the gas phase in that CO_2 is captured in carbonate anions, hence paving an avenue to the practical use of photocatalytic hydrogen production.

Results

The design of the catalytic system. The idea of the present study is to immobilize the photocatalyst particles on the transparent polypropylene (PP) substrate for the reaction of methanol reforming to hydrogen under light (Fig. 1). Such a PP substrate could be folded into multi-layer structures to harvest the incident photons over the whole sample (Fig. 2). In this study, we focused on the hydrogen generation process instead of any specific materials. We hence chose two most well-documented materials, carbon nitride (CN) and TiO_2 , as photocatalysts and commonly-used Pt as the co-catalyst. CN photocatalyst was synthesized from urea while TiO_2 was commercial P25 without further treatment^{1,20-22}. Experimental details can be found in the Supplementary information (SI). Briefly, a sheet of PP was folded into a 32-layer $2 \times 2 \text{ cm}^2$ configuration as the

substrate, cleaned with water and isopropanol and dried before being placed in an oxygen plasma cleaner to increase the hydrophilicity of the surface (Supplementary Fig. 1). Then, for example, 2 mg Pt/CN was loaded on both sides of the PP substrate and dried in an oven at 70 °C before placing in a 30 ml gas-tight reactor (Supplementary Fig. 1). The distribution of catalysts and thereby the light absorption have been carefully tailored by varying the loading of the catalyst and the number of the layers. PP hardly absorbs sunlight (Supplementary Fig. 2), ensuring that the loaded catalyst (Pt/CN or Pt/TiO₂) harvests most incident photons. From scanning electron microscopy (SEM) (Fig. 1c and Supplementary Fig. 3.a-b), CN clusters with a size of 2~10 μm could be discerned on

Fig. 1 Fabrication and characterizations of the multi-layer system. (a) The single PP layer decorated with Pt/CN for methanol reforming to hydrogen under the light. (b) The multi-layer membrane for methanol reforming to hydrogen. Inset: images of a bendable multi-layer membrane before and after deposition of Pt/CN. (c) SEM image of CN on PP membrane. (d) TEM image of Pt on CN.

the PP substrate. The semiconductor photocatalysts were decorated with Pt via photodeposition²⁰, where Pt/CN represents CN decorated with Pt, for instance. The transmission electron microscopy (TEM) images (Fig. 1d and Supplementary Fig. 3c) of Pt/CN show a stacked-layer morphology of CN and Pt clusters with a size of around 2-5 nm. The obtained Pt/CN coating on PP remains robust even after rinsing by water and methanol.

Strong alkaline conditions were reported to prolong the lifetime of photogenerated electrons by quickly eliminating the holes¹⁶. According to our previous findings, the highly concentrated OH⁻ can rapidly react with photoholes to form hydroxyl radicals, which react with alcohol at a high rate¹⁶. Hence, the slow hole transfer process is replaced with two faster ones, leaving long-lived electrons for the efficient reduction of protons to hydrogen¹⁶. By raising the pH (or decreasing the amount of water) in the system, the photocatalytic evolution rate of hydrogen was dramatically increased. The proposed reaction contains only sodium hydroxide, methanol and negligible water, which is a system with an extremely high pH. The photocatalytic investigation was then carried out on the multi-layer system in a 10 ml methanol solution containing NaOH under light irradiation.

The reforming of the alkaline methanol. We first measured the hydrogen production rates on 3% w.t. Pt/CN multi-layer sample in four NaOH methanol solutions containing 3%, 2%, 1% and 0% (v/v) water, respectively, to investigate the influence of water. As the amount of water decreased, both hydrogen production rates and TOF increased (Fig. 2a), due to the kinetically more efficient methanol deprotonation under more alkaline conditions^{16,23,24}. It is important to note that aqueous methanol reforming is endothermal while the reforming of alkaline methanol is exothermal. The system with extra water is thermodynamically more challenging. In the absence of water, the

sample evolved hydrogen at a rate of 241.7 $\mu\text{mol/g s}$ with an average TOF of 6×10^3 moles of hydrogen per mole of Pt per hour, generating visible bubbles during the catalytic process (Fig. 2a and the Supplementary Video). Although no additional water was added in anhydrous methanol, water could be produced *in situ* by oxidation or deprotonation of methanol under highly alkaline conditions^{16,24,25}. Water is a widely-used proton source, however, extra water appears detrimental to photocatalytic hydrogen production from alkaline methanol, where methanol acts as both the proton source and the hole scavenger.

