Gold–indium modified TiO₂ nanocatalysts for photocatalytic CO₂ reduction with H₂ as reductant in a monolith photoreactor

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In this study, CO₂ photoreduction via reverse water gas shift (RWGS) reaction over gold (Au) and indium (In) modified TiO₂ nanocatalysts in a monolith photoreactor has been investigated. Crystalline nanoparticles of anatase TiO₂ were obtained in doped TiO₂ samples with metals deposited over TiO₂ as Au and In⁺ ions. The catalytic performance of metal-doped/TiO₂ catalysts was found to be considerably higher when compared to pure TiO₂. The maximum production of CO as the main product was 8982 μmol g⁻¹ h⁻¹ at selectivity 99% and CO₂ conversion of 9.5% over 0.2 wt.% Au–3.5 wt.% In/TiO₂, and CO₂/H₂ feed ratio 1.5. The CO production over co-metals (Au–In) doped TiO₂ monolithic catalyst was 1.3 times higher than Au/TiO₂, 4.39 times higher than In/TiO₂ and 76 times higher than undoped TiO₂ catalysts. Significantly higher photocatalytic performance of metal-doped TiO₂ was obviously due to fast electron transfer with hindered recombination rates and larger illuminated surface area in monolith channels. The quantum efficiency of CO production through RWGS reaction using Au–In/TiO₂ catalyst was considerably improved (0.79%) than Au/TiO₂ (0.53%) and In/TiO₂ (0.14%) monolithic catalysts. The stability of the reused catalysts for CO production sustained at cyclic runs. This development confirmed higher performance of metal-doped TiO₂ nanocatalysts supported over monolith channels for CO₂ photoreduction via RWGS reaction.

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1. Introduction

Increasing carbon dioxide (CO₂) concentration in the atmosphere is a matter of great concern and any attempt to reduce its emission is of primary importance. The photocatalytic conversion of CO₂ into fuels and/or chemicals has grown into an intense area of research owing to global warming and fossil fuel shortages [1–3]. CO₂ can be reduced with water to CO, CH₂, CH₃OH, CH₂O with photo-technology [4–7]. However, H₂O is a weak reductant and is hardly reducible, thus photoreduction of H₂O to H₂ proceeds preferably through water splitting instead of CO₂ reduction. Large amount of H₂ can be produced by water splitting under sunlight irradiations, thus, it can be available in excess [8,9]. Therefore, CO₂ photoreduction with H₂ through reverse water gas shift (RWGS) reaction is more effective to reduce CO₂ to fuels [10–12].

Among semiconductor materials, securing photocatalysts with high activity, selectivity and quantum yield efficiency is a critical challenge. TiO₂ is more promising owing to numerous advantages such as strong oxidative potential, low cost, available in excess, chemically/thermally stable and non-toxic [13–16]. However, TiO₂ photoactivity is lower because of the fast recombinaction of photoexcited electron (e⁻)–hole (h⁺) pairs. The photocatalytic activity of titanium based photocatalysts can be enhanced by the incorporation of metals. Among different single metals loaded systems Ag [4,17], Pt [18], I [19], Cu [20], Rh [21] and Fe [22] were widely reported for CO₂ photoreduction. Recently, indium (In) is considered as the most effective metal to enhance TiO₂ photoactivity because of multiple oxidation sates and prevent charge recombination [23]. Tahir and Amin [24] reported photocatalytic CO₂ reduction with H₂O vapors over In-doped TiO₂ photocatalyst and found much higher TiO₂ photoactivity in the presence of In-metal. Simultaneous doping or depositing two different types of metal atoms on TiO₂ has attracted considerable interest; since they can improve TiO₂ photoactivity effectively compared to single metal doped TiO₂. Sasikala et al. [25] investigated In and N co-doped TiO₂–Pd nanocomposites for H₂ generation and found significant improvement in TiO₂ activity in the presence of...
co-metal ions. Similarly, Cao et al. [26] reported In$_2$O$_3$/C$_3$N$_4$ hybrid catalyst for efficient CO$_2$ reduction to fuels. Kuo et al. [27] reported water splitting over Ru-In$_2$O$_3$/TiO$_2$ catalyst and found higher TiO$_2$ photoactivity for H$_2$ production in the presence of Ru and In metals.

