Room temperature stable CO$_x$-free H$_2$ production from methanol with magnesium oxide nanophotocatalysts

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Methanol, which contains 12.6 weight percent hydrogen, is a good hydrogen storage medium because it is a liquid at room temperature. However, by releasing the hydrogen, undesirable CO and/or CO$_2$ byproducts are formed during catalytic reforming. We show that alkaline earth metal oxides, in our case MgO nanocrystals, exhibit stable photocatalytic activity for CO/CO$_2$-free H$_2$ production from liquid methanol at room temperature. The performance of MgO nanocrystals toward methanol dehydrogenation increases with time and approaches $\sim$320 $\mu$mol g$^{-1}$ hour$^{-1}$ after a 2-day photocatalytic reaction. The CO$_x$-free H$_2$ production is attributed to methanol photodecomposition to formaldehyde, photocatalyzed by surface electronic states of unique monodispersed, porous MgO nanocrystals, which were synthesized with a novel facile colloidal chemical strategy. An oxygen plasma treatment allows for the removal of organic surfactants, producing MgO nanocrystals that are well dispersible in methanol.

INTRODUCTION

Because of the high mobility of protons, hydrogen can be efficiently converted into electricity by using low-temperature proton exchange membrane fuel cells. However, it is not easy to store and transport pure hydrogen. A liquid methanol–formaldehyde cycle could be useful for storing hydrogen (1)

$$\text{CH}_3\text{OH} \leftrightarrow \text{H}_2(\text{g}) + \text{CH}_2\text{O} \quad (1)$$

Methanol (CH$_3$OH) has a boiling point of 64.7°C and is a liquid under ambient conditions. Formaldehyde (CH$_2$O) has a boiling point of $\sim$19.3°C, so only moderate pressure ($\sim$5 atm) is needed to liquefy it; furthermore, it exhibits 37 weight percent solubility in liquid water. Reaction (1) in a closed loop releases no carbon into the atmosphere (2, 3). The difficulty in reaction (1) lies in efficient methanol dehydrogenation to produce H$_2$ at the site of end use (as opposed to hydrogenation, which can be accomplished centrally), and so far, this has been far from economical. The reported dehydrogenation catalysts to producing hydrogen from methanol mainly include aqueous methanol reforming and pure methanol decomposition. Aqueous methanol reforming, with H$_2$O added for the water-gas (CO) shift reaction, normally requires high temperatures ($\geq$200°C) and pressures ($\geq$25 bar) (4, 5), or mild temperatures (<100°C) but the use of ruthenium complexes (6) or lower-stability metal-organic complexes (7). For pure methanol decomposition, thermal decomposition is achieved at high temperatures (≥160°C) with noble metals (Pt and Pd) (8–12), although photodecomposition has been reported at room temperature with Ti-β and noble metals (Pt, Rh, Ir, Pd, and Au) deposited on TiO$_2$ as photocatalysts. However, the photocatalytic reactions require methanol vapor, and a Pt-TiO$_2$ catalyst is plagued by low H$_2$ yields (<7 $\mu$mol H$_2$ g$^{-1}$ hour$^{-1}$) and low stability (13–15).

Here, we show that magnesium oxide (MgO), a stable and cheap alkaline earth metal oxide that has been used as a photocatalyst for CO$_2$ reduction and organic contaminant degradation, an additive in refractory materials, and an adsorbent for air purification, toxic waste remediation, and biomedicine (16–25), is also an ultrastable photocatalyst for hydrogen production from methanol. We can mass produce monodisperse, porous MgO nanoparticles (NPs) with diameters ranging from 40 to 170 nm that demonstrate stable CO$_x$-free H$_2$ production from liquid methanol near room temperature.

Various wet chemical synthesis strategies have been developed to obtain MgO nanocrystals. Examples include sol-gel processes, hydrothermal/solvothermal methods, polyol-mediated thermolysis reactions, and microwave-assisted synthesis (26–29). However, most of the current routes initially yield hydroxide precursors, such as Mg(OH)$_2$ and Mg$_2$(OH)$_2$CO$_3$, which must be calcinated at high temperatures to produce crystalline MgO. These high-temperature processes are costly and usually result in fusion of NPs into aggregates (30–33). To date, only one study focused on the preparation and properties of nearly monodisperse MgO nanocrystals using an organometallic decomposition method (34). However, the raw materials used in this approach are toxic and expensive. To the best of our knowledge, until now, a facile, environmentally friendly, and inexpensive synthetic route to mass produce well-defined, porous MgO nanocrystals still remains a challenge, and a systematic study on the synthesis and properties of monodispersed, porous MgO nanocrystals has yet to be performed.

