High quantum efficiency of hydrogen production from methanol aqueous solution with PtCu-TiO_2 photocatalysts

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Methanol with the 12.5wt% H_2 content is widely considered as a liquid hydrogen medium. Coupling with water with the 11%% H_2 content, liquid water reforming of methanol for H_2 synthesis is a promising way for on-demand hydrogen production. We demonstrate an atomic-level catalyst design strategy, using synergy between single atoms and nanodots for H_2 production. The PtCu-TiO_2 sandwich photocatalyst achieves a remarkable H_2 formation rate (2383.9 µmol/h) with a high apparent quantum efficiency (AQE 99.2%). Furthermore, the oxidation product is high-value chemical formaldehyde with 98.6% selectivity, instead of CO_2, leading to a nearly zero-carbon-emission process. Detailed investigations indicate a dual-role of copper atoms: an electron acceptor to facilitate photoelectron transfer to Pt, a hole acceptor for the selective oxidation of methanol to formaldehyde, thus avoiding overoxidation to CO_2. The synergy between Pt nanodots and Cu single atoms together reduce the activation energy of this process to 13.2 kJ/mol.

Traditional H_2 generation from methanol steam reforming requires medium temperatures and pressures (e.g. 200-350 °C, 20-50 bar), resulting in high capital cost and high carbon dioxide emission.[1,2] Though substantial effort has been devoted to methanol-reforming, most of the existing cases focused on half-reduction reaction with H_2 as the only interesting product, ignoring the other half-oxidation reaction products which are carbon-containing. Industrially, over 40% methanol has been used for formaldehyde production, and the most common of industrial-scale technologies are Formox and BASF processes based on silver and ironmolybdenum based catalysts, respectively[3] but they again require a relatively high temperature that comes with by-product CO_x.[4,5] Therefore, it remains challenging to realize selective dehydrogenation of methanol to produce formaldehyde with high selectivity besides the reduction product H_2 under moderate conditions.

Photocatalysis offers a clean and sustainable way to drive chemical conversions under very mild conditions.[6,7] Recently, engineering single-atom catalysis has become a promising strategy to achieve high efficiency and tune selectivity of products by modulating atomic configuration to maximize metal atoms.[8–10] Among them, Cu single-atom co-catalyst was preliminarily reported as the most active non-noble metal for photocatalytic methanol-conversion with the impressive H_2 evolution rate of 83.0 μmol/h,[12] while the activity is still lower than the counterpart by thermal catalysis, obviously limited by the amount of Cu single atoms loaded, which is in most cases about 1%.

Here we demonstrate an atomic-level catalyst design strategy using porous MIL-125(Ti) as a substrate and ion-coordination method to promote synergy between Cu single atoms and Pt nanodots for H_2 production from methanol aqueous solution. The optimal PtCu-TiO_2 exhibits H_2 generation activity of 1206.5 μmol/h (see Movie S1) with a formaldehyde synthesis rate of 1166.0 μmol/h and 98% selectivity at room temperature, or 2383.9 μmol/h H_2 production rate with the nearly 100% AQE at 70°C, even comparative to the benchmark thermal catalyst for H_2 production. Particularly, little CO_2 is produced during H_2 production, resulting in a nearly zero-carbon emission process. Such a special catalyst design strategy thus promises extremely efficient H_2 production together with high-value chemical synthesis under very moderate conditions.

Fig. 1A represents mass-specific H_2 generation rates achieved on MOF-derived TiO_2 loaded with various metals, following the order Cu-TiO_2 > Ru-TiO_2 > Ni-TiO_2 > Pt-TiO_2 > Co-TiO_2 > TiO_2, so single-atom Cu improves the H_2 production rate to 656.7 μmol/h, nearly 50 times enhancement and is much better than widely used noble metals under present conditions. The mechanism for this active species is investigated later. Then the optimisation of Cu-TiO_2 was performed (Supplementary Fig. 1-5), including synthesis conditions (solvent, annealing temperature and time *etc.*). The Cu-TiO_2 annealed at 500°C for 3h further improves the H_2 production rate from 656.7 μmol/h to 777.0 μmol/h, due to the optimal crystalline and Cu^+/Cu^{2+} ratio obtained in such condition. To confirm the origin of enhanced activity, MIL-125-derived TiO_2 was also prepared at various temperatures (Supplementary Fig. 6). In addition, Pt-TiO_2 obtained by a widely used photodeposition method exhibits a high activity of 684.5 μmol/h, while still smaller than Cu-TiO_2, again indicating the single atom Cu loaded TiO_2 is the best under current experimental conditions.