Recently, the interest in plasmonic approach in the area of photocatalysis has escalated. In the plasmonic metallic nanostructures, the strong interaction with resonant photons through excitation of localized surface plasmon resonance (LSPR) increased the photoactivity [28,29]. Among the noble metals, gold nanoparticles combined with TiO$_2$ can effectively improve charge separation of photogenerated electron–hole pairs, thus enhancing the overall photocatalysis efficiency of TiO$_2$ under UV-illumination. Noble metal nanoparticles alone can absorb UV–light via inter–band transition. The advantages of Au doped or deposited on TiO$_2$ are: (i) to modify the surface morphologies and structures of TiO$_2$, (ii) to improve e$^-$/h$^+$ pairs separation by performing as electron trap over the TiO$_2$ surface and, (iii) to increase the surface electron activity by localized surface plasma resonance [30,31].

Gold-doped TiO$_2$ nanoparticles were investigated by Mei et al. [32] for photocatalytic CO$_2$ reduction to hydrocarbons with higher TiO$_2$ photoactivity. Gold and copper nanoalloys TiO$_2$ photocatalysts were investigated for photocatalytic CO$_2$ reduction with H$_2$O and found higher photoactivity in the presence of gold metal [33]. Therefore, it is envisaged that gold and indium co-doped TiO$_2$ system would efficiently reduce CO$_2$ through RWGS reaction. The efficient and uniform transformation of the light irradiations over the catalyst surface is crucial in photoreactor design to increase conversion and yield rates. Among the structured photoreactors, monolith containing parallel straight channels can take advantages of distinctive structure, have higher surface area to volume ratio, and efficient light harvesting [34,35]. Monolithic substrate can provide up to 100 times higher specific surface area than other types of catalyst supports having the same outer dimensions [36–38]. Recently, monolith photoreactor has been explored for photocatalytic CO$_2$ reduction with H$_2$O vapors and reported good CO$_2$ conversion efficiency and selectivity [39–41]. Therefore, it is anticipated that RWGS reaction in a monolith photoreactor over co-doped TiO$_2$ catalysts would be appreciable to further CO$_2$ conversion with improved selectivity.

The objective of this study is to test the performance of a monolith photoreactor and photoactivity of co-doped (Au and In) TiO$_2$ nanoparticles for the reduction of CO$_2$ by H$_2$ through RWGS reaction. The factors controlling catalyst activity and products selectivity such as metal loading, CO$_2$/H$_2$ mole ratios, and irradiation time are discussed. Besides, quantum efficiency analysis, possible reaction mechanism and catalyst stability test are also deliberated.

2. Experimental

2.1. Preparation of photocatalysts

A series of gold and indium modified TiO$_2$ catalysts were synthesized using sol–gel method. As shown in Fig. 1, TiO$_2$ sol was prepared by adding a mixture of 15 mL acetic acid and 15 mL isopropanol to mixture containing 20 mL titanium tetra isopropoxide in 60 mL isopropanol under vigorous stirring. The solution was continuously stirred for 24 h to get clear sol. Next, calculated amounts (wt.%) of indium nitrate (In(NO$_3$)$_3$·3H$_2$O) and gold chloride (HAuCl$_4$·3H$_2$O) dissolved in isopropanol were added to the titanium solution and was stirred for 6 h until the thick sol was obtained. All the monoliths were washed with acetone and isopropanol to remove organic residues if any and then dried at 80 °C for 12 h. Before coating, the dried monolith weight was recorded and then dip–coated in the resulting Au–In/TiO$_2$ sol for few seconds. The excess sol inside the monolith channels was blown off using compressed hot air. The coating procedure was repeated to get the desired catalyst loadings. The catalyst-supported monoliths and the remaining sol were dried at 80 °C for 12 h and finally calcined at a rate of 5 °C min$^{-1}$ up to 500 °C and held for 5 h. The actual catalyst loading was measured by subtracting the weight of un-coated monolith from the coated.

Different In and Au doping levels were prepared by varying the quantity of indium nitrate and gold chloride. For single metal ion doping, the amounts of In-used were 2 wt.%, 3.5 wt.%, 5 wt.% and 7 wt.%, while amount of gold used were 0.3 wt.% Au, 0.5 wt.% Au and 0.7 wt.% Au. For co-doping, gold doping levels were 0.1 wt.%, 0.2 wt.% and 0.3 wt.% at fixed In-doping (3.5 wt.%). For comparison, un-doped TiO$_2$ was prepared according to the same procedure.