Fig. 2. Photocatalytic methanol reforming to hydrogen. (a) Hydrogen production rates and TOF as a function of the amount of water in the multi-layer system. (b) Hydrogen production rates and TOF of the multi-layer system (32-fold), the slurry system and the slurry with PP flakes with inset images. The error bars represent standard deviations (SD).

In contrast to the multi-layer system, the conventional slurry system used as a reference showed 30 times lower hydrogen production rate and TOF (Fig 2b). Such a dramatic difference indicates that the well-distributed photocatalyst on the multi-layer system can utilize the incident photons much more efficiently compared to a slurry system under identical conditions. In the slurry system, the anhydrous alkaline methanol system also showed 20 times higher activity compared with a typical aqueous photocatalytic system containing 10% methanol (Supplementary Table 1, Entry 5-6). To exclude the suspicion that the PP substrate might react with the Pt/CN, we sliced a piece

of PP substrate (32-fold $2\times 2\text{ cm}^2$, pre-treated under identical conditions). We added it into a reference Pt/CN stirred slurry (Fig. 2b). No significant improvement in the hydrogen production rate was observed, indicating the stability of the PP substrate. In the absence of Pt decoration, a membrane with 2 mg CN only released a tiny amount of hydrogen (Supplementary Fig. 4). In further control experiments (Supplementary Fig. 4 and Supplementary Table 1), negligible hydrogen was detected without light, catalysts or methanol, indicating that such an exothermal reaction is not spontaneous but need to be triggered by the incident photons. Illumination can naturally raise the temperature of a reactor to $60\sim 70\text{ }^\circ\text{C}$ ^{13,26,27}. Another possible reason for the temperature rise is due to the exothermic methanol reforming with alkali reaction. Thus, the temperature of the present system could also reach up to $70\text{ }^\circ\text{C}$. However, no catalytic activity was observed when the reactor was held at $70\text{ }^\circ\text{C}$ under dark conditions (Supplementary Fig. 4), confirming that light is a necessary trigger.

In a multi-layer structure, when incident photons pass through the first front layer, only a fraction is absorbed by the small amount of catalysts on each side, while most photons reach the second layer. Some photons will be reflected to the first layer to excite the catalysts again while the rest is absorbed by the second layer or passes further (Supplementary Fig. 5a). As such, a multi-layer structure not only prevents aggregation of CN and reduces scattering but also enhances light utilization. The remote layers absorb fewer photons than the layers near the light source, so the amount of the catalyst and the number of layers should be balanced. Therefore, we tuned the number of stacking layers from 32 to 16 to 8 (2.0, 1.0 and 0.5 mg of Pt/CN, respectively) to manage the light propagation inside the system. The optimal hydrogen production was achieved on a 16-fold membrane (Supplementary Fig. 5b), and the TOF was further increased to 4.4×10^4 mole of hydrogen per mole of Pt per hour with a hydrogen formation rate of $189\text{ }\mu\text{mol/g.s}$.

Platinum is the cost determinant of such a methanol-reforming system. Excess Pt shields the surface of CN from incident photons and decreases the number of individual sites by forming large clusters. Therefore, it is crucial to use these active sites adequately to maximize the TOF. One method is to load Pt-decorated CN powder on the PP. In this case, some Pt sites were presumably embedded inside the CN clusters (Fig. 3a left), out of the reach of the protons at the methanol/CN interface and thus wasted for activity. Therefore, to decorate Pt selectively on the surface of CN, CN was first coated on the membrane. Then Pt was *in situ* photodeposited on CN (Fig. 3a right).

Fig. 3. Effect of various parameters on the multi-layer systems for methanol reforming. (a) Hydrogen production rates and TOF as a function of the Pt loading methods. Left: typical loading method, Pt dispersed randomly in CN. Right: *in situ* loading method, Pt selectively loaded on the interface of methanol/CN. (b) Hydrogen production rates and TOF as a function of the amount of Pt *in situ* loaded on CN. (c) Hydrogen production rates and TOF as a function of different photocatalysts coated with *in situ* Pt co-catalyst. (d) Approaching long-term methanol reforming on 0.03% Pt/CN under weak light conditions. TTN: total turnover number. The error bars represent SD.