Pt was then introduced to further promote the activity and more importantly stability via the synergy between Cu and Pt.[12] Pt increases Cu-TiO_2 activity to 1206.5 μmol/h H_2 when its loading amount is 0.5wt% (Supplementary Fig. 7), The optimised PtCu-TiO_2 shows 89 times higher activity than pristine TiO_2. Fig. 1B and Supplementary Fig. 8 show the initial catalytic activity change with time over different photocatalysts with an order of PtCu-TiO_2 (1206.5 μmol/h) > Cu-TiO_2 (777.0 μmol/h) > Pt-TiO_2 (684.5 μmol/h) > TiO_2 (13.5 μmol/h). The observed activity of Pt-TiO_2 and Cu-TiO_2 is much higher than pure TiO_2, ascribing to co-catalyst loading. Cu-TiO_2 exhibits higher activity than Pt-TiO_2, ascribing to bifunctional Cu where Cu^{2+} acts as an electron acceptor for H_2 generation and Cu^+ serves as hole-extraction sites for methanol-oxidation as proved later. Furthermore, the activity of PtCu-TiO_2 was tested from 25°C to 70°C, showing an increasing trend with the rise of temperature. The control experiment (Supplementary Fig. 9-10) shows no generation of H_2 at 70°C under dark, ruling out the thermal catalysis contribution under this condition. Next, Fig. 1C shows the oxidation product selectivity over obtained photocatalysts. HCHO is the main oxidation product, along with a trace amount of CO and CO_2. The reference TiO_2 shows a selectivity of 80% toward HCHO, similar to the reported selectivity of TiO_2.[13–15] Comparatively, introducing Pt on TiO_2 does not increase the selectivity to formaldehyde while single atoms Cu increases the selectivity to 99%, probably due to the mitigated overoxidation by Cu introduction. PtCu-TiO_2 shows a similar selectivity to Cu-TiO_2 (up to 98.6%), further suggesting the vital role of Cu atoms, with the formaldehyde synthesis rate of 1871.5 μmol/h at 60°C and 2259.5 μmol/h at 70°C (Supplementary Fig. 11). The selectivity to other oxidation products is 0.77% for HCOOH, 0.56 % for CO_2, and 0.06 % for CO when operating at 70°C. The AQE is the most reliable criterion for photocatalysis, which was determined in Fig. 1D and Supplementary Fig. 12. One can see that the AQE reached 99.2% at 70°C, a record in this area.

The reducibility and stability of photocatalysts are very important. In most cases, a few hours or maximum one day photocatalysts' stability were reported.[16–18] Herein PtCu-TiO_2 stability was studied by 7 consecutive day runs (Fig. 1E). PtCu-TiO_2 exhibits a steady activity over 14 cycles, suggesting its excellent stability. The slight activity fluctuation is likely due to methanol concentration changes caused by the process of purging and catalyst particles stuck to the stirring bar. In comparison, the stability of Cu-TiO_2 shows an obvious decrease of more than 60% after five cycles (Supplementary Fig. 13). MP-AES and X-ray photoelectron spectroscopy (XPS) were carried out (Supplementary Table 1-2), evidencing that Pt nanodots loading enables Cu to be more active and stable than pure Cu, assuring long-term stability of PtCu-TiO_2. The activity of PtCu-TiO_2 was also compared with reported efficient catalysts in methanol dehydrogenation by both photocatalysis and thermal catalysis (Fig. 1F, Supplementary Table 3). PtCu-TiO_2 represents a remarkably high activity, e.g. 1206.5 μmol/h and 2383.9 μmol/h at 25°C and 70°C, respectively, much higher than the reported photocatalysts (Supplementary Table 3) so far. Such H_2 evolution activity is also comparable to the benchmark Pt/MoC operated at 150°C and under 6 MPa, where CO_2 was produced as the major oxidation product.[19] Different from the benchmark thermal catalysis, high valuable chemical formaldehyde is synthesized in this study (Supplementary Table 4). The activation energy of TiO_2 and PtCu-TiO_2 were measured (Supplementary Fig. 14), indicating PtCu greatly promotes H_2 production, matching well with the observed activity.

The X-ray powder diffraction (XRD) was used to analyse the crystallinity and phase composition of Cu-TiO_2 (**Error! Reference source not found.**A). The XRD spectrum presents mixed-phase of anatase and rutile of MOF-derived TiO_2 while Cu-TiO_2 shows pure anatase phase although they have the same calcination temperature (500°C), suggesting Cu anchoring might stabilise the anatase phase.[20] The spectra reveals that higher calcination temperature results in more rutile formation. No characteristic peaks associated with Cu are observed in all Cu-TiO_2 samples although the high amount of 1.53% Cu is loaded, attributing to highly dispersed Cu. **Error! Reference source not found.**B shows Raman spectra, where the signals of E_g, B_{1g}, A_{1g} are assigned to anatase TiO_2.[21] As the temperature increasing, all samples start to exhibit vibrational modes at 445 cm^{-1}, and the signal at 608 cm^{-1} keeps arising from 500°C to 600°C. This phenomenon demonstrates that the primary bonding environment of anatase remains unchanged, but more rutile TiO_2 appears when further heating, in line with XRD.