Here, we demonstrate an inexpensive and green approach to synthesizing monodispersed, porous monocrystalline MgO NPs (Scheme 1) using magnesium acetylacetonate dihydrate [Mg(acac)$_2$·2H$_2$O]. The size of the porous MgO nanocrystals can be tuned from ~40 to 170 nm, all showing ultraviolet (UV) to blue emissions under UV light excitation.
that indicates high density of mid-gap surface electronic states. After oxygen plasma treatment, we modified the surfaces of as-obtained MgO NPs, improving their surface purity and hydrophilicity. The superior activity in CO$_2$-free H$_2$ production from MgO NPs was associated with the local photoexcitation and charge separation among MgO defect energy levels, where excited holes oxidize methanol to generate protons that subsequently get reduced by hot electrons to produce H$_2$.

RESULTS

Synthesis and characterization of monodispersed porous MgO nanocrystals

The synthesized MgO NPs have an exclusively face-centered cubic phase [periclase type, space group: Fm$ar{3}$m, JCPDS (Joint Committee on Powder Diffraction Standards): 45-0946], as confirmed by powder x-ray diffraction (XRD) analysis (Fig. 1A) for various-sized MgO NPs, with the calculated crystal parameters $a = b = c = 4.211$ Å. No diffraction peaks from other chemical species, such as Mg(OH)$_2$ or MgCO$_3$, are detectable in all the samples. The average particle sizes of MgO NPs determined by XRD using the Debye-Scherrer equation to the (200) reflection were around 40, 85, 115, and 170 nm, respectively. Sharpening of the diffraction peaks indicates the increased crystallinity of MgO NPs with increasing size.

Figure 1B shows a transmission electron microscopy (TEM) image of as-synthesized MgO nanocrystals; the MgO NPs are relatively monodispersed with an average size of ~85 nm (inset for a histogram of particle diameters). This suggests retention of capping ligands on the nanocrystal surfaces, as validated by Fourier transform infrared (FTIR) spectroscopy (fig. S1). The scanning electron microscopy (SEM; fig. S2A) image shows that the MgO NPs are spherically shaped. Energy-dispersive x-ray (EDX) spectroscopy (fig. S2B) confirms that stoichiometric MgO is formed with an atomic ratio of Mg/O = 1:1. The size of the MgO NPs was readily controlled by varying the reaction temperature and time. For instance, with 2 mmol of Mg(acac)$_2$·2H$_2$O as the precursor in oleylamine/oleic acid/1-octadecene (OM/OA/ODE) = 4:1:5 (molar ratio), a reaction time of 30 min at 265°, 280°, 300°, or 320°C produced MgO NPs with an average diameter of ~40 nm (Fig. 1C), ~85 nm (Fig. 1D), ~115 nm (Fig. 1E), or ~170 nm (Fig. 1F), respectively, which is well consistent with the XRD analysis (Fig. 1A). Moreover, as indicated by the TEM images in Fig. 1, the as-obtained MgO NPs gradually became smooth as the reaction temperature was elevated. Under a fixed reaction temperature of 265°C, the thermolysis of 2 mmol of Mg(acac)$_2$·2H$_2$O in OM/OA/ODE = 4:1:5 (molar ratio) for 60 min produces MgO NPs with a size of ~60 nm (fig. S3A). When the reaction temperature was raised to 280°C with all other conditions unchanged, the size of MgO NPs increased to ~100 nm (fig. S3B). Our results show that the size of the as-obtained MgO NPs did not significantly change with the reaction time (30 to 60 min) and when the temperature was kept constant at 300° or 320°C (Fig. 1E versus Fig. S3C and Fig. 1F versus fig. S3D). This suggests a temperature-driven "size-focusing" process with increasing reaction temperature (35).
The crystal structure of the individual MgO NPs was determined with high-resolution TEM (HRTEM) imaging and selected-area electron diffraction (SAED), as shown in Fig. 2. Figure 2A represents a typical TEM image for a single MgO NP; an amorphous surface layer can be clearly observed at the edge of the MgO NPs (inset of Fig. 2A). This amorphous surface layer may result from the applied capping ligands (OM and OA), which is consistent with the FTIR spectroscopy (fig. S1). The enlarged TEM image in the inset of Fig. 2A and the high-angle annular dark-field scanning TEM (HAADF-STEM) image in Fig. 2B demonstrate the local variation in density due to the porous nature of the MgO NPs. As seen in Fig. 2C, the HRTEM images taken from Fig. 2A show clear rock salt crystal lattice along the [100]. The observed interplanar distances between the lattice fringes are 0.21 and 0.15 nm, corresponding to the (200) and (220) planes of MgO, respectively. The SAED pattern acquired on a single MgO NP displays a single set of clear diffraction spots (Fig. 2D), confirming the monocrystalline nature of the porous MgO NPs (36).

