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Photothermal catalytic H₂ production over hierarchical porous CaTiO₃ with plasmonic gold nanoparticles

Xinti Yu^{1,#}, Zechuan Yu^{2,#}, Heng Zhao¹, Ian D. Gates¹, Jinguang Hu^{1*}

¹Department of Chemical and Petroleum Engineering, University of Calgary, Calgary T2N 1N4, Canada.

²School of Civil Engineering and Architecture, Wuhan University of Technology, Wuhan 430070, Hubei, China.

[#]Both Authors contributed equally.

*Correspondence to: Prof. Jinguang Hu, Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary T2N 1N4, Canada. E-mail: jinguang.hu@ucalgary.ca

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Abstract

The synergistic promotion by photocatalysis and thermocatalysis is a promising approach for sustainable hydrogen (H₂) production. Herein, we rationally design a perovskite-based catalyst with three-dimensionally ordered macroporous structure (3DOM CaTiO₃-Au) for photothermal catalytic H₂ production from different substrates. The hierarchical 3DOM structure facilitates light harvesting and mass diffusion of the substrates, while the gold nanoparticles (Au NPs) promote charge separation. The photogenerated and hot electrons are oriented accumulated on the surface of Au NPs. The non-metallic gold species [Au(I)] show more activity for H₂ evolution. As a result, 3DOM CaTiO₃-Au exhibits excellent activity for H₂ production from glycerol and other substrates with hydroxyl groups. The present work demonstrates a feasible approach to improve sustainable H₂ production by rationally designing and fabricating efficient photothermal catalysts.

Keywords: 3DOM CaTiO₃, plasmonic Au NPs, photothermal catalysis, H₂ production, mechanism investigation

INTRODUCTION

Hydrogen (H₂), a clean and sustainable energy vector, has been widely recognized as a promising alternative to traditional fossil fuels^[1]. Currently, about 96% of H₂ is produced from the steam reforming process, which



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requires a huge amount of energy input and results in CO₂ emission^[2]. Comparably, solar-driven water splitting is a more energy-saving and sustainable approach for H₂ generation^[3-8]. However, the present water splitting activity has been greatly limited by the energetically and kinetically demanding process of O₂ evolution reaction (OER)^[9,10]. In the present work, numerous investigations have been conducted to replace the OER with organic photo-oxidation, which could not only reduce the energy demand for H₂ generation but also provide an alternative to simultaneously produce value-added chemicals^[11-17].

To realize the above scenario, the rational design of dual-functional photocatalysts is highly desired. The excellent candidate should have multiple abilities in light harvesting, enhanced charge separation and favorable surface reaction kinetics^[18,19]. In terms of light harvesting, the hierarchically porous structure stands out due to the multiple scattering effect, prolonging the interaction between incident photons with photocatalytic materials^[20-22]. Three-dimensionally ordered macroporous (3DOM) structure has been extensively applied in photocatalytic applications because of its outstanding competence in improving light absorption and facilitating mass diffusion^[23-26]. Our previous investigation has revealed the significant promotion in photocatalytic H₂ production by CaTiO₃ perovskite with 3DOM structure and carbon quantum dots as cocatalysts, which exhibited comparable activity as 3DOM CaTiO₃-Au^[27]. Considering the excellent photo- and thermal effects of perovskite and gold nanoparticles, it could be foreseen that H₂ production activity would be significantly boosted with the synergistic promotion by photocatalysis and thermocatalysis^[28,29].

Limited by the high Gibbs free energy of most chemical reactions, the overall activity of most photocatalysis is still in the primary stage^[30]. Herein, photothermal catalysis with the assistance of heating to improve the solar-to-hydrogen efficiency has begun to emerge in most recent years^[31-33]. Metal nanomaterials with localized surface plasmon resonance (LSPR) effect have been widely utilized in photothermal applications, such as gold^[34]. The widely recognized mechanism in this case is the photo-assisted thermocatalysis, in which the local temperature on these metal nanomaterials could be as high as > 70 °C under irradiation, thereby enhancing reaction kinetics^[35]. However, the synergistic promotion of H₂ generation could only achieve 2-5 folds as the LSPR of these metal nanomaterials generates a limited number of active electrons, which would be partially transferred to the conduction band of the contacted semiconductors^[36]. Due to the sluggish H₂ evolution reaction on the surface of semiconductor compared with metal materials, photo-assisted thermocatalysis still has significant scope for improvement. From this point of view, accumulating more electrons on the surface of plasmonic gold nanoparticles with extra heating from activated semiconductor materials is a feasible approach to further improve the activity of H₂ production. Besides, non-metallic gold species (Au^{δ+}) have been reported to have improved activity for photocatalytic reactions^[37]. The internal mechanism has not been systematically investigated.

In the present work, we demonstrate the synergistic catalysis of photocatalysis and thermocatalysis for H₂ production by conducting the experiment under light irradiation and at a controlled temperature. 3DOM CaTiO₃ is firstly synthesized by the colloid-template method and gold nanoparticles (Au NPs) are then loaded on the surface to obtain the photothermal catalyst. The as-prepared 3DOM CaTiO₃-Au exhibits hierarchically porous structure in long range and shows significant improvement in visible light absorption due to the LSPR effect. As a result, the 3DOM CaTiO₃-Au shows excellent H₂ production (145.2 μmol) from photothermal glycerol reforming, which is about 57 times and 13 times higher than that from thermocatalysis and photocatalysis, respectively. The oriented accumulation of photothermal electrons on the surface of Au NPs with oxidized species greatly reduces the energy barrier for hydrogen evolution. The present work demonstrates an example of boosting hydrogen production by coupling photocatalysis with thermocatalysis with the rational design of a catalyst.