Then scanning electron microscope and transmission electron microscopy (TEM) were carried out to investigate the morphology of photocatalysts. TiO_2 (Supplementary Fig. 15A-B) presents a disk-type shape in the 200-500 nm range, while PtCu-TiO_2 (**Error! Reference source not found.**A, Supplementary Fig. 15C-D) remains a similar morphology with a rougher surface due to PtCu deposition. Furthermore, **Error! Reference source not found.**B reveals that disk-like PtCu-TiO_2 is nanoporous and bright dots on TiO_2 matrix are assigned to Pt dots with a diameter around 1-3 nm. The measured lattice spacings (**Error! Reference source not found.**C, Supplementary Fig. 16) are 0.35 nm, 0.18nm and 0.226 nm corresponding to TiO_2 (101), TiO_2 (200) and Pt (111), matching well with the corresponding diffraction. To reveal the Cu state in PtCu-TiO_2, line profiles are shown in **Error! Reference source not found.**D. Line 1 only shows Ti, while line 2 contains both Ti and Cu, indicating highly dispersed Cu atoms in TiO_2 (**Error! Reference source not found.**E, Supplementary Fig. 17). The STEM-EDS mapping (**Error! Reference source not found.**G) confirms Cu is highly dispersed in TiO_2, while Pt concentration is much less than Cu, which is further verified by point analysis (Supplementary Fig. 18). The aberration-corrected high-angle annual dark-filed STEM is then performed on an equivalent sample of Rh-TiO_2 to confirm the successful preparation of Rh single atoms via this method (Supplementary Fig. 19). This also suggests that Cu single atom can exist on TiO_2 surface.

The extended X-ray absorption fine structure (EXAFS) was used to further investigate local coordination environment of Cu and Pt (Fig. 4A-B, Supplementary Fig. 20-21). The Fourier-transformed k^2-weighted EXAFS spectra of Cu K-edge (**Error! Reference source not found.**A) shows that the position at 1.5**Å** (not corrected in phase) is assigned to C-O shell of CuO, while two peaks at 2.45**Å** and 2.73**Å** (not corrected in phase) correspond to Cu-O-Cu of Cu_2O. Note that the main peak of Cu-O bond for both Cu-TiO_2 and PtCu-TiO_2 is located in the mid of CuO and Cu_2O, indicating that Cu carries the mixed feature of Cu^+ and Cu^{2+}. Moreover, no Cu-Cu and the second shell Cu-O-Cu configuration are observed, confirming isolated Cu atoms exist in catalysts. Furthermore, EXAFS data-fitting results (Supplementary Table 5) show that the Cu-O coordination number (CN=3.4 for PtCu-TiO_2, CN=3.5 for Cu-TiO_2) is quite different from that of CuO (CN=4), Cu_2O (CN=2) and Cu-Cu bond (CN=12), indicating atomic Cu species. Moreover, the binding length Cu-O in PtCu-TiO_2 (1.94Å) is very close to that of CuO, probably due to the presence of Pt enabling the recovery of Cu^{2+}. The Fourier-transformed k^2-weighted EXAFS spectra of Pt L_{III}-edge reveal that the Pt-Pt shell profile (**Error! Reference source not found.**B) of PtCu-TiO_2 (2.3**Å**, not corrected in phase) is slightly different from that of Pt foil (2.4**Å**, not corrected in phase), probably attributing to the presence of Pt-Cu bond. There are three neighbouring shells in PtCu-TiO_2: Pt-Pt (CN=8.5), Pt-Cu (CN=2.4), and Pt-O (CN=0.9), consistent with elementary mapping. As speculated, Pt-Cu formation may result in electron transfer between Pt and Cu atoms. Wavelet transform analysis was then performed to further determine the coordination environment of Cu and Pt on TiO_2 (Supplementary Fig. 22-23). In brief, EXAFS results support that highly dispersed Cu single atoms were partially coupled with Pt dots in PtCu-TiO_2 while the other single atoms Cu exist as Cu-O species.

