Hybrid Cu$_x$O–TiO$_2$ Heterostructured Composites for Photocatalytic CO$_2$ Reduction into Methane Using Solar Irradiation: Sunlight into Fuel

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Supporting Information

ABSTRACT: Photocatalytic CO$_2$ conversion to fuel offers an exciting prospect for solar energy storage and transportation thereof. Several photocatalysts have been employed for CO$_2$ photoreduction; the challenge of realizing a low-cost, readily synthesized photocorrosion-stable photocatalytic material that absorbs and successfully utilizes a broad portion of the solar spectrum energy is as yet unmet. Herein, a mesoporous p-type/n-type heterojunction material, Cu$_x$O–TiO$_2$ (x = 1, 2), is synthesized via annealing of Cu/Cu$_2$O nanocomposites mixed with a TiO$_2$ precursor (TiCl$_4$). Such an experimental approach in which two materials of diverse bandgaps are coupled provides a simultaneous opportunity for greater light absorption and rapid charge separation because of the intrinsic p–n heterojunction nature of the material. As detailed herein, this heterostructured photocatalyst demonstrates an improved photocatalytic activity. With the CO$_2$ reduction of our optimal sample (augmented light absorption, efficacious charge separation, and mesoporosity) that utilizes no metal cocatalysts, a remarkable methane yield of 221.63 ppm·g$^{-1}$·h$^{-1}$ is achieved.

1. INTRODUCTION

The continuous increase in atmospheric CO$_2$ concentration is considered to be a key driver that induces climate change. The prospect of unwanted climate change or climate heating—desertification has compelled investigations into the means to normalize atmospheric CO$_2$ concentrations. As is well known, CO$_2$ is a highly stable molecule, requiring significant energy input for its reduction. In this regard, sunlight is considered to be the most useful energy source for promoting CO$_2$ conversion into useful hydrocarbon products, such as methane or ethane, offering the possibility of turning sunlight into fuels compatible with the current energy infrastructure.

During the past several decades, titanium dioxide (TiO$_2$) has received much attention as a photocatalyst because of its abundant availability, nontoxicity, photocorrosion resistance, and excellent charge transport properties. However, the TiO$_2$ bandgap of 3.2 eV limits its absorption to the ultraviolet region, making it utilize only 4% of the entire solar spectrum. To reduce the TiO$_2$ bandgap such that it absorbs a greater portion of the solar spectrum energy while maintaining its commendable properties, various strategies have been investigated, such as anion doping, loading of noble metals like Pt, Pd, Au, and so forth to act as cocatalysts, and coupling of TiO$_2$ with low-bandgap semiconductors. Composites of Cu$_2$O and TiO$_2$ have been utilized for hydrogen evolution, CO$_2$ photoreduction, and photodegradation of volatile organic compounds and as visible light-responding photocathodes. Therefore, we believe that coupling TiO$_2$ with a suitable low-bandgap semiconductor, our interest herein, can result in a broad-spectrum visible light-absorbing material with improved photocatalytic activities. The present hybrid photocatalyst based upon Cu$_x$O–TiO$_2$ showcases a performance better than those of the previously reported studies on Cu$_x$O–TiO$_2$ for CO$_2$ photoreduction into methane.

Herein, we report the synthesis and the photocatalytic application of a mesoporous p–n heterojunction composite material without metal cocatalyst sensitization, as commonly used. Our material is composed of p-type Cu$_x$O (CuO and Cu$_2$O) with a bandgap of ∼1.35–1.7 eV, coupled with n-type TiO$_2$. The Cu$_x$O–TiO$_2$ photocatalyst is prepared using a facile and inexpensive two-step process: briefly, Cu/Cu$_2$O nanocomposites are synthesized via thermal decomposition, which are then vigorously mixed with titanium tetrachloride (TiCl$_4$) under an argon atmosphere, forming a gelatinous solution. The calcination under air of this gelatinous solution results in a highly mesoporous Cu$_x$O–TiO$_2$ composite.