RESULTS AND DISCUSSION

The fabrication process of 3DOM CaTiO₃-Au is illustrated in [Figure 1A](#). Briefly, the obtained polystyrene spheres by the surfactant-free emulsion polymerization method are assembled into a colloid template. The precursor containing Ca(NO₃)₂ and titanium (IV) isopropoxide then fills the voids of the template, accompanied by the simultaneous hydrolysis reaction. After calcination in air with gradient programs, the 3DOM CaTiO₃ is obtained with CaCO₃ impurity on the surface. Finally, gold nanoparticles are loaded on the acid-washed 3DOM CaTiO₃ by sodium borohydride reduction method. As the quality of colloid template plays a vital role in the formation of 3DOM structure, the assembled polystyrene spheres are first characterized by scanning electron microscopy (SEM). The highly ordered assembly of polystyrene spheres is revealed in [Figure 1B](#). [Figure 1C](#) displays the low-resolution SEM image of the fabricated 3DOM CaTiO₃, which is an assembly of relatively uniform three-dimensionally ordered macroporous structure. The framework of 3DOM CaTiO₃ is constructed by porous nanosheet, which has been well explained in our previous investigation [[Figure 1D](#)]. Transmission electron microscopy (TEM) images at low resolution also reveal the hierarchically porous structure with well-distributed gold nanoparticles [[Figure 1E and F](#)]. The statistical result of the gold nanoparticles shows a broad size distribution and they concentrate in 8 nm [[Supplementary Figure 1](#)]. The high crystallinity could be revealed by the distinguished lattices with a spacing of 0.27 nm, corresponding to the (112) crystal facet of orthorhombic CaTiO₃ [[Figure 1G](#)]. The element mappings reveal the uniform distribution of each element in the structure [[Supplementary Figure 2](#)].

[Figure 2A](#) shows the XRD patterns of the 3DOM CaTiO₃ and 3DOM CaTiO₃-Au. CaTiO₃ phase was confirmed by the comparison between the XRD patterns and the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 01-078-1013. The as-fabricated CaTiO₃ has pure phase and good crystallinity. All diffraction peaks can be assigned to the orthorhombic structure. The inset in [Figure 2A](#) is the partial enlarged detail and the peak around 38.3° corresponds to the (111) lattice plane of Au, which reveals the presence of Au in CaTiO₃. The XRD patterns of the CaTiO₃ unwashed by diluted nitric acid are shown in [Supplementary Figure 3](#). In addition to CaTiO₃, the impurity CaCO₃ was also observed. The Ca²⁺ outside the crystal structure of CaTiO₃ interacted with CO₂ to form CaCO₃ during the calcination process. The initial molar ratio of Ca and Ti was 1:1, and the formation of CaCO₃ indicated the presence of cation defects in the crystal structure^[38].

The optical properties of 3DOM CaTiO₃ and 3DOM CaTiO₃-Au have been measured by UV-vis diffuse reflectance spectroscopy and the corresponding spectra are shown in [Figure 2B](#). The optical band gap values obtained through the linear fitting of tails from the UV-vis spectra are shown in the inset of [Figure 2B](#). All the samples are of the same size and thickness. The strong absorption at a wavelength range below 400 nm matches the intrinsic inter-band transition absorption of orthorhombic CaTiO₃^[39]. As shown in the inset of [Figure 2B](#), the band gap of as-fabricated 3DOM CaTiO₃ is approximately 3.25 eV, corresponding to an optical absorption edge of 382 nm. After the introduction of AuNPs, the light absorption is greatly improved. The broad peak at 540 nm of 3DOM CaTiO₃-Au composite corresponds to surface plasmon resonance (SPR) absorption of Au nanoparticles.

The chemical states on the surface of catalysts have been investigated by X-ray photoelectron spectroscopy (XPS), where characteristic peaks of Ca, Ti, O, Au and C are observed in the general survey scan [[Supplementary Figure 4A](#)]. All the XPS data has been calibrated by C 1s at 284.8 eV [[Supplementary Figure 4B](#)]. The pristine 3DOM CaTiO₃ and the modified composite of 3DOM CaTiO₃-Au show the unchanged binding energies of Ti 2p and O 1s [[Supplementary Figure 4C and D](#)]. However, a significant shift to lower binding energy in Ca 2p spectra is identified with the loading of Au NPs onto the