In the present synthesis, the combination of different capping ligands was found to play a key role in obtaining monodispersed porous MgO nanocrystals. For example, aggregated MgO NPs (fig. S4A) were produced when 2 mmol of Mg(acac)_2·2H_2O was used as a precursor for a reaction at 280°C for 30 min, with the sole use of OM as the capping ligand and ODE as the solvent. In pure OA and ODE, almost no solid matter appeared after the precipitation treatment. In addition, we found that different ratios of solvents had great influence on the dispersibility of the porous MgO nanocrystals (fig. S4, B to D).

High yields of monodispersed porous MgO nanocrystals were only obtained at an optimized OM/OA/ODE ratio of 4:1:5 (Fig. 1B) because of a well-maintained balance between nucleation and growth during synthesis.

Through manipulation of capping ligands, solvents, and their relative ratios, we have successfully synthesized size-controlled monodispersed porous MgO NPs. One unique characteristic of MgO is its chemical stability, which is essential for long-term performance under strong illumination. To remove surface capping ligands, we used an oxygen plasma treatment on dried MgO powders. As an example, fig. S1 shows a comparison between the FTIR spectrum of the 85-nm MgO NPs before (black) and after (red) treatment. The oxygen plasma treatment thus efficiently modifies the nanomaterial surface by removing the organic capping ligands.

Figure 3 shows the room temperature UV-vis (visible) absorption and photoluminescence (PL) spectra for MgO NPs. Figure 3A shows the UV-vis absorption spectra of MgO NPs for MgO NPs of different sizes. All of the colloidal MgO NPs exhibited continuous absorption across the UV wavelength range, with two broad absorption peaks centered around 220 nm (5.6 eV) and 270 nm (4.6 eV). These peaks arise from the excitation of O^2− surface anions on the edge (fourfold coordinated) and on the corner (threefold coordinated) of the nanocrystal (37, 38), respectively. Although MgO is a wide-band gap insulator (E_g = 7.8 eV) (39, 40), optical transitions in the visible range were observed for our porous MgO NPs. Figure 3B shows PL spectra of MgO NPs at an excitation wavelength of 270 nm. The broad spectra covering from 300 to 450 nm indicate the presence of structural defects, such as oxygen vacancies (41–43), in the insulating MgO. All of the various sizes of the MgO NPs exhibited a strong visible blue emission if under 365-nm UV irradiation (fig. S5).

**Stable H₂ production from liquid-methanol photodecomposition near room temperature**

The photocatalytic activity for hydrogen production from high-purity liquid methanol at room temperature was examined for the MgO NPs (see Materials and Methods for details). The excitation wavelength dependence was studied by using various long-pass filters. As shown in Fig. 4A, there is no H₂ production when 530- or 380-nm long-pass filters are used. However, full-wavelength illumination (200 to 2500 nm) resulted in the production of H₂. This result is consistent with photoactivity arising from 220- and 270-nm excitation of the MgO nanocrystals (Fig. 3A). Hydrogen production was sensitive to MgO concentration in methanol. Figure 4B shows that suspensions of
~0.38 mg ml$^{-1}$ exhibit the best performance. Lower concentrations likely dilute the concentration of intermediate products, radicals, and/or protons because of the lower availability of surface active sites or photoexcited charges from MgO, resulting in a lower performance. On the other hand, high concentrations can cause light blocking/screening between the adjoining MgO nanocrystals, thus lowering light-harvesting efficiency. This is further supported by the fact that MgO’s absorbance of light rises much slower compared with its concentration increase (fig. S6A).

The H$_2$ production yields for various sizes of MgO nanocrystals are presented in fig. S6. Among the different sizes, the highest H$_2$ production rates (~55 μmol g$^{-1}$ hour$^{-1}$) occur from 85-nm MgO NPs. The higher surface area of the smaller-sized MgO nanocrystals (85 nm), as compared to the larger-sized MgO nanocrystals (115 and 170 nm), leads to an enhanced photocatalytic reaction with methanol. The surface area was verified using the Brunauer-Emmett-Teller (BET) method: the 40-, 85-, 115-, and 170-nm-sized MgO NPs have surface areas of 28.5, 19.7, 17.4, and 13.9 m$^2$ g$^{-1}$, respectively (fig. S7).

**Fig. 4.** H$_2$ production from methanol photodecomposition based on ~85-nm MgO nanocrystals. (A) Illumination wavelength effect using the long-wave pass filters with different cut-on wavelengths. (B) MgO concentration effect with constant 3 mg of MgO powder dispersed in different volumes of methanol. (C) Performance endurance of H$_2$ production by continuing to use the same MgO (3 mg)/methanol (8 ml) reaction materials for the whole three-cycle testing. (D) XRD pattern for MgO after a total 48-hour photocatalytic reaction.
The smallest-sized MgO nanocrystals (40 nm), with the largest BET surface area, did not yield the highest H₂ production rate per weight. This is most likely the result of the lower crystal quality of 40-nm-sized MgO nanocrystals (fig. S8) as compared to the 85-nm-sized MgO nanocrystals (Fig. 2D). The production of H₂ from pure MgO nanocrystals indicates that photoexcited electrons and holes in the surface defect energy levels of MgO can be harvested to oxidize methanol and reduce the generated protons (H⁺) for H₂ production. At the same time, this result demonstrates that an oxygen plasma treatment is an effective method to remove the organic surfactants from nanomaterials synthesized via this oil phase strategy. After oxygen plasma treatment, MgO crystals have hydrophilic surfaces and become dispersible in polar liquids, such as methanol and water. This method enhances the direct contact between the MgO nanocrystal surface and methanol, enabling a more efficient photo Reaction.