With an identical amount of Pt (0.3% w.t. CN), the *in situ* Pt loaded sample exhibited a doubled activity compared with the sample with Pt-decorated CN sample (Fig. 3a). As the loading ratio varied from 1% to 0.3%, the TOF increased by 13% (Fig. 3b). Reducing the amount of Pt to 0.03% w.t. of CN, the TOF reached 5×10^5 mole of hydrogen per mole of Pt per hour. Interestingly, the 0.01% Pt/CN sample produced hydrogen with a TOF reaching 1.8×10^6 mole of hydrogen per mole of Pt per hour with an internal quantum yield of 21% at 365 nm. This dramatic enhancement is due to selective deposition of exposed Pt active sites on the surface of photocatalysts.

To investigate the compatibility of our system with different photocatalysts, we loaded TiO_2 nanoparticles onto a multi-layer PP substrate using identical methods (Supplementary Fig. 5c). A reproducible hydrogen production rate of $170.2 \mu\text{mol/g s}$ was measured on Pt/ TiO_2 (Fig. 3c and Supplementary Fig. 5d), corresponding to a TOF of 1.2×10^6 mole of hydrogen per mole of Pt per hour. The comparable performance observed on Pt/ TiO_2 and Pt/CN indicates that the key for the remarkable activity is the intrinsic beneficial anhydrous alkaline methanol reforming reaction and the multi-layer structure photocatalytic system. The present catalytic approach is a general method to speed up the hydrogen production from methanol, and it does not depend on special semiconductors. The hydrophilicity of semiconductors also influences the photocatalytic activities in aqueous systems. In this water-free system, semiconductors with low hydrophilicity might also be used for hydrogen production.

The practical potential of the system. Moreover, the long-term stability of such a multi-layer system loaded with Pt/CN was evaluated. In a 30 ml reactor, the rapid production of hydrogen markedly increases the pressure (c.a. 23.2 ml H_2 produced per hour on 1 mg 0.01% w.t. Pt/CN)

when the long-term test was carried out on 0.01% w.t. Pt/CN under full light power. Therefore, to minimize the change in pressure, we decreased light intensity. With reduced light intensity, the activity remained an initial TOF of 1.2×10^4 moles of hydrogen per mole of Pt per hour, still comparable to the benchmark of thermal catalysis³. Such a system stayed robust for ten hours, demonstrating the potential for long-term use (Fig. 3d). The slight decline of TOF over ten cycles was owing to the reduced transparency of solution due to the generated Na_2CO_3 ²⁸, which is poorly soluble in methanol (Supplementary Fig. 6). Such transparency issues could be addressed by effectively separating and recycling Na_2CO_3 from the system. The consumption of NaOH in the system also accounted for the decay in the activity.

Another additional advantage of the present system is the *in situ* collection of CO_2 . Negligible CO_x (CO_2 or CO) was detected in the gas phase during the reaction (Fig. S7), indicating that CO_2 was captured into carbonate rather than directly emitted into the headspace. More importantly, the danger of presence of CO is mitigated. CO , a well-known poison for the Pt catalysts²⁹, is absent in this system, allowing for a clean feed of pure hydrogen for fuel cells. In particular, methanol could be sustainably produced via the reduction of CO_2 ³⁰⁻³² and the oxidation of methane³³⁻³⁵ while NaOH could be regenerated from Na_2CO_3 (see Supplementary Texts), making the present system economical and sustainable³⁶.

Two reports have achieved CO_x -free liquid methanol photodecomposition to formaldehyde and hydrogen: $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ (8)^{37,38}. Although it avoids the production of CO_x , it has been found not ideal in terms of H_2 production activity³⁷. The reported hydrogen evolution rates of these systems are relatively low ($320 \mu\text{mol g}^{-1} \text{h}^{-1}$ and $617 \mu\text{mol g}^{-1} \text{h}^{-1}$, without reported TOF). The present study both prevents CO_x release and reaches a very high hydrogen evolution rate (up to $3.5 \text{ mol g}^{-1} \text{h}^{-1}$) and TOF. The superior performance in the present study is due to the intrinsic

design of the reforming of alkaline methanol, which is based on a different strategy from the photodecomposition of methanol.