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During the ambient-atmosphere calcination process, (1) TiCl$_4$ oxidizes to form TiO$_2$; (2) Cu/Cu$_2$O nanocomposites are oxidized, forming Cu$_x$O (CuO and Cu$_2$O); and (3) organic ligands used in the synthesis of Cu/Cu$_2$O nanocomposites are removed, providing a firm heterojunction formation between Cu$_x$O and TiO$_2$ with a well-defined mesoporous morphology. A schematic diagram showing our experimental approach is shown in Figure 1.

We test the resulting photocatalyst for its ability to promote the ambient-temperature photoconversion of CO$_2$ and water vapor to hydrocarbons and to discover a high rate conversion of CO$_2$ to, almost exclusively, methane without the use of noble metal codopants. For the purpose of optimization, various samples of Cu$_x$O–TiO$_2$ are prepared with various amounts of TiCl$_4$ (TiO$_2$ precursor), namely, CT03, CT05, CT07, and CT09 corresponding to 0.3, 0.5, 0.7, and 0.9 mL of TiCl$_4$, respectively, mixed with 20 mL of Cu/Cu$_2$O nanocomposites dispersed in toluene. To the best of our knowledge, for the first time, hybrid mesoporous p-type Cu$_x$O (CuO and Cu$_2$O) coupled with n-type TiO$_2$ for photocatalytic conversion of CO$_2$ into hydrocarbon fuels without using metal cocatalysts is introduced.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Cu$_x$O–TiO$_2$ Composites. The X-ray powder diffraction (XRD) patterns of pure CuO, pure TiO$_2$ (synthesized from TiCl$_4$), and Cu$_x$O–TiO$_2$ samples are shown in Figure 2. The XRD patterns of the Cu$_x$O–TiO$_2$ samples mainly show an intense peak at 20 = 26.2$^\circ$, corresponding to d$_{101}$ of anatase TiO$_2$, confirming the presence of anatase TiO$_2$ as well as a relatively small amount of Cu/Cu$_x$O nanocomposites in the Cu$_x$O–TiO$_2$ samples. This result, we assume, is likely due to the low crystallinity and high dispersion of Cu/Cu$_x$O species on TiO$_2$ surfaces. From the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the representative sample CT07, 2 wt % Cu is determined, which corresponds to approximately 80% of the Cu content obtained using the data from the field emission scanning electron microscopy (FE-SEM) energy-dispersive spectroscopy (EDS) technique (Figure S5).

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images of the Cu$_x$O–Cu$_2$O nanocomposites and a representative Cu$_x$O–TiO$_2$ sample (CT07) are shown in Figure 3. The as-synthesized Cu$_x$O–Cu$_2$O nanocomposites show excellent size uniformity (Figure 3A) with the selected area electron diffraction (SAED) pattern showing d$_{111}$ planes for both CuO and Cu. The HR-TEM image (Figure 3B) shows respective lattice fringes for CuO and Cu metal, which are well-matched with the SAED pattern. To check the mesoporosity of the Cu$_x$O–TiO$_2$ sample, FE-SEM and HR-TEM images of the sample CT07 can be seen in Figures S2 and S3, respectively. Furthermore, the STEM elemental mapping of the CT07 sample further (Figure S4) confirms the presence of CuO and TiO$_2$ within the mesoporous Cu$_x$O–TiO$_2$ composite.
The UV−vis diffuse reflectance spectra (UV−vis DRS) of pure TiO2 and Cu−TiO2 samples (Figure 4A) exhibit two prominent changes: (1) pure TiO2 is unable to absorb visible light, whereas the UV−vis DRS spectra of the modified samples exhibit a shift in the absorption edge to longer wavelengths (400−600 nm), which is attributed to the formation of a heterojunction between CuO and TiO2;14,15 and (2) the absorption band in the near infrared (600−1000 nm) is observed because of the Cu loading and thus is attributed to a 2Eg → 2T2g interband transition in the CuII clusters deposited over TiO2.16

The bandgap values of all samples are estimated using Tauc plots (Figure 4B) and are listed in Table 1. The variation in the bandgap can be attributed to the amount of Cu/Cu2O present. The bandgap of the composites gradually increases with an increase in the TiCl4 content; the lowest value was 3.09 eV for sample CT03 containing 0.3 mL of TiCl4 mixed in a 20 mL Cu/Cu2O solution.