The H₂ production from MgO NPs is stable, and the rate actually improves with time (Fig. 4C and fig. S9). This is in contrast to many H₂ production systems, which often deteriorate in performance over time (5, 7, 15, 44, 45). To test MgO’s performance stability, we monitored product analysis of the same MgO/methanol system under photocatalytic reaction over the course of 2 days. To avoid undesirable gas leakage from the capped septum of a reactor during periodic syringe removal of products from the cell, the reaction system was interrupted and then vented in fume hood between testing cycles. During the first cycle, the produced H₂ rises steadily, increasing with time. After the interruption following cycle 1, the production of H₂ continues and its rate increases with time in cycle 2. Hydrogen production continues in cycle 3, although to a lesser extent in rate increase. Notably, the rate reaches ~320 μmol g⁻¹ hour⁻¹ at the end of a 2-day photocatalytic reaction. The local temperature induced by the lamp illumination around the photoreactor was observed to vary from 25° to 37°C over the 2-day reaction period. Note here that the temperature does not rise with illumination time strictly linearly: the temperature is relatively high, ~37°C, around noon and does not surpass 33°C during other times. The temperature therefore did not affect the performance, and the rising performance during the first 24-hour reaction (Fig. 4C and fig. S9) occurred as the surface sites on MgO NPs were gradually activated while the reaction was ongoing. On the basis of our experimental results, MgO nanocrystals are extremely stable under operating conditions for H₂ production near room temperature. This is attributed not only to the large band gap and high chemical stability of MgO (the heat of formation is 601.24 kJ mol⁻¹ of oxygen, in contrast to 469.36 kJ mol⁻¹ of oxygen for TiO₂) but also to photocatalytic surface states. To our knowledge, this work is the first to demonstrate catalytic methanol photodecomposition using the surface states of a dielectric oxide nanomaterial synthesized with a low-cost, high-throughput, green process.

**Insight into H₂ production from MgO/methanol**

Figure 5 proposes a mechanism for the H₂ production of MgO in methanol (46, 47). In this figure, the black dotted lines close to the central solid line represent the broad emission feature of MgO. For comparison, the energy scale versus E_vac is scaled to the redox potential versus the normal hydrogen electrode (46, 47). The oxidation potential for methanol, ~−4.3 eV versus E_vac at pH 7, is indicated by the dashed pink line. Absolute energy levels for emission and absorption are set on the basis of the fact that MgO NPs have photocatalytic activity in H₂ production. This requires that the oxidation potential of methanol lies between the energy levels of excitonic electrons and holes in the absorption region of MgO. Surface-bound electron-hole pairs from threefold/low-coordinate surface sites of MgO NPs are ionized after absorption of UV light mainly at 220 nm (5.6 eV) and 270 nm (4.6 eV) (see Fig. 3A) (37, 38, 43). For simplicity, only the energy levels in the absorption region relating to the 270-nm peak are illustrated in Fig. 5. The energy level of the photogenerated holes of MgO is over ~−8 eV, negative to the oxidation potential of methanol at ~−4.3 eV versus the vacuum energy level E_vac at pH 7 (48). This enables photogenerated holes to oxidize CH₂OH and generate intermediate hydroxalkyl radical, ·CH₂OH. These dynamically unstable radicals are easily oxidized to formaldehyde (CH₂=O) (3, 49). During the two-step oxidation, two protons are generated and reduced to H₂ from the electrons residing in surface states of MgO. This H₂ production behavior is closely correlated with the unique structure of our synthesized MgO nanocrystals. As shown in fig. S10, we compared time-dependent H₂ production between MgO in this work, commercial MgO, commercial SiO₂, and commercial TiO₂ (P25) NPs. The sizes of commercial MgO, SiO₂, and TiO₂ are about 80 to 100 nm, 30 to 60 nm, and 20 to 40 nm, respectively. Before H₂ production, all samples are treated with the same O₂ plasma. With the continuous light illumination time for 24 hours, H₂ produced from commercial SiO₂ is only 0.4 μmol, and that from commercial MgO reaches 1.1 μmol. However, MgO in this work can reach 2.4 μmol, which is 2.2 and 6.0 times of that from commercial MgO and SiO₂, respectively. Compared with SiO₂ and MgO, commercial TiO₂ (P25) produced H₂ more efficiently at first but slowed down after 12-hour reaction and was surpassed by MgO in this work after 16 hours. This indicates an undependable performance from commercial TiO₂ (P25). The low performance of commercial SiO₂ implies that O₂ plasma...
treatments itself does not make a notable contribution to H₂ production in this work; O₂ plasma treatment is mainly used to make MgO nanocrystals hydrophilic. The obviously more H₂ produced from the MgO in this work, as compared with commercial MgO, demonstrates that the unique structure with low-coordinate surface sites of our MgO directly contributes to efficient H₂ production from methanol under photocatalytic reaction.