Fig. 4 Gas-phase methanol reforming on the multi-layer systems. (a) Left: schematic of the multi-layer membrane for gas-phase methanol reforming to hydrogen under light. Right: an image of the methanol vapor reforming setup on multi-layer membrane coated with Pt/CN/NaOH. (b) Hydrogen production rates and TOF comparison on liquid-phase and gas-phase methanol reforming system. The error bars represent SD.

More strikingly, the multi-layer structure exhibited the activity to reform gas-phase methanol to hydrogen. Instead of using 10 ml methanol solution, we placed a vial containing 1.5 ml methanol to generate its vapor inside the reactor. NaOH was loaded together with Pt/CN on PP (16-layer 0.01% w.t. Pt/CN), providing a local highly alkali-rich environment (Fig. 4a). Although the amount of reactants compared to the liquid-phase system was reduced, this gas-phase configuration still produces a comparable rate of hydrogen production. This implies a more efficient utilization of reactants than the liquid-phase one (Fig. 4b). The enhanced activity is attributed to the better contact between the catalyst particles and the methanol vapor. Such a gas-phase methanol reforming system with a high TOF offers a potential solution to feed fuel cells in practical vehicles (see Supplementary Texts for further details).

Conclusion

In summary, we have shown an efficient process to produce hydrogen from water-free alkaline methanol. We demonstrated that the reaction reaches a hydrogen evolution rate of $\sim 1 \mu\text{mol/s}$ and a TOF of 1.8×10^6 mole of hydrogen per mole of Pt per hour on multi-layer architecture loaded with Pt/CN or Pt/TiO₂ under light illumination. The TOF is two orders of magnitude better than reported for the thermal catalytic approach. Herein, anhydrous methanol and alkali work as both the proton source and hole scavenger, where light has a kinetic role as a trigger for the reaction. In addition, the proposed layered system shows superior performance to the commonly-used slurry systems without the need for agitation. The high rate of hydrogen production is attributed to the intrinsic thermodynamically favorable reaction, the prevention of particle aggregation, the light management and the efficient utilization of Pt active sites. Moreover, the system could sustainably reform both liquid and gas phase of methanol to feed pure hydrogen to fuel cells. Furthermore, the earth abundance of raw materials for the plastic and urea, the ink-printing technique to deposit catalysts on the membrane and the compatibility of the gas-phase device with a flow system enable the scalable fabrication and hold promise for broad and practical applications.

Methods

Material synthesis

All chemicals are purchased from Sigma-Aldrich. In a typical carbon nitride synthesis, urea was placed in a lidded high-quality alumina crucible, then placed inside a furnace, and heated at a ramp rate of 5°C min^{-1} and finally held at 600°C for 4 h. Water, HCl, and NaOH were used to wash the produced powders to remove all unreacted and potentially detrimental surface species.

Fabrication of a multi-layer membrane.

10 mg carbon nitride powder (with or without Pt deposition) was dispersed in 15 ml ethanol and sonicated (50 W) for 1 hour before use. To fabricate a multi-layer membrane, a piece of polypropylene substrate was folded to *e.g.* 16-fold of $2 \times 2 \text{ cm}^2$ size and washed by water and isopropanol. Then it was dried at room temperature before placing in a plasma cleaner to promote the hydrophilicity of the surface. Then the folded membrane was placed into a 30 ml reactor. The CN-ethanol (or Pt/CN-ethanol) dispersion was added into

the reactor and the membrane was submerged in the dispersion for 1 min to create the surface adsorption of the catalyst on PP. Then the dispersion was taken out and the wet membrane with surface adsorption of the catalyst was dried in an oven at 70 °C. The coating procedure was performed on both sides of the membrane for three times. Then the coated membrane was transferred to another clean 30 ml reactor for photocatalysis.

Photocatalyst characterization.

UV/Vis absorption was measured with a Varian Carry 5000 UV-Vis-NIR spectrometer. The morphology of the photocatalyst was characterized by a JEOL JEM-1011 TEM operating at a 100 kV accelerating voltage. High-resolution images in the TEM mode and the HAADF-STEM mode were recorded with an FEI Titan 80-300 operating at 300 kV.

Photocatalytic reactions.