In situ XPS of PtCu-TiO_2 during photocatalysis was performed to study compositional changes (Fig. 2C). The peaks at 932.1 eV and 952.1 eV are attributed to Cu^+ while other peaks at 934.1 eV and 954.1 eV are assigned to Cu^{2+}. The spectra evidence that Cu^+ and Cu^{2+} coexist in Cu-TiO_2 and PtCu-TiO_2.[22] During irradiation, the Cu^+/Cu^{2+} ratio shows an increase from 2.60 to ca. 4.05, revealing that Cu^{2+} traps electrons. For Pt 4f (**Error! Reference source not found.**D), the binding energy of Pt $4f^{5/2}$ and Pt $4f^{7/2}$ are 71.2 eV and 75.3 eV, corresponding to Pt^0, while that of 74.2 eV and 76.4 eV correspond to Pt^{4+}, probably due to the oxidized state (PtO_2).[23] The Pt/Pt^{4+} during irradiation remains the same but the binding energy of Pt^0 shifts by 0.2 eV toward lower binding energy, suggesting that Pt surface becomes electron-rich.[24] Besides, the binding energy of Pt^{4+} remains almost the same, indicating that electrons are trapped by Pt^0 instead of Pt^{4+}. This suggests that only Pt located on Cu extract photoelectrons, likely from Cu^+ to become electron-rich sites, proving the synergy between Cu and Pt for a remarkably stable catalytic process. Further, elemental chemical states of Cu-TiO_2 and PtCu-TiO_2 were investigated (Supplementary Table 6). The correlation between Cu^+/Cu^{2+} ratio and H_2 formation rate (Supplementary Fig. 24) represents high H_2 production rates can be attained when Cu^+/Cu^{2+} ranges from 0.64 to 1.60, might revealing that both Cu^+ and Cu^{2+} are active sites.

The UV-vis diffuse reflectance spectra of samples are shown in Supplementary Fig. 25, where loading both Cu and Pt exhibit a similar band absorption to TiO_2. Fig. 4C shows Electron paramagnetic resonance (EPR) spectra, where Cu-TiO_2 and PtCu-TiO_2 exhibit similar strong peaks attributing to $I = 3/2$ of Cu^{2+}.[25] Upon irradiation, the decreased intensity of the Cu^{2+} signal implies Cu^{2+} traps electrons to form an EPR-silent Cu^+. PtCu-TiO_2 exhibits the same trend but weaker intensity reduction, revealing that electrons further transfer from Cu^+ to Pt, leading to the subsequent partial Cu^{2+} recovery or that original Cu^+ is oxidised to Cu^{2+} by holes. In addition, the photoelectrochemical study was performed to investigate the charge carrier transfer (Supplementary Fig. 26-28), indicating that Cu facilitates water/methanol oxidation or works as hole acceptors on the anode. Similar phenomenon is also observed by time-resolved photoluminescence (Supplementary Fig. 29 and Table 7). Operando UV−vis−NIR diffuse-reflectance spectroscopy was used to further investigate the synergy of Cu and Pt (Supplementary Fig. 30), indicating that Cu, Pt and PtCu serve as efficient electron capture, highly matching with the electron transfer pathway suggested.

In situ EXAFS was performed to probe the density of orbital states involved in electron transitions, revealing the charge transfer pathway. Ti L-edge and O K-edge EXAFS absorption features of photocatalysts were acquired under dark (Supplementary Fig. 31) and during irradiation (Fig. 4D). Under irradiation, TiO_2 exhibits a weak Ti L-edge signal, attributed to electron excitation from O *2p* to Ti *3d* under irradiation and leads to a more-occupied Ti 3*d* orbital. The intensity ratio under irradiation against dark (I_{UV}/I_{dark}) of Ti L-edge follows the order Cu-TiO_2 > PtCu-TiO_2 > Pt-TiO_2 > TiO_2 (Fig. 4F). A slightly bigger I_{UV}/I_{dark}(Ti) in Pt-TiO_2 indicates that Pt acts as an electron-trapping site. Impressively, Cu-TiO_2 exhibits the largest I_{UV}/I_{dark}(Ti), indicating Cu most effectively abstract electrons from TiO_2. Considering electrons backflow from Pt to TiO_2 under dark as discussed above, slightly enhanced Ti L-edge intensity in Pt-TiO_2 is reasonable due to the two-way flow of electrons. The I_{UV}/I_{dark}(Ti) of PtCu-TiO_2 is bigger than Pt-TiO_2 but smaller than Cu-TiO_2, due to the combination effect of Cu and Pt involving one-way electron capture and electron backflow. This supports the claim that single-atom Cu^{2+} species are inserted between Pt and TiO_2, so Cu^{2+} in PtCu-TiO_2 can not only accept electrons and transfer them to Pt but also mitigate electrons backflow from Pt to TiO_2. All samples show increased O K-edge absorption under irradiation, but with various intensity changes, due to the combination of charge excitation and charge transfer. A slightly increased O K-edge feature is presented in TiO_2 (Fig. 4D), arising from a less-occupied O 2p orbital caused by photoelectron excitation. The I_{UV}/I_{dark}(O) of Pt-TiO_2 is the largest, as electrons are excited from O2p to Ti 3d, then transfer to Pt, leading to a much less-occupied O 2*p* orbital. Interestingly Cu-TiO_2 with one way electron-trapping ability has a smaller I_{UV}/I_{dark}(O) than Pt-TiO_2, due to that Cu^+ works as the efficient hole-capture site besides Cu^{2+} as an electron acceptor. As such, holes in O 2p orbital after electron excitation are abstracted by Cu^+, reducing the possibility of O K-edge absorption. A similar case exists in PtCu-TiO_2, where its I_{UV}/I_{dark}(O) is very close to that of Cu-TiO_2, further suggesting the role of Cu^+ for hole-trapping. These in-situ results clearly indicate that PtCu is an efficiency electron sink, and the proposed charge flow is described in Supplementary Fig. 33. Further, Density Functional Theory calculation was performed to present the reaction pathway (Supplementary Fig. 34-35), where electrons transfer to Cu^{2+} followed by mobility to Pt for H_2 evolution and meanwhile CH_3OH oxidation occurs on Cu^+.