Aqueous methanol reforming, one of the methanol dehydrogenation reactions, produces carbon dioxide (CO₂) via the water-gas shift reaction. Conversely, complete decomposition of methanol generates carbon monoxide (CO) and H₂ (5). In our MgO/methanol reaction system, neither CO₂ (fig. S11, A and C) nor CO (fig. S12, A and B) was observed in the products. On the basis of this observation, the two main products from MgO/methanol after photodecomposition are H₂, as observed from the chromatogram of fig. S11A, and CH₂O. This indicates that methanol, catalyzed by MgO, is not completely photodecomposed. Although this partial decomposition of methanol is not ideal in terms of H₂ production capacity, the CH₂O product is a convenient liquid in a closed loop (under ~5-atm pressure), as opposed to CO₂ or CO gases. Note here that there is a trace of unknown gaseous component (fig. S11A), which is attributed to the impurities in methanol because this component is also produced after illumination of pure methanol (fig. S11B). Additionally, negligible amounts of oxygen are also present because of the manual injection of gas into the gas chromatograph. Furthermore, to check whether methanol itself produces H₂ under UV light illumination (50), H₂ production was monitored from 8 ml of methanol in the absence of the MgO photocatalyst. As shown in fig. S5B, the amount of H₂ produced is only ~0.1 μmol after 10-hour reaction, which is only 2.5% of that (~4 μmol) produced from the MgO/methanol (3 mg of MgO dispersed in 8 ml of methanol). The negligible H₂ produced from pure methanol starts to saturate after a 9-hour reaction (fig. S6B), which implies that the hydrogen is probably produced from the impurities in methanol that eventually decomposed to the inactive species. This saturation in H₂ production is in contrast to the increasing H₂ production for MgO/methanol (Fig. 4C and fig. S9). MgO not only exhibited stable performance; its crystal structure was well maintained after the 48-hour photocatalytic reaction. This is confirmed by the XRD taken after 48 hours of operation, which is still well matched to the standard pattern of JCPDS: 45-0946, as shown in Fig. 4D.

DISCUSSION

Here, we demonstrate to have successfully synthesized porous, monocristalline MgO NPs via a green and cheap thermolysis process with high yields. The diameter of the MgO nanocrystals can be well controlled from 40 to 170 nm, and these nanocrystals exhibit intense defect-induced blue luminescence under UV excitation. To widen the application of MgO synthesized via an oil phase solution process, we successfully used an oxygen plasma treatment to remove the capping ligands and increase hydrophilicity and dispersion in polar liquids, such as methanol and water. The resulting MgO NPs are photocatalysts for liquid-methanol photodecomposition, resulting in fast CO₂-free H₂ production. The ultrastable catalytic activity for CO₂-free H₂ production demonstrated herein points to new paths to develop environmentally friendly and scalable photocatalysts.

MATERIALS AND METHODS

Chemicals
Magnesium 2,4-pentanedionate hydrate [Mg(acac)₂·2H₂O, >98%, Alfa Aesar], OM (70%, Sigma-Aldrich), OA (90%, Sigma-Aldrich), ODE (>90%, Sigma-Aldrich), ethanol [analytical reagent (AR)], acetone (AR), glycerin (AR), and cyclohexane (AR) were used as received without further purification.

Synthesis of porous MgO NPs
The synthesis of the 85-nm-sized porous MgO NPs was used as an example. A slurry containing 2 mmol (0.445 g) of Mg(acac)₂·2H₂O, 16 mmol (4.288 g) of OM, 4 mmol (1.128 g) of OA, and 20 mmol (5.05 g) of ODE in a three-necked flask (100 ml) was heated to 140°C to remove water and oxygen, thus forming a homogeneous light yellow solution. The resulting mixture was heated to 280°C under N₂ and kept at that temperature for 30 min. Upon cooling to room temperature, the nanocrystals were precipitated by adding an excess of ethanol and glycerin (volume ratio of 4:1) and separated from the solution by centrifugation (10,000 rpm, 10 min), followed by drying in an oven at 60°C. The glycerin was used to remove impurities, such as NaCl. The as-prepared dried nanocrystals could be dispersed in various nonpolar organic solvents, such as cyclohexane and toluene. The average yield of nanocrystals was around 55%.