The photoluminescence (PL) spectra of TiO2 (synthesized from the TiCl4 precursor), Cu/Cu2O nanocomposites, and the sample CT07 can be seen in Figure 5. Pure TiO2 depicts a sharp peak around 385 nm because of emission from band-to-band recombination with other peaks appearing in the range of 400−600 nm, attributed to the electron transitions from the inter-bandgap defect levels.17,18 Cu/Cu2O nanocomposites exhibit a UV emission peak at 380 nm and a visible emission peak at 520 nm, attributed to the recombination of electron−hole pairs in free excitons or deep-level defects and photogenerated electrons in CuO, respectively.19,20 For the sample CT07, the visible emission peak for CuO at 520 nm is quenched as compared to that of Cu/Cu2O nanocomposites, thereby suggesting the formation of a p−n junction at the interface, resulting in a reduced rate of recombination.

The Brunauer−Emmett−Teller (BET) surface areas and pore-size distributions are measured for all CuO−TiO2 samples (Figure S6), with their values displayed in Table 1. CT07 shows the largest surface area (26.95 m2·g−1), approximately 2.4 times higher than that of CT03 (11.05 m2·g−1). It is observed that on increasing the amount of TiCl4, the surface area decreases, possibly because of the increased aggregation induced by the higher amounts of the Ti precursor.

Further evidence for CuO−TiO2 formation comes from an X-ray photoelectron spectroscopy (XPS) analysis of the sample CT07. Figure 6A shows the Ti 2p region with two intense peaks at 457.6 and 464.0 eV, corresponding to Ti 2p3/2 and Ti 2p1/2 states, respectively, ensuring the presence of Ti4+ ions.21 The satellite shoulder peaks appearing at higher binding energies are assumed to be because of the Ti4+ state in the Ti−O−Cu structure.22 The Cu 2p region (Figure 6B) exhibits Cu 2p1/2 and Cu 2p3/2 main peaks appearing around 933.0 and 953.0 eV, respectively, corresponding to CuII and CuI states, respectively.23

Table 1. Photocatalytic and Textural Properties of the CuO−TiO2 Samples

| Sample | \(S_{\text{BET}}\) (m²·g⁻¹) | Pore volume \(v\) (cm³·g⁻¹) | Bandgap \(E_g\) (eV) | Amount of CH4 evolved \(E_{\text{f}}\) (ppm·g⁻¹·h⁻¹) |
|--------|-----------------|-----------------|-----------------|-----------------|
| CT03   | 11.05           | 0.115           | 3.09            | 23.33           |
| CT05   | 16.49           | 0.102           | 3.12            | 55.07           |
| CT07   | 26.95           | 0.094           | 3.15            | 221.63          |
| CT09   | 22.95           | 0.164           | 3.2             | 168.03          |

*aThe surface areas of the samples are determined by using the BET equation to a relative pressure \(P/P_0\) range of 0.05−0.35 of the adsorption isotherm. *Barrett−Joyner−Halenda (BJH) equation using the desorption isotherm is used to calculate the pore volume. *Tauc plots are made for bandgap energy estimation. *Amount of CH4 evolved is calculated using eq 7.

Figure 4. (A) UV−vis DRS of all samples showing red shift in the CuO−TiO2 samples attributed to the formation of a CuO−TiO2 heterojunction and absorption in the 600−1000 nm range because of CuO intrinsic absorptions. (B) Corresponding Tauc plots for the bandgap estimation of the CuO−TiO2 samples.

Figure 5. PL emission spectra of pure TiO2, Cu/Cu2O nanocomposites, and the sample CT07.
953.0 eV, with satellite peaks at 942.5 and 962.5 eV, respectively. The main Cu 2p peaks are further deconvoluted into four peaks, where peak 1 and peak 3 are assigned to the Cu+ species (Cu2O), whereas peak 2 and peak 4 are associated with the Cu 2+ species (CuO). The satellite peaks are attributed to the ligand-to-metal charge transfer, an important indicator of the presence of Cu2+ species by an open 3d shell, which is not observed for Cu+ or metallic Cu0 species because of their completely filled 3d shell. Furthermore, the energy gap between peak 2 and peak 4 is 20.0 eV, which matches well with the standard value of 20.0 eV for CuO. The Cu 2p XPS data suggest the presence of two phases, that is, CuO and Cu2O in the as-prepared samples.