A reaction scheme for methanol conversion on PtCu-TiO_2 is proposed (Fig. 5). When electrons and holes are excited in TiO_2 followed by the transfer. Single-atom Cu^{2+} traps electrons to form Cu^+, which migrate to Pt as a reduction reaction site and meanwhile Cu^+ recovers to Cu^{2+}. In parallel, left holes are extracted by Cu^+ in another site of TiO_2 surface to form Cu^{2+} that is the oxidation reaction site, which has a moderate oxidation potential compared with photoholes themselves in the valance band of TiO_2, avoiding methanol overoxidation to CO_2. One can see that Cu^{2+}-Pt is for electron-trapping while Cu^+ is responsible for hole-trapping. Next protons (H^+) are reduced into H_2 in electron-rich Pt(e^-) sites and dispersed Cu^{2+} react with methanol to produce formaldehyde. After reaction, the catalyst recovers to the original state. The extraordinary H_2 production activity obtained by PtCu-TiO_2 can be ascribed to the bifunctional Cu species with the assistance of Pt, where Pt loading helps proton reduction and regeneration of Cu^{2+} while the atomic hole-acceptor (Cu^+) for selective methanol-oxidation to formaldehyde, leading to efficient H_2 generation in a nearly zero CO_2 emission process.

In summary, this work reports a benchmark performance of methanol conversion by the synergy of Pt nanodots and atomic Cu on TiO_2, resulting in the highest H_2 evolution activity of 2383.9 μmol/h, leading to an AQE of 99.2% at 365 nm, together with a high oxidation product formaldehyde synthesis rate of 2259.5 μmol/h with ca. 98.6% selectivity while the selectivity to CO is very small about 0.06%. Interestingly, the bifunctional Cu controls methanol-oxidation to form formaldehyde with high selectivity, eliminating CO_2 emission during H_2 production. The characterization results reveal that PtCu-TiO_2 sandwich structure provides a unique electron transfer path where Cu^{2+} acts as an electron bridge to transport electrons to Pt, thus driving protons reduction, resulting in a very low activation energy (13.2 kJ/mol). This work explores dual-site single-atom catalysts and synergy between single atoms and nanodots to maximize atom utilization and realises highly selective and stable production of valuable products (both green H_2 and formaldehyde), opening an important avenue for atomic catalyst design with high efficiency and stability for both reduction and oxidation reactions.

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Author contributions: J. Tang designed and supervised the entire project and oversaw all discussions. H. Wang conducted the catalysts preparation, sample characterisations, activity tests. H. Qi carried out the EXAFS and fitted the data. X. Li contributed to the EPR discussion. T. Miao helped to collect data and discussion of UV-Vis-NIR diffuse-reflectance spectra. S. Jia carried out DFT calculation and X. Zhang supervised the process. X. Sun collected Ti, O EXAFS data and W. Huang supervised the process. L. Xiong performed Aberration-corrected high angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM). S. Wang collected all TEM data. X. Liu, A. Wang and T. Zhang supervised the EXAFS data collection and fitting. The manuscript was written through collective contributions from all authors. All authors approved the final version of the manuscript.