Characterization
TEM images were acquired with a Hitachi HT7700 transmission electron microscope operated at 100 kV. HRTEM micrographs and STEM images were obtained with a Philips Tecnai F20 FEG (field emission gun)–TEM operated at 200 kV. SEM images were characterized through a Quanta F250. Samples for TEM analysis were prepared by drying a drop of cyclohexane solution containing the nanocrystals on the surface of a carbon-coated copper grid. The XRD patterns were obtained using Rigaku D/MAX-RB with monochromatized Cu Kα radiation (λ = 1.5418 Å) and 2θ ranging from 20° to 80°C. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer. UV-vis absorption spectra were measured on a PerkinElmer Lambda 35 UV-vis spectrophotometer. PL spectra were recorded on a Hitachi F-4600 spectrofluorophotometer at room temperature. Nitrogen adsorption-desorption isotherms were measured on a Micromeritics TriStar 3000 porosimeter (mesoporous characterization) and Micromeritics ASAP 2020 (microporous characterization) at 77 K. All MgO NPs samples were outgassed at 160°C for 6 hours under vacuum before measurements. The specific surface areas were calculated on the basis of the BET method. Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with a Shimadzu/Kratos AXIS Ultra DLD spectrometer, using the He(I) radiation (21.21 eV) from a He discharge lamp. Peaks were recorded with a constant energy of 5 eV and a step size of 0.05 eV. The pressure in the analysis chamber was maintained at 4.3 × 10⁻⁹ torr.

Measurement of H₂ production
Here, four kinds of materials/powders were tested for the photocatalytic hydrogen production, including MgO nanocrystals with sizes of 40, 85, 115, and 170 nm. Note here that, before the photocatalytic experiments, all the MgO powders were treated with the same oxygen plasma for 1 hour to generate hydrophilic surfaces by removing the hydrophobic organic ligands. The photocatalytic hydrogen production experiments were performed in a ~16-ml quartz flask under...
atmospheric pressure at room temperature. For hydrogen production testing, 3 mg of MgO powder was dispersed in pure methanol (anhydrous, 99.8% from Sigma-Aldrich) with its volume varied from 2 to 10 ml, followed by sonication for ~45 min. Then, the quartz flask was sealed with silicone rubber septum, and then the reaction suspension in the flask was degassed with pure nitrogen gas for ~30 min to remove the air inside, keeping the reaction suspension in an inert environment. After degassing, the quartz flask with reaction suspension was transferred and placed before the light source. A 1000-W mercury lamp (MAX-1000, Newport Corporation) was used as a broadband light source covering the wavelength band between 200 and 2500 nm, to trigger the photocatalytic reaction. The light illumination intensity on the flask was ca. 388 mW cm⁻². The hydrogen was analyzed by gas chromatography (Agilent 7890A) with the installed gas valve system. During multiple-cycle performance endurance testing, the reaction material MgO/methanol in the reactor was sonicated for ~30 min, and then the whole reaction system was sealed for the subsequent ~30-min degassing to drive away air before the H₂ production testing.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/9/e1501425/DC1