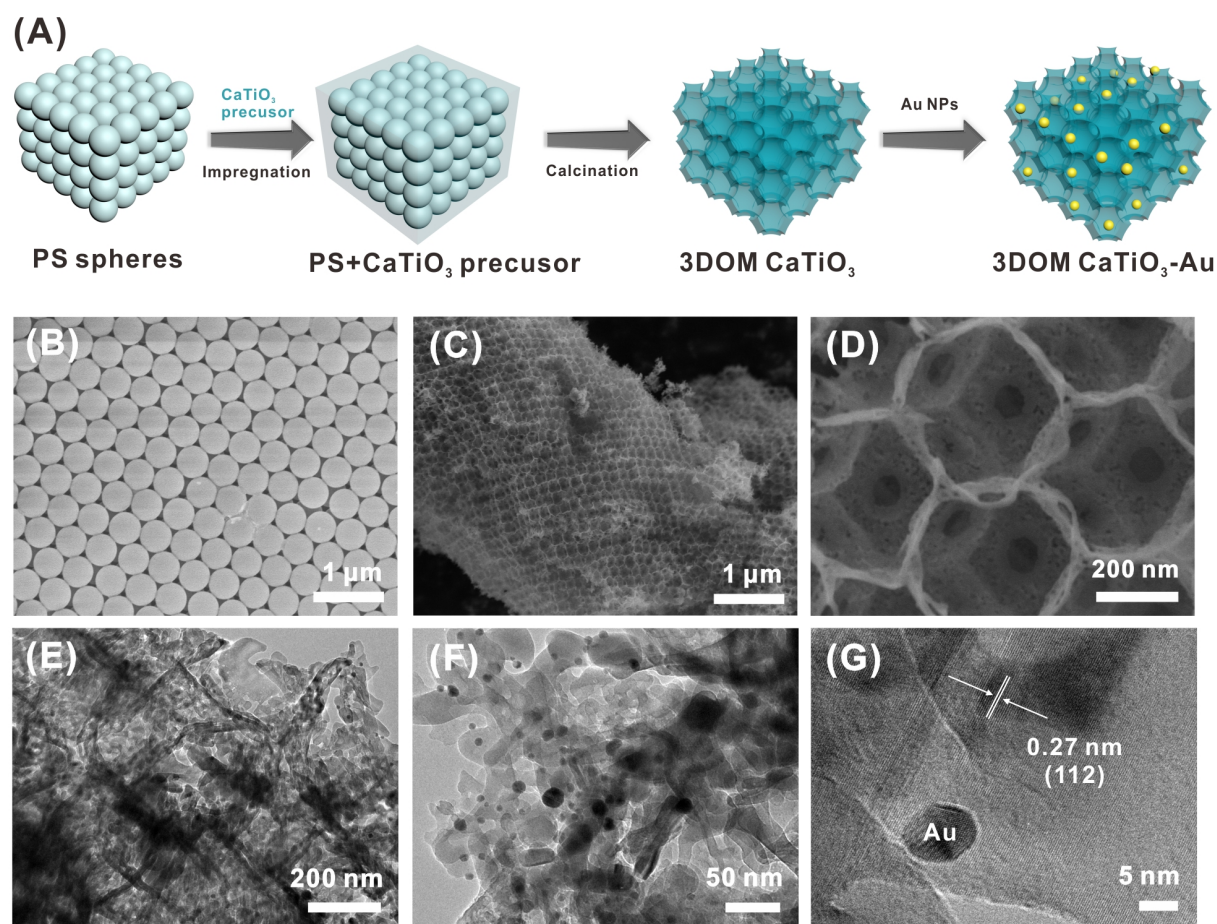


Figure 1. (A) Schematic illustration of the fabrication process of 3DOM CaTiO₃-Au, SEM images of (B) assembled polystyrene spheres; (C) 3DOM CaTiO₃ with low resolution; (D) 3DOM CaTiO₃ with high resolution; (E) and (F) Low-resolution TEM images of 3DOM CaTiO₃-Au; (G) high-resolution TEM image of 3DOM CaTiO₃-Au.

surface of CaTiO₃, indicating the spontaneous electron transfer due to the formation of Schottky junctions [Figure 2C]^[40]. More importantly, the oxidized species of gold is also identified apart from the metallic state, which is consistent with our previous investigation [Figure 2D]^[37]. The relative percentage of Au (I) is calculated to be around 3.2%. The detected Ti-OH in the O 1s spectra indicated the presence of oxygen vacancy in both 3DOM CaTiO₃ and 3DOM CaTiO₃-Au, which could be further revealed by the electron paramagnetic resonance (EPR) results [Supplementary Figure 5]. Noticeably, the intensity of oxygen vacancy increases with the introduction of gold nanoparticles, which may attribute to the high reduction ability of sodium borohydride.

The activity of as-prepared catalysts was evaluated by thermos-photocatalytic glycerol reforming for H₂ production. To reveal the synergistic promotion of thermocatalysis and photocatalysis, H₂ production over different catalysts was first investigated *via* thermocatalysis at 100 °C and photocatalysis, respectively. CaTiO₃ and 3DOM CaTiO₃ produce a similar amount of H₂ after 11 h reaction (0.47 μmol and 0.52 μmol respectively), indicating the negligible contribution of 3DOM structure in thermocatalytic H₂ production of pristine CaTiO₃ [Figure 3A]. With the loading of gold nanoparticles, the amount of H₂ significantly increases to 2.55 μmol after 11 h reaction, which is probably attributed to the mass diffusion property of hierarchical 3DOM structure. Another feature of 3DOM structure is light harvesting, which facilitates activating CaTiO₃ to produce more electrons and holes^[41]. The promotion of H₂ production of 3DOM