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Figure captions

Fig. 1 | H_2 production from liquid water reforming of methanol by photocatalysis. A, The mass-specific H_2 generation rates achieve on MOF-derived TiO_2 loaded with various metals, herein Cu serves as the most efficient reaction sites. Herein M-TiO_2 was calcined at 450°C for 4h and experiments were performed at 25°C. **B**, Photocatalytic activity of the single atom or bimetallic species, indicating that PtCu co-loading remarkably improves the activity. Cu-TiO_2 was prepared at 500°C for 4h. **C**, The products selectivity of different catalysts, showing the formaldehyde (whose selectivity is shown by orange colour) is the main oxidation product and its selectivity over PtCu-TiO_2 is up to 98%. Herein experiments were performed at 25°C. The error bar is the standard error of the mean (SEM), where it is 1206.5 +/- 47.9 μmol/h and n=3. **D**, The AQE of the optimal PtCu-TiO_2 at low temperatures with the error bar, close to 100% quantum efficiency achieved. The error bars are 56.2 +/- 0.2% SEM for 25°C, 73.4 +/- 2.6% SEM for 40°C, 83.1+/- 3.7% SEM for 50°C, 96.6 +/- 2.5% SEM for 60°C, where n=2. **E**, 7-day run of stability test of the PtCu-TiO_2 catalyst (each day run 2 cycles during daytime, as H_2 production rate was too high so we had to stop experiments in the nighttime for safety reason). **F**, The activity summary of the reported benchmark photo- and thermo- catalysts clearly indicates that PtCu-TiO_2 remarkably outperforms all photocatalysts and is comparable to the best thermal catalysts. The error bar is 1206.5 +/- 47.9 μmol/h and n=3. (1) $_{0.75\%}$Cu-TiO_2,[8] (2) i-Pt-TiO_2,[26] (3) $Ni(OH)_2/TiO_2$,[27] (4) $_{34\%}$Cu-TiO_2,[28] (5) $_{3\%}$Li-TiO_2,[29] (6) FP-$_{0.5\%}$Pt-TiO_2,[30] (7)$_{0.188\%}$Pt-NYTiO_2,[31] (8) $_{1.5\%}$Cu- TiO_2, [11] (9) Pt-TS-1 zeolite,[32] (10) Cu-Zn-Ti,[33] (11) $_{2\%}$Pt-TiO_2,[19] (12) $_{2\%}$Pt-Al_2O_3,[19] (13) $_{2\%}$$Pt_1$/MoC.[19] The quantum efficiency of all representative photocatalysts are indicated in the parenthesis behind.

Fig. 2 | Physical characterisation of the photocatalysts. A, XRD and **B**, Raman spectra of TiO_2 and Cu-TiO_2. **C**, The in-situ XPS Cu 2p spectra of PtCu-TiO_2 before and during irradiation, indicating that Cu^{2+} is in-situ reduced to the active site Cu^+. **D**, The XPS Pt 4f spectra of PtCu-TiO_2 before and during irradiation.

Fig. 3 | Morphology observation of the catalysts. A, SEM, **B**, ADF STEM with Pt marked by yellow circles, **C-D**, high revolution TEM lattice images of PtCu-TiO_2 with TiO_2 (101) and Pt (111) crystalline, indicating the formation of PtCu-TiO_2. The corresponding line scan profile marked in **D**, with **E** blue lines 1 (only Ti) and **F** line 2 (with two bright points of Cu atoms marked by green circles). **G**, ADF STEM of PtCu-TiO_2 and the corresponding element mapping, showing much more highly dispersed Cu than Pt in the catalyst.

Fig. 4 | Chemical characterisation of the photocatalysts. **A**, The Fourier transform of k^2-weighted EXAFS spectra at the K-edge of Cu-TiO_2, PtCu-TiO_2, Cu foil and CuO. **B**, The Fourier transform of k^2-weighted EXAFS spectra at the LIII-edge of Pt-TiO_2, PtCu-TiO_2, Pt foil and PtO_2. **C**, The electron paramagnetic resonance (EPR) of Pt-TiO_2, Cu-TiO_2 and PtCu-TiO_2. The Cu^{2+} signal decrease is more evident in Cu-TiO_2 than PtCu-TiO_2 (Insert), indicating that electrons likely further transfer from Cu^+ to Pt, leading to the partial Cu^{2+} restoring. Ti L-edge and O K-edge EXAFS spectra of **D**, TiO_2, and **E**, PtCu-TiO_2 under dark and during irradiation. **F**, Ratio of Ti L-edge or O K-edge intensity in the modified samples under light irradiation to that under dark condition.

Fig. 5| The possible mechanism of photocatalytic methanol and water conversion on PtCu-TiO_2 for both H_2 and valuable chemicals production instead of CO_2

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Methods

MIL-125 preparation: Typically, a certain amount of terephthalic acid was dissolved in N,N dimethylacetamide (DMF) followed by the introduction of ethanol [34]. Then the required amount of titanium butoxide was added into the above solution dropwise to form a uniform mixture and then transferred to a Teflon-lined stainless-steel autoclave at 130 °C for 20 hours. After extraction and cooling down, the precipitate was separated, washed by dimethylformamide and methanol using centrifuging at a centrifugal force of 1236.26 × g for 5 min. The solvent was removed by vacuum oven at room temperature to collect MIL-125.