REFERENCES AND NOTES

1. G. A. Olah, A. Goeppert, G. K. Surya Prakash, Beyond Oil and Gas: The Methanol Economy (Wiley-VCH, Weinheim, ed. 2, 2009).
2. K.-i. Aika, H. Sekiya, A. Ozaki, Selectivities of group VIII metals for the hydrogenation of formaldehyde and the effect of support and promoter. Chem. Lett. 12, 301–304 (1983).
3. R. Hirschi, A. Eichler, J. Hafner, Hydrogenation of ethylene and formaldehyde on Pt (111) and PtₕFₕ₂ (111): A density-functional study. J. Catal. 226, 273–282 (2004).
4. J. W. Shabaker, R. R. Davda, G. W. Huber, R. D. Cortright, J. A. Dumescic, Aqueous phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. J. Catal. 215, 344–352 (2003).
5. D. R. Pal, R. A. Dagle, J. D. Holliday, Methanol steam reforming for hydrogen production. Rev. Chem. 107, 3992–4021 (2007).
6. M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexlcr, H. Junge, S. Gladisli, M. Beller, Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide. Nature 495, 85–89 (2013).
7. E. Alberico, P. Sprotmoll, C. Cords, M. Nielsen, H.-J. Drexlcr, W. Baumann, H. Junge, M. Beller, Selective hydrogen production from methanol with a defined iron pincer catalyst under mild conditions. Angew. Chem. Int. Ed. 52, 14162–14166 (2013).
8. Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo, M. Haruta, Low-temperature decomposition of methanol to carbon monoxide and hydrogen with low activation energy over Pd₂/Zeolite catalyst. Catal. Lett. 44, 189–191 (1997).
9. Y. Matsumura, K. Tanaka, N. Tode, T. Yazawa, M. Haruta, Catalytic methanol decomposition to carbon monoxide and hydrogen over nickel supported on silica. J. Mol. Catal. A Chem. 152, 157–165 (2000).
10. W. I. Shen, Y. Matsumura, Low-temperature methanol decomposition to carbon monoxide and hydrogen catalysed over cationic palladium species in Pd/Co₂O₃. Phys. Chem. Chem. Phys. 2, 1519–1522 (2000).
11. J. C. Brown, E. Gulati, Hydrogen production from methanol decomposition over Pt/Al₂O₃ and ceria promoted Pt/Al₂O₃ catalysts. Catal. Commun. 5, 431–436 (2004).
12. W. Cui, I. Feng, C. Xu, S. Lü, F. Qiu, Hydrogen production by photocatalytic decomposition of methanol gas on Pt/TiO₂ nano-film. Catal. Commun. 5, 533–536 (2004).
13. W. Cui, C. Xu, S. Zhang, L. Feng, S. Lü, F. Qiu, Hydrogen evolution by photocatalysis of methanol vapor over Ti-beta. J. Photochem. Photobiol. A 175, 89–93 (2005).
14. G. Halasi, G. Schubert, F. Solymosi, Comparative study on the photocatalytic decomposition of methanol on TiO₂ modified by N and promoted by metals. J. Catal. 294, 199–206 (2012).
15. A. Gazsi, G. Schubert, T. Băngsă, F. Solymosi, Photocatalytic decomposition of methanol and ethanol on Au supported by pure or N-doped TiO₂. J. Photochem. Photobiol. A. 271, 45–55 (2013).
16. C.-J. Jia, Y. Liu, H. Bongard, F. Schüth, Very low temperature CO oxidation over colloidally deposited gold nanoparticles on Mg(OH)₂ and MgO. J. Am. Chem. Soc. 132, 1520–1522 (2010).
17. K. Teramura, T. Tanaka, H. Ishikawa, Y. Kohno, T. Funabiki, Photocatalytic reduction of CO₂ to CO in the presence of H₂ or CH₄ as a reductant over MgO. J. Phys. Chem. B 108, 346–354 (2004).
18. H. Niu, Q. Yang, K. Tang, Y. Xie, Large-scale synthesis of single-crystalline MgO with bone-like nanostructures. J. Nanopart. Res. 8, 881–886 (2006).
19. A. Khaleli, P. N. Kapoor, K. J. Klubande, Nanocrystalline metal oxides as new adsorbents for air purification, Nanostruct. Mater. 11, 459–468 (1999).
20. R. Richards, W. Li, S. Decker, C. Davidson, O. Koper, V. Zaikovski, A. Volodin, T. Rieker, K. J. Klubande, Consolidation of metal oxide nanocrystals. Reactive pellets with controllable pore structure that represent a new family of porous, inorganic materials. J. Am. Chem. Soc. 122, 4921–4925 (2000).
21. C. Feldmann, S. Matschulho, S. Ahlert, Polyol-mediated synthesis of nanoscale Mg(OH)₂ and MgO. J. Mater. Sci. 42, 7076–7080 (2007).
22. M. Huang, D.-Q. Li, Y.-J. Lin, M. Wei, D. G. Evans, X. Duan, Controllable preparation of nano-MgO and investigation of its bactericidal properties. J. Inorg. Biochem. 99, 986–993 (2005).
23. S. Utamapanya, K. J. Klubande, J. R. Schlup, Nanoscopic metal oxide particles/clusters as chemical reagents. Syntheses and properties of ultrathin surface area magnesium hydroxide and magnesium oxide. Chem. Mater. 3, 175–181 (1991).
24. Y. Ding, G. Zhang, H. Wu, B. Hai, L. Wang, Y. Qian, Nanoscale magnesium hydroxide and magnesium oxide powders: Control over size, shape, and structure via hydrothermal synthesis. Chem. Mater. 13, 435–440 (2001).