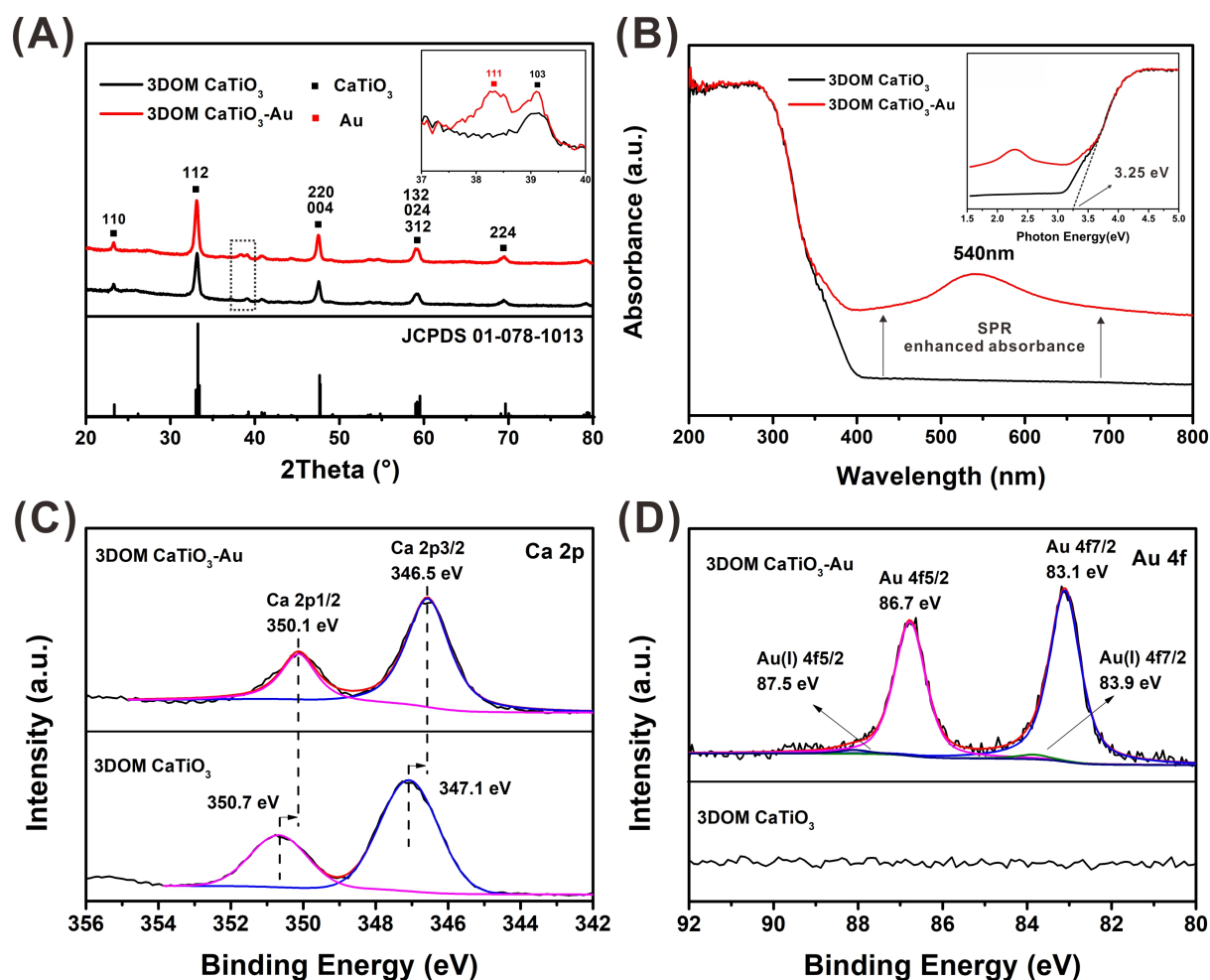


Figure 2. (A) XRD patterns; (B) UV-vis absorption spectra, high-resolution XPS spectra of (C) Ca 2p; and (D) Au 4f of 3DOM CaTiO₃ and 3DOM CaTiO₃-Au.

structure could be revealed by the performance of CaTiO₃ (0.26 μmol) and 3DOM CaTiO₃ (0.70 μmol) under the Xenon lamp irradiation [Figure 3B]. After loading gold nanoparticles, about 30 folders and 17 folders in H₂ production after 11 h reaction is achieved for CaTiO₃-Au (7.89 μmol) and 3DOM CaTiO₃-Au (11.67 μmol), respectively. The synergistic enhancement is further realized by coupling thermocatalysis at 100 °C and photocatalysis for all the four catalysts. The amount of H₂ generation at 11-h reaction for CaTiO₃, 3DOM CaTiO₃, CaTiO₃-Au and 3DOM CaTiO₃-Au is boosted to 18.91 μmol, 40.60 μmol, 90.41 μmol and 145.2 μmol, respectively [Figure 3C]. The comparison in H₂ production for each catalyst under different reaction conditions further demonstrates the significant promotion by photothermal approach [Supplementary Figures 6-9 and Supplementary Table 1]. Compared to bare photocatalysis and thermocatalysis, the H₂ generation over 3DOM CaTiO₃-Au by photothermal catalysis is enhanced by about 12 and 58 folders, respectively. The effect of gold loading on the thermo-photocatalytic H₂ production was further investigated by changing the volume of used HAuCl₄. The variation of gold loading is revealed to have a negligible effect on H₂ production for CaTiO₃-Au without 3DOM structure. While 3DOM CaTiO₃-Au exhibits significant relation with the gold loading and 205.9 μmol of H₂ is produced at the 11-h reaction when the actual loading of gold was 1.90 wt% [Figure 3D], which is more efficient compared to the CaTiO₃-based catalyst in literature [Supplementary Table 2]. The reaction temperature is

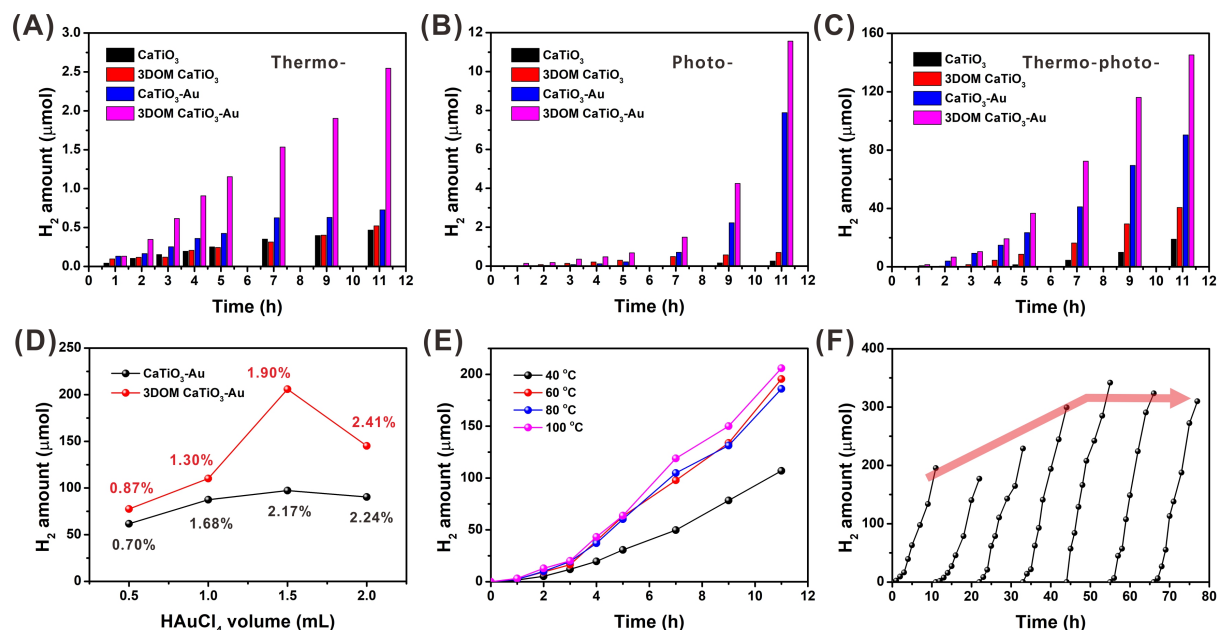


Figure 3. H₂ production over different catalysts via (A) thermocatalysis (100 °C); (B) photocatalysis; (C) thermo-photocatalysis (100 °C); (D) thermo-photocatalytic H₂ production over 3DOM CaTiO₃-Au prepared by different volumes of HAuCl₄ (actual loading of Au is labeled); (E) thermo-photocatalytic H₂ production over 3DOM CaTiO₃-Au prepared by 1.5 mL of HAuCl₄ under different reaction temperatures; and (F) long-time cycling test.