Figure 6. XPS of the sample CT07 showing (A) the Ti 2p region with characteristic Ti peaks assigned to Ti 2p3/2 and Ti 2p1/2 (B) characteristic Cu 2p peaks and satellite peaks assuring the presence of Cu2O and CuO, and (C) the O 1s region exhibiting three peaks located at 529.7, 531.2, and 532.3 eV corresponding to Ti−O, O−H, and C−O bonds, respectively.

2.2. Photocatalytic Conversion of CO2 into Methane and Its Proposed Mechanism. Photocatalytic CO2 conversion into hydrocarbon fuels is used to test the CuO−TiO2 sample. Pure TiO2 (synthesized from the TiCl4 precursor) and pure bulk CuO are used as reference samples. Analysis of the products obtained from all samples using gas chromatography (GC) predominantly shows methane as the main hydrocarbon product. Figure 7 shows that the methane production rate after each sample is illuminated for 1 h of solar illumination. When CuO is coupled with TiO2, all samples show an increase in the CH4 yield. With an increasing amount of TiCl4 for the synthesis of CuO−TiO2, the amount of CH4 evolution increases, reaching a maximum value with CT07. A further increase in TiCl4 beyond CT07 decreases the CH4 yield, which we believe is due to the low surface area of CT09 limiting active sites to interact with the CO2 molecules. CT07 exhibits a methane evolution of 221.63 ppm·g⁻¹·h⁻¹, a value which is 11.1 times and 22 times higher than for pure CuO (20.01 ppm·g⁻¹·h⁻¹) and TiO2 (9.94 ppm·g⁻¹·h⁻¹), respectively. It is noted that this yield is better than those of our previously reported photocatalysts utilized for CO2 conversion into methane.

Figure 7. Rates of CH4 evolution measured under simulated solar irradiation for pure TiO2, pure CuO, and all CuO−TiO2 samples. The sample CT07 shows the highest methane evolution rate of 221.63 ppm·g⁻¹·h⁻¹. The control test of the CT07 sample in an Ar/H2O(g) mixture exhibits negligible CH4 evolution.
The rate of CH₄ production is calculated for all Cu₃O−TiO₂ samples using eq 7, as listed in Table 1. Control tests performed by illuminating CT07 in an Ar/H₂O(g) atmosphere under similar irradiation conditions show a negligible amount of CH₄ evolution. Thus, it can be inferred from the control experiment that CH₄ evolved during the normal experiments is due to the photoreduction of CO₂ and not because of the oxidation of surface-bound organics.

The stability of the representative sample CT07 is measured by its repeated testing for five cycles (Figure S11). The representative sample CT07 shows good stability without any acute decrease in the methane production rate: hence, one can see that the rate of CO₂ reduction on the fifth test is approximately 88% that of the first.

An elucidation based upon experimental results and on the literature that reported the energy levels and the suggested process for the conversion of CO₂ and water vapor into methane is shown in Figure 8. As revealed by XPS data, Cu₃O−TiO₂ contains both Cu₂O and CuO, the conduction band edges of which are both more negative than TiO₂. Thus, upon illumination within the Cu₃O−TiO₂ photocatalyst, generation of electrons (e⁻) and holes (h⁺) takes place, whereby the electrons in p-type Cu₂O can easily flow to the conduction band of TiO₂ to contribute to the photoreduction of adsorbed CO₂, whereas the photogenerated holes migrate in the opposite direction to oxidize the adsorbed H₂O, releasing H⁺ and O₂.