The multi-layer membrane coated with CN was folded and placed in a 30 ml glass vial reactor (inner diameter = 25 mm). 2g NaOH was dissolved in 10 ml methanol to form the NaOH methanol solution. The solution was purified to remove Na₂CO₃ by centrifuge at 5000 rpm for 5 min. Then the clear solution was added to the 30 ml reactor and purged with Argon for 15 min before placing under the light irradiation of 450 W Xenon lamp (FL-1039/40, AUX LAMP). In a typical slurry system (with 600 rpm agitation under ambient conditions 25 °C), 2 mg Pt/CN nanoparticles were dispersed in 10 ml NaOH methanol solution in a 30 ml glass vial.

For the typical photodeposition method, a certain amount of CN powder with H₂PtCl₆ precursor was added into the reactor containing 10 ml 10% methanol/water solution, sealed and purged with Ar and irradiated by a 450W Xenon light source (FL-1039/40, AUX LAMP) for 2 hours. For the *in-situ* photodeposition method, CN was firstly coated on PP multi-layer membrane and placed in the reactor containing 10 ml NaOH methanol solution, sealed and purged with Ar and irradiated by a 450W Xenon light source (FL-1039/40, AUX LAMP) for 12 min. Then the reactor was purged with Ar again before evaluation of activity.

The system was purged by Argon before irradiation using a 450W Xenon light source (FL-1039/40, AUX LAMP). The headspace of the reactor was analyzed by Shimadzu GC2014 gas chromatography (GC) coupled with a thermal conductivity detector (TCD). Periodic measurements are taken manually by a syringe to determine the H₂ production. For the evaluation of H₂ generation, each time 10 µl of the sample headspace was taken to the GC through Teflon-lined septum at the top of the reactor. The H₂ formation rate is expressed as the molar amount evolved per second of illumination and per gram of catalysts. The H₂ formation rates are calculated from the average values of at least 3 repeats for each sample. The error bars represent SD.

In a NaOH methanol solution slurry, the activity of hydrogen production reached 7.8 µmol/gs, which is ~20 times higher than the commonly-used system with 10% methanol aqueous solution (0.4 µmol/gs). As such, the photocatalytic hydrogen generation rate measured on a Pt/CN in NaOH methanol solution (7.8 µmol/gs) outnumbered the reported benchmark hydrogen evolution rates and TOF on Pt/CN (3.6 µmol/gs, Extended Data Table 1)³⁹, although the latter was measured under vacuum conditions, which often improves the hydrogen evolution yield significantly^{1,10}.

Calculation of internal quantum efficiency

The internal quantum yields for Pt/CN photocatalyst was measured using 365 nm LED light. The internal quantum yields are defined by the following equation:
$$IQY = \frac{\text{number of reacted electrons}}{\text{number of the absorbed photons}} \times 100\%.$$
 Two electrons are consumed by per hydrogen molecule evolved: $2e^- + 2H^+ \rightarrow H_2$. As a result, the internal

quantum efficiency can be estimated by the equation: $IQY = \frac{N_{H_2} \times 2 \times N_A}{H_a \times A \times \frac{\lambda}{hc} \times t}$, where: N_{H_2} is the amount of hydrogen under time t (s), N_A is the Avogadro's number, H_a is the average intensity of absorbed light, obtained by the subtraction of the transmitted intensity from the incident intensity measured by a detector. A is the irradiation area (4 cm^2), h is the Planck's constant, c is the speed of light, λ is the wavelength of the incident light, t is the time.

Calculation of turnover frequency (TOF)

The TOF is calculated from the hydrogen production amount ($R \text{ } \mu\text{mol/s} \times 10^{-6} \times 3600 \text{ s/h}$) and Pt amount (mol) as follows:

$$TOF = \frac{R \text{ } \mu\text{mol/s} \times 10^{-6} \times 3600 \text{ s/h}}{Pt \text{ mol}}$$

For example, for the 0.01% Pt/CN sample, 0.51 nmol Pt was added in the system. Meanwhile, 93.6 μmol H_2 was produced during a 6-min irradiation. The turnover number is thus 1.84×10^5 during 6 minutes, corresponding to a TOF of $1.84 \times 10^6 \text{ mol } H_2 \text{ per mol Pt per hour}$. The TOF is calculated from the average of at least 3 repeats for each sample.

Chemical reactions involved in the main text

Methanol production from CO_2 and water (1) and methanol aqueous reforming to hydrogen (2), which stepwise release oxygen and hydrogen, add up to water splitting (3).

In photocatalysis, methanol is usually used as hole scavenger (4) to promote the hydrogen production from water by reduction of protons (5), where (4) and (5) add up to (2).