then changed to investigate its relationship with H₂ production [Figure 3E]. 3DOM CaTiO₃-Au exhibits similar activity when the temperature is above 60 °C, while the activity greatly reduces when the temperature is 40 °C. This indicates that 60 °C may be the threshold to fully activate 3DOM CaTiO₃-Au to produce active electrons for H₂ production. It should be mentioned that CO₂ was not observed during the reaction, indicating the absence of overoxidation. Some liquid products at extremely low concentrations were detected by high-performance liquid chromatography (HPLC) [Supplementary Figure 10]. However, the glycerol conversion was negligible (< 2%). The contribution of glycerol to H₂ production could be revealed by the control experiment in which pure water without glycerol is used as the reactant [Supplementary Figure 11]. It clearly shows that significant enhancement in H₂ production is achieved with the addition of glycerol, revealing the role of sacrificial agent of glycerol. The stability of 3DOM CaTiO₃-Au is tested at 60 °C during the long-time cycling reaction. In the first five cycles, 3DOM CaTiO₃-Au shows gradually increased activity and good stability could be revealed by the repeatability in H₂ production [Figure 3F].

To explain the internal reason for the gradual enhancement in H₂ production during the first five cycles, the used catalyst 3DOM CaTiO₃-Au was collected and characterized for its morphology and chemical state. The 3DOM structure in the long range is kept well after catalytic reaction and a little collapse could also be observed in the high-resolution SEM image [Figure 4A and B]. A significant change in the chemical state of gold is observed [Figure 4C]. Other elements have almost the same chemical state after catalytic reaction [Supplementary Figure 12]. The relative percentage of Au (I) increases from 3.2% to 8.7% after catalytic reaction. Electrostatic potential (ESP) difference is calculated by the addition of two oxygen atoms above the gold [Figure 4D]. The region near the binding site of proton overlaps the region with increased electrostatic potential, suggesting that the electron binding affected by the change in ESP would be relevant to chemical reactions involving hydrogen and electron. Contribution from the elevated ESP to the binding of an electron is 10 to 19 kcal/mol, which suggests a stronger electron binding capability of charged gold ions

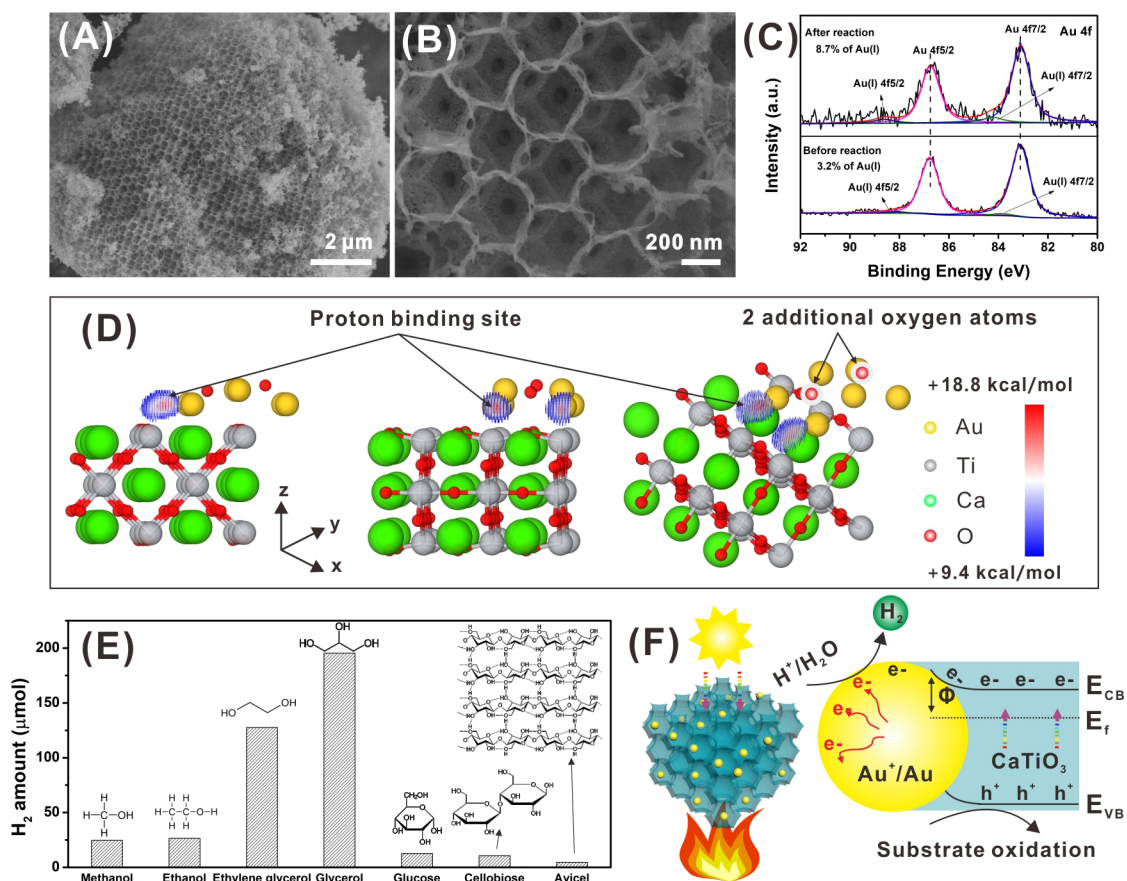


Figure 4. (A and B) SEM images of 3DOM CaTiO₃-Au after photocatalytic reaction; (C) XPS Au 4f spectra of 3DOM CaTiO₃-Au before and after photocatalytic reaction; (D) electrostatic potential difference brought by oxidation of gold atoms (the left and the middle are cross-section view of yz and xz plane, respectively). The right is a 3-D view of the electrostatic potential difference. The positive values indicate an elevated electrostatic potential by the addition of oxygen atoms); (E) H₂ production from different substrates; and (F) the proposed mechanism.