The photoreduction of CO₂ is a complex process. Initially, the adsorption of CO₂ takes place over the semiconductor surface, leading to an activation of the CO₂ molecule for reduction. Although CO₂ is a linear molecule, its adsorption on a photocatalyst surface transforms it into a bent structure, with a decrease in the lowest unoccupied molecular orbital (LUMO) level of CO₂, thus offering a lower barrier for accepting electrons under illumination. When light is illuminated upon the CO₂-adsorbed photocatalytic material, the photoexcited electrons generated are injected to the adsorbed CO₂ to proceed with the reduction reactions, with the formation of various intermediate free radicals and products. Among the various CO₂ photoreduction mechanisms proposed, the carbene pathway is the most widely accepted pathway for yielding CH₄ and/or CH₃OH as the main products. The literature for the carbene pathway mechanism is well-defined and is considered reliable based on the investigations made using electron spin resonance (ESR) and electron paramagnetic resonance (EPR) experimental techniques. The carbene pathway begins with the injection of a single electron into the adsorbed CO₂, forming an anion radical CO₂•⁻. Such a single electron reduction of CO₂ to an anion radical CO₂•⁻ possesses a strong negative electrochemical potential of −1.9 V versus a normal hydrogen electrode (NHE). Hence, with such a high potential required for this step, it seems highly improbable for the semiconductors to proceed with the reduction. Therefore, at this stage, it is considered that as soon as the CO₂•⁻ radical is formed, it reacts with the protons H⁺ (provided by water oxidation via filling holes) and photogenerated electrons to produce intermediate radicals and products. Such a process is known as “proton-assisted multielectron reduction” and is generally acceptable for the CO₂ photoreduction process. The radicals and products produced at the intermediate stages further undergo a series of proton-assisted multielectron reductions, finally yielding CH₄ as the main product. Thus considering the proton-assisted multielectron reduction via the carbene pathway, we propose a possible route for CO₂ photoreduction, a schematic view of which is shown in Figure 8.

\[
\text{Cu}_3\text{O} + \text{H}_2\text{O} \xrightarrow{h^+} \text{Cu}_3\text{O}^- + \text{H}_2
\]

The rate of CH₄ production is calculated for all Cu₃O−TiO₂ samples using eq 7, as listed in Table 1. Control tests performed by illuminating CT07 in an Ar/H₂O(g) atmosphere under similar irradiation conditions show a negligible amount of CH₄ evolution. Thus, it can be inferred from the control experiment that CH₄ evolved during the normal experiments is due to the photoreduction of CO₂ and not because of the oxidation of surface-bound organics.

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\[
\text{Cu}_3\text{O} - \text{TiO}_2 \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow H^+ + \text{OH}^-
\]

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^{•^-}
\]

\[
\text{CO}_2^{•^-} + e^- + H^+ \rightarrow \text{CO} + \text{OH}^-
\]

\[
\text{CO} + 2e^- + H^+ \rightarrow \text{C} + \text{OH}^-
\]

\[
\text{C} + 4e^- + 4\text{H}^+ \rightarrow \text{CH}_4
\]

3. EXPERIMENTAL SECTION

3.1. Synthesis of Mesoporous Cu₃O−TiO₂ Heterostructured Composites. The synthesis of mesoporous
Cu$_2$O–TiO$_2$ heterostructured composites was carried out using a simple impregnation step. An already prepared Cu/Cu$_2$O nanocomposite solution (6 mL) (details in Supporting Information) was dispersed in 20 mL of anhydrous toluene in a rubber-capped vial and degassed for 30 min under vacuum to remove any air dissolved in the solution and filled with an inert gas (Ar). The degassed solution was transferred into the glove box, followed by a dropwise addition of a certain amount of 1 M titanium(IV) chloride solution (0.3, 0.5, 0.7, and 0.9 mL of TiCl$_4$) to the degassed solution. The color of the solution changes from dark green to dark yellow. After 1 h of reaction, a well-dispersed solution mixture of dark yellow Cu/Cu$_2$O nanocomposite and TiCl$_4$ was formed and is allowed to oxidize spontaneously in air for 30 min under stirring. A change in the color of the mixture from dark yellow to reddish brown is observed. The gel-type mixture of Cu/Cu$_2$O nanocomposite and TiCl$_4$ was dried under air at 70 °C and then subsequently calcined in a tubular furnace at 400 °C, at a ramping rate of 6 °C/min under air flow (20 cc/min) for 3 h. The annealing process oxidizes both the Cu/Cu$_2$O nanocomposite and TiCl$_4$ forming Cu$_2$O–TiO$_2$ (where $x = 1$ or 2), a well-known oxidation process that has been reported earlier. The Cu$_2$O–TiO$_2$ samples obtained with 0.3, 0.5, 0.7, and 0.9 mL of TiCl$_4$ were labeled as CT03, CT05, CT07, and CT09, respectively.