25. A. Subramaniam, G. V. Kumar, A. Sai Sathya Priya, T. Vasudevan, Polyol-mediated thermolysis process for the synthesis of MgO nanoparticles and nanowires. Nanotechnology 18, 225601 (2007).
26. S. Makhlud, R. Dror, Y. Nitzan, Y. Abramovich, R. Jelinek, A. Gedanken, Microwave-assisted synthesis of nanocrystalline MgO and its use as a bactericide. Adv. Funct. Mater. 15, 1708–1715 (2005).
27. K. Zhu, J. Hu, C. Küber, R. Richards, Efficient preparation and catalytic activity of MgO (111) nanospheres. Angew. Chem. Int. Ed. 44, 7435–7439 (2005).
28. O. B. Koper, I. Lajardic, A. Volodin, K. J. Klubande, Alkaline-earth oxide nanoparticles obtained by aerogel methods. Characterization and rational for unexpectedly high surface chemical reactivities. Chem. Mater. 9, 2468–2480 (1997).
29. P. P. Fedorov, E. A. Tkachenko, S. V. Kuznetsov, V. V. Voronov, S. V. Lavrishchev, Preparation of MgO nanoparticles. Inorg. Mater. 43, 502–504 (2007).
30. C. Yan, D. Xue, Novel self-assembled MgO nanosheet and its precursors. J. Phys. Chem. B 109, 12358–12361 (2005).
31. H. R. Moon, J. I. Urban, Methanol steam reforming for hydrogen production. Angew. Chem. Int. Ed. 48, 6278–6281 (2009).
32. X. Peng, J. Wickham, A. P. Alivisatos, Kinetics of II-VI and III-V colloidal semiconductor nano-crystal growth: “Focusing” of size distributions. J. Am. Chem. Soc. 120, 5343–5344 (1998).
33. F. Wang, C. Li, L.-D. Sun, C.-H. Xu, J. Wang, J. C. Yu, C.-H. Yan, Porous single-crystalline palladium nanoparticles with high catalytic activities. Angew. Chem. Int. Ed. 51, 4872–4876 (2012).
37. S. Stankic, M. Sterrer, P. Hofmann, J. Bernardi, O. Diwald, E. Knözinger, Novel optical surface properties of Ca²⁺-doped MgO nanocrystals. Nano Lett. 5, 1889–1893 (2005).
38. M. Sterrer, T. Berger, O. Diwald, E. Knözinger, Energy transfer on the MgO surface, monitored by UV-induced H₂ chemisorption. J. Am. Chem. Soc. 125, 195–199 (2003).
39. R. C. Whited, W. C. Walker, Exciton spectra of CaO and MgO. Phys. Rev. Lett. 22, 1428–1430 (1969).
40. M. Klaua, D. Ullmann, J. Barthel, W. Wulfhekel, J. Kirschner, R. Urban, T. L. Monchesky, A. Enders, J. F. Cochran, B. Heinrich, Growth, structure, electronic, and magnetic properties of MgO/Fe (001) bilayers and Fe/MgO/Fe (001) trilayers. Phys. Rev. B 64, 134411 (2001).
41. G. H. Rosenblatt, M. W. Rowe, G. P. Williams Jr., R. T. Williams, Y. Chen, Luminescence of F and F⁺ centers in magnesium oxide. Phys. Rev. B 39, 10309–10318 (1989).
42. E. Feldbach, R. Jaaniso, M. Kodu, V. P. Denks, A. Kasikov, P. Liblik, A. Maaroos, H. Mändar, M. Kirm, Luminescence characterization of ultrathin MgO films of high crystallinity prepared by pulsed laser deposition. J. Mater. Sci. Mater. Electron. 20 (Suppl. 1), 321–325 (2009).
43. P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödli, F. Bechstedt, M. Scheffler, C. G. Van de Walle, First-principles optical spectra for F centers in MgO. Phys. Rev. Lett. 108, 126404 (2012).
44. C. G. Silva, R. Juárez, T. Marino, R. Molinari, H. García, Influence of excitation wavelength (UV or Visible light) on the photocatalytic activity of titania containing gold nanoparticles for the generation of hydrogen or oxygen form water. J. Am. Chem. Soc. 133, 595–602 (2011).
45. Y. Hou, A. B. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl, I. Chorkendorff, Layered nanojunctions for hydrogen-evolution catalysis, Angew. Chem. Int. Ed. 52, 3621–3625 (2013).
46. C. G. Zoski, Handbook of Electrochemistry (Elsevier, Amsterdam, 2007).
47. S. Linic, P. Christopher, D. B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. Nat. Mater. 10, 911–921 (2011).
48. M. J. Berr, P. Wagner, S. Fischbach, A. Vaneski, J. Schneider, A. S. Sucha, A. L. Rogach, F. Jäckel, J. Feldmann, Hole scavenger redox potentials determine quantum efficiency and stability of Pt-decorated CdS nanorods for photocatalytic hydrogen generation. Appl. Phys. Lett. 100, 223903 (2012).
49. A. A. Ismail, L. Robben, D. W. Bahnemann, Study of the efficiency of UV and visible-light photocatalytic oxidation of methanol on mesoporous RuO₂–TiO₂ nanocomposites. Chemphyschem 12, 982–991 (2011).
50. K. I. Öberg, R. T. Garrod, E. F. van Dishoeck, H. Linnartz, Formation rates of complex organics in UV irradiated CH₃OH-rich ices. Astron. Astrophys. 504, 891–913 (2009).

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