compared to the pristine gold atoms. Considering that the elevated ESP locates near the hydrogen binding site, we expect that the charged gold ions would exhibit a higher reactivity. The H₂ production from different substrates over 3DOM CaTiO₃-Au is also investigated. As the number of hydroxyl groups in the molecular structure from methanol to glycerol increases, the activity of H₂ production also increases [Figure 4E]. However, when the glucose and cellobiose with five and eight hydroxyl groups are used as the substrate, the H₂ production performance is greatly reduced, mainly due to the poor accessibility of these substrates with large dimensional structures to the catalyst^[42,43]. Further inhibition of H₂ evolution is observed when cellulose with a more complex structure is used as the substrate. Therefore, the H₂ production performance is not only related to the number of hydroxyl groups but also the complexity of substrate structure. A brief mechanism is proposed herein [Figure 4F]. Under light irradiation, the electrons of CaTiO₃ are activated to conduction band, while the holes stay on the valence band. Due to the high work function of Au, the photogenerated electrons are then transferred to the surface of Au. With the assistance of extra heating, more electrons are accumulated from CaTiO₃ and the Au NPs also generate active hot electrons. All the electrons on the surface of Au NPs trigger the proton reduction reaction to produce H₂, while the substrate oxidation reaction is proceeded by the holes on the valence band.

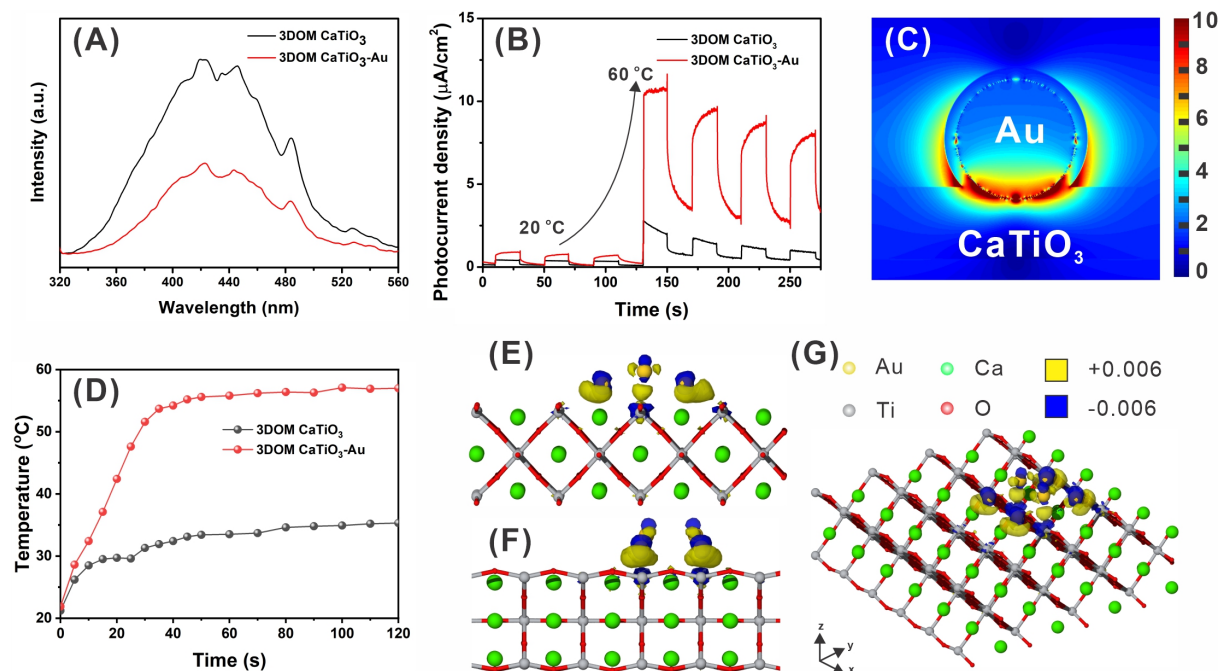


Figure 5. (A) PL; (B) photocurrent of 3DOM CaTiO_3 and 3DOM $\text{CaTiO}_3\text{-Au}$ under different temperatures; (C) simulated electromagnetic field intensity distribution; (D) temperature of the catalyst with different light irradiation times for 3DOM CaTiO_3 and 3DOM $\text{CaTiO}_3\text{-Au}$. Isosurfaces of electronic density difference at the perovskite-gold interface from the cross-section view of (E) yz and (F) xz plane; (G) 3-D view of positive-value and negative-value isosurface in yellow and blue, respectively.