### 3.2. Photocatalyst Characterization

XRD studies were performed using a Panalytical, Empyrean diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å) in the range of 2Θ = 10°–90° at $1°$/min. Surface morphologies and composition were observed using a field emission scanning electron microscope (Hitachi S-4800) equipped with an EDS attachment. High-resolution images were obtained using a field emission transmission electron microscope (FE-TEM, Hitachi HF-3300) operating at 300 kV, where the samples were prepared on a Ni grid.

The surface areas of the products were analyzed using the BET method (Micromeritics ASAP 2000 apparatus) at −196 °C. XPS (Thermo VG, K-alpha) with Al Kα line operating at 148 606 eV as the X-ray source was used to study the surface composition and oxidation states of Cu$_2$O–TiO$_2$. The optical properties of the samples were studied using UV–vis DRS Cary series (Agilent Technologies) with an attached diffuse reflectance accessory. PL was measured using a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies), $\lambda_{ex} = 300$ nm for all samples. The copper content in the photocatalyst was deduced using the ICP-AES analysis using a Thermo Scientific iCAP 7400 duo ICP-AES instrument.

### 3.3. Photocatalytic CO$_2$ Conversion

The photocatalytic CO$_2$ conversion experiment, an empty photoreactor (stainless steel; volume = 15.4 cm$^3$) was purged with CO$_2$ gas (1000 ppm in He) and vacuum simultaneously to remove any air or other impurities before and after the loading of the photocatalyst. The photocatalyst (50 mg) was loaded into the photoreactor; moist CO$_2$ gas (1000 ppm in He) was passed through a water bubbler, which then enters the photoreactor. The photocatalyst-loaded photoreactor, filled with a mixture of CO$_2$ and H$_2$O vapors mixture, was then illuminated by a 100 W Xenon solar simulator (Oriel, LCS-100) with an AM1.5 filter for 1 h, and the reaction products (500 µL) were analyzed using a Shimadzu GC-2014 gas chromatograph (Restek Rt-Q Bond column, ID = 0.53 mm, and length = 30 m) equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. Figure S1 shows the schematic of the experimental setup for the photocatalytic CO$_2$ reduction. The hour-normalized photocatalytic CH$_4$ evolution rate is calculated using eq 7.

$$\text{Rate of CH}_4\text{ evolution} = \frac{\text{amount of CH}_4\text{ produced (ppm)}}{\text{amount of photocatalyst used (g)}}$$

Five cycles of CO$_2$ photoreduction were performed to test the stability of the same sample; after every test, the photoreactor was purged with Ar gas and vacuum, then re-filled with CO$_2$ gas (1000 ppm in He), followed by a 1 h illumination for the next testing cycle.

### 4. Conclusions

In summary, hybrid Cu$_2$O–TiO$_2$ photocatalysts are prepared via a facile experimental approach comprising two steps, that is, synthesis of Cu/Cu$_2$O nanocomposites followed by mixing with TiCl$_4$ and subsequent oxidation. The as-prepared samples are characterized using analytical techniques including XRD, TEM, UV–vis DRS, PL, BET, and XPS. A red shift in the light absorption is observed for the Cu$_2$O–TiO$_2$ samples, mainly attributed to the formation of nanoscale heterojunctions between Cu$_2$O and anatase TiO$_2$, providing a better charge separation and an increase in the optical absorption. Among the Cu$_2$O–TiO$_2$ samples, the sample CT07 produces the highest CH$_4$ yield with production rates, 11.1 and 22 times higher than pure CuO and TiO$_2$, respectively.

The improved photocatalytic activity can be attributed to (1) the improved light absorption with a significant red shift in the absorption wavelength; (2) formation of p–n heterojunctions with suitable band edge positions for the improved separation of the photogenerated charge; and (3) large surface areas to promote interfacial reactions. A further increase in the TiCl$_4$ amount, sample CT09, resulted in a decrease in the CH$_4$ evolution rate, which we believe is due to a reduced surface area and a wider bandgap.

Our material synthesis strategy of hybrid Cu$_2$O–TiO$_2$ recommends coupling of low-bandgap materials with large-bandgap materials as an efficient approach for the design of high-performance photocatalysts.
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