M-TiO_2 preparation: MIL-125 was well dispersed in DI water via sonication, followed by the addition of metal-salt with the designed weight ratio (e.g. 0.75wt% metal on MIL-125). After stirring for 2 hours, the mixture was centrifuged at a centrifugal force of 1236.26 × g for 5 min to obtain metal-MIL-125 (named the ion-coordination method). The TiO_2 with various metal loading (including Fe, Co, Ni, Cu, Ru, Pt) was obtained by calcination of the solid at different temperatures (400-600 °C) in a muffle oven to form M-TiO_2. Various Cu ratios were loaded on MIL-125 followed by the calcination to obtain Cu-TiO_2, which was later determined by MP-AES as 0.16%, 0.85%, 1.53%, 1.82%, and 2.42%. The $_{1.53\%}$Cu-TiO_2 was named as Cu-TiO_2 in the manuscript and this text unless specifically mentioned. To investigate the condition affect, different calcination temperatures and times were applied for Cu-TiO_2 synthesis. For pure TiO_2, MIL-125 was directly put in a muffle furnace (Carbolite, CWF 1300) for annealing at 500°C for 3h.

PtCu-TiO_2 synthesis: Pt was induced on Cu-TiO_2 by an in situ photodeposition method. Typically, 5 mg Cu-TiO_2 and 0.5wt.% of H_2PtCl_6 were dispersed into 40mL 70% methanol aqueous solution. Then the above solution was purged with argon for 20 min to remove oxygen and then sealed for 365 nm LED-induced postdeposition to form PtCu-TiO_2. The preparation of Pt-TiO_2 was the same procedure as the above except using TiO_2 as the substrate. It is worth mentioning that the samples for characterization were obtained by 30 min irradiation using 50mg Cu-TiO_2 to obtain a good signal to noise. From MP-AES, the Pt amount of PtCu-TiO_2 and Pt-TiO_2 was analysed to be 0.25% and 0.17%. The optimal sample $_{1.53\%}$Cu$_{0.25\%}$Pt-TiO_2 was named as PtCu-TiO_2 while $_{0.17\%}$Pt-TiO_2 was named as Pt-TiO_2 in the manuscript and this text unless specifically stated.

Photocatalysis: The hydrogen generation experiments from the methanol-water mixture were carried out under 365 nm LED irradiation (Perfect Light, Beijing). Usually, 5 mg material and 40 mL 70% methanol solution was added into a 175 mL reactor followed by the illumination. The temperature was kept at room temperature (20°C) using a water bath. For the long-term stability test, the sample always remained in the reactor for the test. During the stability test, in run 7, 0.5 mL methanol was added due to the methanol evaporation during argon purging. Then, in run 10, 4 mL 70% methanol was added to maintain the same solution volume. From run 10-14, 0.1 ml methanol was introduced before each reaction due to consumption of methanol. The gases H_2 was analysed by gas chromatography Varian 430-GC with a FID detector. A FID equipped with methanizer in another GC (Varian 450) was used to quantify the concentration of CO_2 and CO. The solution after certain reaction time was sampled for formaldehyde and formic acid detection using ultraviolet-visible diffuse reflectance spectroscopy (an acetylacetone method [35]) and ion chromatography (Eco IC, Column Metrosep A Supp 5), respectively.

Apparent quantum efficiency (AQE) measurement: The AQE calculation follows $\varphi = \frac{nR}{I}$, where n, R, and I are the involved electrons number, the hydrogen evolution rate and the amount of incident photons, respectively [36]. For all measurements, the irradiation window diameter was 4 cm and the incident light intensity was measured to be 3.5 mW cm^{-2}. The temperature was controlled by a stirring hot plate for measurement at the different reaction temperature. The experiment was carried out a few times under 10 min (600s) light irradiation. The average produced H_2 at 25°C, 40°C, 50°C, 60°C and 70°C were 22.6 µmol, 29.5 µmol, 34.4 µmol, 38.8 µmol and 41.6 µmol in the reactor (175 mL), respectively. The AQE at 70°C was measured under 3.65 mW/cm^2 light irradiation and the produced H_2 in the reactor was 41.6 µmol. Taking the AQE at 70°C as an example, the detailed calculation was shown below.

$$I = \frac{E\lambda}{hc} \times S = \frac{3.65 \times 10^{-3} \times 600 \times 365 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} \times 3.14 \times 2 \times 2 = 5.05 \times 10^{19}$$

$$\varphi = \frac{nR}{I} = \frac{2 \times 41.6 \times 10^{-6} \times 6.02 \times 10^{23}}{5.05 \times 10^{19}} \times 100\% = 99.2\%$$