To reveal the improvement in charge separation after the introduction of Au NPs, steady photoluminescence (PL) spectra of 3DOM CaTiO_3 and 3DOM $\text{CaTiO}_3\text{-Au}$ are collected with the excitation wavelength of 400 nm. 3DOM $\text{CaTiO}_3\text{-Au}$ exhibits much reduced PL intensity, indicating the significant inhibition of photogenerated electrons and holes [Figure 5A]. To check the effect of temperature on the charge generation, transient photocurrent is measured. Both 3DOM CaTiO_3 and 3DOM $\text{CaTiO}_3\text{-Au}$ show excellent responses to light irradiation [Figure 5B]. When the temperature of the electrolyte increases from 20 °C to 60 °C, more than 10 folds in photocurrent are achieved for 3DOM $\text{CaTiO}_3\text{-Au}$, revealing the generation of more electrons with the assistance of extra heating. To visually understand the charge separation, the electromagnetic field is simulated on a single Au nanoparticle [Figure 5C]. It is clear that the charge density on the surface of Au is much higher than that of CaTiO_3 and the highest electromagnetic field intensity is located at the interface of Au and CaTiO_3 , indicating the formation of electron transfer channel at the interface and the immigration of active electrons from CaTiO_3 to Au. The photothermal effect of the catalyst is recorded by measuring the temperature of the 3DOM CaTiO_3 and 3DOM $\text{CaTiO}_3\text{-Au}$ with different light irradiation times [Figure 5D]. Combined with the corresponding IR thermal images [Supplementary Figure 13,] it clearly shows the significant contribution to the photothermal effect by the gold nanoparticles. The electronic density difference brought by the addition of gold to perovskite is evaluated in real space and plotted [Figure 5E-G]. The isosurface in yellow encloses a space with enriched electronic density. We expect that this region favors proton binding. We place a hydrogen atom near the binding site and calculate that the total energy difference between the compound and individual components (the perovskite-gold model and a single hydrogen atom) is about -76.70 kcal/mol near gold and -93.48 kcal/mol near gold ions, which further indicates that oxidized gold species facilitate the H_2 evolution.

CONCLUSIONS

In summary, 3DOM CaTiO₃ is successfully fabricated by the colloid template method and Au NPs with partially oxidized species [Au(I)] are loaded to obtain 3DOM CaTiO₃-Au as the efficient catalyst for photothermal H₂ production. The 3DOM structure facilitates light harvesting and mass diffusion property, while the Au NPs help to improve the charge separation. As a result, 3DOM CaTiO₃-Au with optimized Au loading exhibits boosted activity for H₂ generation by the synergistic promotion of photocatalysis and thermocatalysis. Considerable H₂ is also achieved when the substrates are changed into biomass derivatives. The oriented accumulation of electrons on the surface of Au NPs and the presence of Au(I) species are revealed to be the key factors. The present work provides a rational catalyst design to boost hydrogen production through synergistic photocatalysis and thermocatalysis.

DECLARATIONS

Authors' contributions

Made substantial contributions to conception and design of the study, performed data analysis and interpretation, and wrote the draft of manuscript: Yu X

Performed data acquisition and provided administrative, technical, and material support: Zhao H

Performed DFT calculation: Yu Z

Discussed and revised the manuscript: Gates ID, Hu J

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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REFERENCES

1. Majumdar A, Deutch JM, Prasher RS, Griffin TP. A framework for a hydrogen economy. *Joule* 2021;5:1905-8. [DOI](#)
2. Chen S, Pei C, Gong J. Insights into interface engineering in steam reforming reactions for hydrogen production. *Energy Environ Sci* 2019;12:3473-95. [DOI](#)
3. Wang Z, Li C, Domen K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem Soc Rev* 2019;48:2109-25. [DOI](#) [PubMed](#)
4. Thalluri SM, Bai L, Lv C, Huang Z, Hu X, Liu L. Strategies for semiconductor/electrocatalyst coupling toward solar-driven water splitting. *Adv Sci (Weinh)* 2020;7:1902102. [DOI](#) [PubMed](#) [PMC](#)
5. Wang Y, Vogel A, Sachs M, et al. Current understanding and challenges of solar-driven hydrogen generation using polymeric photocatalysts. *Nat Energy* 2019;4:746-60. [DOI](#)
6. Zhang P, Tian Z, Kang Y, et al. 10 nm Corrugated TiO₂ nanowire arrays by monomicelle-directed assembly for efficient hole extraction. *J Am Chem Soc* 2022;144:20964-74. [DOI](#) [PubMed](#)
7. Gao M, Zhang T, Ho GW. Advances of photothermal chemistry in photocatalysis, thermocatalysis, and synergetic