In the present study, water-free methanol was used to produce hydrogen and fix CO_2 into carbonate via (6).

Potential approach to recycle NaOH

One may argue that NaOH is also a cost determinant. Here we propose a process to regenerate NaOH. In the presence of NaOH, this system captures CO_2 and forms Na_2CO_3 precipitate. Besides using Na_2CO_3 for further purposes, it is envisaged that the collected Na_2CO_3 could also naturally react with earth abundant $Ca(OH)_2$ to form $CaCO_3$ due to its smaller solubility and regenerate NaOH via the process: $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \downarrow$ (7). The collected $CaCO_3$ could be directly buried to store CO_2 and NaOH is produced.

$CaCO_3$ could also be decomposed to CaO and CO_2 under electro-thermal heating with the electricity produced by solar energy. Then CaO could be naturally converted to $Ca(OH)_2$ again to regenerate NaOH, while CO_2 is released under control to e.g. produce methanol (1) again. Hence, the proposed cycle to regenerate NaOH can be completed. The overall total reaction is again carbon-neutral. Such a process

involves all abundant and inexpensive reactants driven by renewable energy such as light and is therefore sustainable.

Estimation of Pt usage for practical vehicles.

Although how this strategy would work in practice is a complicated question related to both science and engineering, we still can roughly estimate the usage of Pt for a commercial proton-exchange membrane fuel cell (PEMFC) vehicle. The reported hydrogen consumption and range of the Toyota Mirai 2017 vehicle are 1 kg H₂ per 100 km (at a speed of about 100 km h⁻¹) and 500 km, respectively.³ To fuel such a vehicle, the fuel tank used in traditional cars could be filled with methanol. Given the hydrogen-consumption rate of Mirai (1 kg h⁻¹) and the Pt-normalized hydrogen-production rate (1,800,000 mol H₂ per mol Pt per hour) of the 0.01%Pt/CN catalyst, around 54.2 mg Pt should meet the requirements of Mirai per hour, which corresponds to approximately 542 g of 0.01% Pt/CN catalyst. The present system requires much less Pt compared to the previous benchmark, which requires 6 g Pt, and 3,000 g catalyst to achieve the same hydrogen production rate³.

Data availability

Supporting data is available in the Supplementary Information. Raw data is available from the corresponding authors upon reasonable request.

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Author contributions

Y. W. prepared the materials and carried out the photocatalytic measurements. E.-P. Y. performed electron microscopy measurements. Y. W. and E.-P. Y. developed the multi-layer devices. Y. W. wrote the manuscript with input from E.-P. Y., J. K. S and J. F. All authors contributed to discussions. ⁺ These authors contributed equally.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Fabrication and characterizations of the multi-layer system. (a) The single PP layer decorated with Pt/CN for methanol reforming to hydrogen under the light. (b) The multi-layer membrane for methanol reforming to hydrogen. Inset: images of a bendable multi-layer membrane before and after deposition of Pt/CN. (c) SEM image of CN on PP membrane. (d) TEM image of Pt on CN.

Figure 2

Photocatalytic methanol reforming to hydrogen. (a) Hydrogen production rates and TOF as a function of the amount of water in the multi-layer system. (b) Hydrogen production rates and TOF of the multi-layer system (32-fold), the slurry system and the slurry with PP flakes with inset images. The error bars represent standard deviations (SD).

Figure 3

Effect of various parameters on the multi-layer systems for methanol reforming. (a) Hydrogen production rates and TOF as a function of the Pt loading methods. Left: typical loading method, Pt dispersed randomly in CN. Right: in situ loading method, Pt selectively loaded on the interface of methanol/CN. (b) Hydrogen production rates and TOF as a function of the amount of Pt in situ loaded on CN. (c) Hydrogen production rates and TOF as a function of different photocatalysts coated with in situ Pt co-catalyst. (d) Approaching long-term methanol reforming on 0.03% Pt/CN under weak light conditions. TTN: total turnover number. The error bars represent SD.

Figure 4

Gas-phase methanol reforming on the multi-layer systems. (a) Left: schematic of the multi-layer membrane for gas-phase methanol reforming to hydrogen under light. Right: an image of the methanol vapor reforming setup on multi-layer membrane coated with Pt/CN/NaOH. (b) Hydrogen production rates and TOF comparison on liquid-phase and gas-phase methanol reforming system. The error bars represent SD.

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