Characterization: The powder X-ray diffraction (XRD) patterns of the samples were measured in a Stoe STADI-P instrument (2° to 40°, step 0.5° at 5.0 s/step) using Mo Kα1 (wavelength 0.70930 Å, 50 kV and 30 mA). Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were acquired by a Shimadzu UV-Vis 2550 spectrophotometer fitted with an integrating sphere, using Standard barium sulfate as a reference. The morphology and microstructure were investigated by the scanning electron microscope (SEM) (Sirion 200). Transmission electron microscopy images and high-angle annular dark-field (HAADF) STEM were acquired on JEOL 2100F analytical TEM operated at 200 kV. The aberration-corrected high-angle annual dark-filed scanning transmission electron microscopy (AC-HAADF-STEM) analysis was performed on a JEOL JEM-ARM200F equipped with a CEOS probe corrector, with a guaranteed resolution of 0.08 nm. Electron spin resonance (EPR) spectra were collected from MS-5000 spectrometer. The *in situ* XPS data of PtCu-TiO_2 was obtained from PHI 5000 VersaProbe II Scanning XPS Microprobe with six multichannel plates using a 365 nm light source (3000 eV). The XPS data of Cu-TiO_2 obtained at various temperatures and PtCu-TiO_2 were recorded from a Kratos Axis SUPRA XPS fitted with a monochromatic Al kα X-ray source (1486.7 eV), a spherical sector analyser and three multichannel resistive plates, 128 channel delay line detectors. Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans recorded at a pass energy of 20 eV._All data was collected at 150W and a spot size of 700 x 300 µm. Data were analysed using CasaXPS and the spectra were calibrated with C1s peak at 284.8 eV. The XPS spectra for Cu-TiO_2 before and after the reaction were collected from a Thermo Scientific NEXSA XPS system with an Al Kα X-ray source. Raman spectra were measured using a Renishaw inVia Raman microscope. The lifetime of the photogenerated charge carriers was acquired by a time-resolved fluorescence decay spectroscopy (FL-1039A/40A) using 320 nm and 450 nm as the excitation and emission wavelengths. The determination of metal amount was performed by microwave plasma atomic emission spectrometry (MP-AES Agilent 4200). Photo-electrochemical test was carried out by a three-electrode electrolytic cell, where the FTO electrode coated with the photocatalyst worked as the working electrode, the platinum plate acted as the counter electrode, and the Ag/AgCl electrode acted as the reference electrode. A 150 W xenon lamp was used as the arc light source and 70 mL of 0.5 M Na_2SO_4 solution with 10% methanol served as the electrolyte. In detail, the photocurrent test was performed using a potentiostatic technique with a switching period of 2 s. The scan rate for the cycling voltammetry was 2mV/s. The electrochemical impedance spectra were collected using the same three-electrode system with the following parameters: at 0 V vs. Ag/AgCl and amplitude 10 mV. The X-ray absorption spectra including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the K-edge of Cu and L_{III}-edge of Pt of the samples, were collected at the BL 14W1 of Shanghai Synchrotron Radiation Facility (SSRF), China. The Cu and Pt foil was employed to calibrate the energy. The spectra were collected at fluorescence mode at room temperature. The Athena software package was used to analyse the data. The detailed Density Functional Theory (DFT) calculation was shown in the supporting information.

Steady-state UV−vis−NIR diffuse-reflectance spectroscopy: The signal detection was performed by a Cary 5000 UV-vis-NIR spectrometer, which was equipped with a Praying Mantis accessory. A filter (>395 nm) was installed before the sample beam detector, avoiding the reflection of excitation light caused by the samples. The reactor was equipped with three quartz windows with 2mm thickness (Crystran, QPZ15-2). One was for excitation light passing and the other two were for the light transmission. In the system, the 300 W Xe lamp (Newport, model 67005) with a filter (325-385 nm, Thorlabs, FGUV UG1) and a 365 nm bandpass filter (Comar) served as the irradiation source. Argon, dry air and methanol acted as an insert reference, electron consumer and hole scavengers, respectively. For all measurements, the reactor was sealed for measurements after 30 min gas feeding via a flow rate of 100 mL/min, achieving an adsorption/desorption balance.

***In situ* NEXAFS measurements:** *In situ* NEXAFS measurements in the total electron yield mode were performed at the Photoemission Endstation (BL10B) in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. This beamline is connected to a bending magnet and equipped with three gratings that cover photon energies from 100 to 1000 eV with a typical photon flux of 1 × 1010 photons/s and a resolution (E/ΔE) better than 1000 at 244 eV. Spectra were collected at energies from 455 to 477 eV for Ti L-edge NEXAFS spectra and 515 to 575 eV for O K-edge NEXAFS spectra in a 0.2 eV energy step. UV light illumination was accomplished using a 320 nm LED lamp placed at 15 cm in front of the sample. The NEXAFS raw data were processed as the following: firstly, the photon energy was calibrated from the 4f spectral peak of a freshly sputtered gold wafer, then a line was subtracted to set the pre-edge as zero, and finally the spectrum was normalized to yield an edge-jump to one.

Data and materials availability: All data are available in the manuscript or the supplementary information.

Methods-only references

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