- photocatalysis for solar-to-fuel generation. *Nano Res* 2022;15:9985-10005. DOI
8. Gao M, Peh CK, Zhu L, Yilmaz G, Ho GW. Photothermal catalytic gel featuring spectral and thermal management for parallel freshwater and hydrogen production. *Adv Energy Mater* 2020;10:2000925. DOI
 9. Jamesh M, Harb M. Tuning the electronic structure of the earth-abundant electrocatalysts for oxygen evolution reaction (OER) to achieve efficient alkaline water splitting - a review. *J Energy Chem* 2021;56:299-342. DOI
 10. Liu Y, Luo X, Zhou C, et al. A modulated electronic state strategy designed to integrate active HER and OER components as hybrid heterostructures for efficient overall water splitting. *Appl Catal B Environ* 2020;260:118197. DOI
 11. Uekert T, Pichler CM, Schubert T, Reisner E. Solar-driven reforming of solid waste for a sustainable future. *Nat Sustain* 2021;4:383-91. DOI
 12. Zhao H, Li CF, Liu LY, et al. n-p Heterojunction of TiO₂-NiO core-shell structure for efficient hydrogen generation and lignin photoreforming. *J Colloid Interf Sci* 2021;585:694-704. DOI PubMed
 13. Zhao H, Li CF, Yong X, et al. Coproduction of hydrogen and lactic acid from glucose photocatalysis on band-engineered Zn_{1-x}Cd_xS homojunction. *iScience* 2021;24:102109. DOI PubMed PMC
 14. Nwosu U, Wang A, Palma B, et al. Selective biomass photoreforming for valuable chemicals and fuels: a critical review. *Renew Sust Energ Rev* 2021;148:111266. DOI
 15. Wang J, Kumar P, Zhao H, Kibria MG, Hu J. Polymeric carbon nitride-based photocatalysts for photoreforming of biomass derivatives. *Green Chem* 2021;23:7435-57. DOI
 16. Wu X, Luo N, Xie S, et al. Photocatalytic transformations of lignocellulosic biomass into chemicals. *Chem Soc Rev* 2020;49:6198-223. DOI PubMed
 17. Li Y, Zhang D, Qiao W, et al. Nanostructured heterogeneous photocatalyst materials for green synthesis of valuable chemicals. *Chem Synth* 2022;2:9. DOI
 18. Toe CY, Tsounis C, Zhang J, et al. Advancing photoreforming of organics: highlights on photocatalyst and system designs for selective oxidation reactions. *Energy Environ Sci* 2021;14:1140-75. DOI
 19. Ma J, Liu K, Yang X, et al. Recent advances and challenges in photoreforming of biomass-derived feedstocks into hydrogen, biofuels, or chemicals by using functional carbon nitride photocatalysts. *ChemSusChem* 2021;14:4903-22. DOI
 20. Chen LH, Li Y, Su BL. Hierarchy in materials for maximized efficiency. *Natl Sci Rev* 2020;7:1626-30. DOI PubMed PMC
 21. Liu J, Zhao H, Wu M, et al. Slow photons for photocatalysis and photovoltaics. *Adv Mater* 2017;29:1605349. DOI PubMed
 22. Baba T. Slow light in photonic crystals. *Nature Photon* 2008;2:465-73. DOI
 23. Zhao H, Wu M, Liu J, Deng Z, Li Y, Su B. Synergistic promotion of solar-driven H₂ generation by three-dimensionally ordered macroporous structured TiO₂-Au-CdS ternary photocatalyst. *Appl Catal B Environ* 2016;184:182-90. DOI
 24. Zhao H, Yu X, Hu G, et al. Confined synthesis of BiVO₄ nanodot and ZnO cluster co-decorated 3DOM TiO₂ for formic acid production from the xylan-based hemicellulose photorefinery. *Green Chem* 2021;23:8124-30. DOI
 25. Zhao H, Li C, Yu X, et al. Mechanistic understanding of cellulose β-1,4-glycosidic cleavage via photocatalysis. *Appl Catal B Environ* 2022;302:120872. DOI
 26. Liu J, Guo Y, Hu Z, et al. Slow photon-enhanced heterojunction accelerates photocatalytic hydrogen evolution reaction to unprecedented rates. *CCS Chem* 2022:1-13. DOI
 27. Zhao H, Liu J, Li C, et al. Meso-microporous nanosheet-constructed 3d com perovskites for remarkable photocatalytic hydrogen production. *Adv Funct Mater* 2022;32:2112831. DOI
 28. Mateo D, Morlanes N, Maity P, Shterk G, Mohammed OF, Gascon J. Efficient visible-light driven photothermal conversion of CO₂ to methane by nickel nanoparticles supported on barium titanate. *Adv Funct Mater* 2021;31:2008244. DOI
 29. Song C, Wang Z, Yin Z, Xiao D, Ma D. Principles and applications of photothermal catalysis. *Chem Catal* 2022;2:52-83. DOI
 30. Li Y, Xue J, Shen Q, et al. Construction of a ternary spatial junction in yolk-shell nanoreactor for efficient photo-thermal catalytic hydrogen generation. *Chem Eng J* 2021;423:130188. DOI
 31. Li X, Zhao S, Duan X, et al. Coupling hydrothermal and photothermal single-atom catalysis toward excellent water splitting to hydrogen. *Appl Catal B Environ* 2021;283:119660. DOI
 32. Gao M, Zhu L, Peh CK, Ho GW. Solar absorber material and system designs for photothermal water vaporization towards clean water and energy production. *Energy Environ Sci* 2019;12:841-64. DOI
 33. Zhang T, Meng F, Gao M, et al. Multi-interfacial catalyst with spatially defined redox reactions for enhanced pure water photothermal hydrogen production. *EcoMat* 2021:3. DOI
 34. Liu H, Shi L, Zhang Q, et al. Photothermal catalysts for hydrogenation reactions. *Chem Commun (Camb)* 2021;57:1279-94. DOI PubMed
 35. Zhou L, Swearer DF, Zhang C, et al. Quantifying hot carrier and thermal contributions in plasmonic photocatalysis. *Science* 2018;362:69-72. DOI
 36. Ng SWL, Gao M, Lu W, Hong M, Ho GW. Selective wavelength enhanced photochemical and photothermal H₂ generation of classical oxide supported metal catalyst. *Adv Funct Mater* 2021;31:2104750. DOI
 37. Zhao H, Liu P, Wu X, et al. Plasmon enhanced glucose photoreforming for arabinose and gas fuel co-production over 3DOM TiO₂-Au. *Appl Catal B Environ* 2021;291:120055. DOI
 38. Wegmann M, Watson L, Hendry A. XPS analysis of submicrometer barium titanate powder. *J Am Ceram Soc* 2004;87:371-7. DOI
 39. Cai J, Cao A, Huang J, et al. Understanding oxygen vacancies in disorder-engineered surface and subsurface of CaTiO₃ nanosheets on

- photocatalytic hydrogen evolution. *Appl Catal B Environ* 2020;267:118378. DOI
40. Zhu C, Wang AL, Xiao W, et al. In situ grown epitaxial heterojunction exhibits high-performance electrocatalytic water splitting. *Adv Mater* 2018;30:e1705516. DOI PubMed
 41. Chang Y, Yu K, Zhang C, et al. Ternary CdS/Au/3DOM-SrTiO₃ composites with synergistic enhancement for hydrogen production from visible-light photocatalytic water splitting. *Appl Catal B Environ* 2017;215:74-84. DOI
 42. Wu X, Zhao H, Khan MA, et al. Sunlight-driven biomass photorefinery for coproduction of sustainable hydrogen and value-added biochemicals. *ACS Sustain Chem Eng* 2020;8:15772-81. DOI
 43. Hao H, Zhang L, Wang W, Zeng S. Facile modification of titania with nickel sulfide and sulfate species for the photoreformation of cellulose into hydrogen. *ChemSusChem* 2018;11:2810-7. DOI PubMed