2.2. Catalyst characterization

Information about the crystallographic structure of the samples showing peak positions and unit cell parameters was obtained using powder X-ray diffraction (XRD) on Bruker D8 advance diffractometer. Cu-Kα radiation was used, operating at 40 kV and 40 mA with a scan range of 15°–70° (2θ), a scan speed of 1.2° (2θ) per min, wavelength (λ) of 1.54 Å and a step size of 0.02. The crystallite sizes were calculated using Scherrer equation $\tau = \frac{k\lambda}{β\cosθ}$, where $\tau$ is the thickness of crystallite (nm). The morphology of nanocatalysts coated over the monolith channels was estimated using scanning electron microscopy (SEM) carried out with JEOL JSM6390 LV SEM instrument. The morphology of the catalyst samples were visualized using a high resolution transmission electron microscope (HRTEM) (FEI-Tecnai G2). The Brunauer–Emmett–Teller (BET) specific surface area and pore size of the catalysts were measured by N$_2$ adsorption–desorption isotherms at 77 K using a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. All the samples were degassed at 250 °C for 4 h. The XPS measurement was performed using Omicron.
Fig. 2. Schematic of experimental setup for photocatalytic CO₂ reduction with H₂ through RWGS reaction in a monolith photoreactor.

DAR 400 analyzer. The photocatalyst was fixed to the sample holder using carbon tape. Ultraviolet–visible (UV–vis) diffuse reflectance absorbance spectra of the samples were determined using Agilent, Cary 100 UV–Vis spectrophotometer equipped with an integrated sphere. Initially, blank runs were conducted to correct the baseline. The absorbance spectra were analyzed at ambient temperature in the wavelength range of 200–800 nm. The band gap energies of the photocatalysts were determined from the extrapolation of Tauc plot to the abscissa of photon energy.

2.3. Photocatalytic CO₂ reduction

The photocatalytic CO₂ reduction with H₂ as a reducing agent under UV-light was conducted in a cylindrical stainless steel reactor with a total volume of 150 cm³ as shown in Fig. 2. All the monolithic supports (Pingxiang Meitao Company, China) used were cylindrical in shape, having dimensions of 60 mm in diameter and 20 mm in length. The catalyst coated ceramic monoliths with channel per square inch (CPSI) 200 were inserted inside the stainless steel chamber, equipped with a quartz window for passing light irradiations from the reflector lamp at the top. The light source used was a 200 W Hg lamp for UV irradiations source with light intensity of 150 mW cm⁻². A cooling fan at the top and sides of the lamp removed the lamp heat. The light intensity was measured with an online optical process monitor ILT OPM-1D and a SED008/W sensor. After performing a leak test with helium (He) at 2 bars pressure for 8 h, the reactor was purged using helium (He) flow before gas mixtures (CO₂, H₂ and He, purity=99.99%) was passed through the reactor for 1 h at a flow rate of 100 mL/min to saturate the catalyst. All the experiments were carried out in a batch mode. The H₂ concentration was fixed at 20 mol.%, while CO₂ concentrations of 10, 20, 30 and 40 mol.% were used to control the CO₂/H₂ ratios at 0.5, 1.0, 1.5 and 2.0, respectively. He gas was

Fig. 3. XRD spectra of un-doped and metal-doped TiO₂ nanoparticles with different metals concentrations.
Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cell parameter (Å)</th>
<th>Cell volume (Å³)</th>
<th>Crystallite size (nm)</th>
<th>Elemental analysis (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = b</td>
<td>c</td>
<td></td>
<td>In</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.764</td>
<td>9.486</td>
<td>134.39</td>
<td>18.73</td>
</tr>
<tr>
<td>2 wt.% In–TiO₂</td>
<td>3.769</td>
<td>9.474</td>
<td>134.40</td>
<td>14.45</td>
</tr>
<tr>
<td>3.5 wt.% In–TiO₂</td>
<td>3.773</td>
<td>9.462</td>
<td>134.66</td>
<td>10.30</td>
</tr>
<tr>
<td>5 wt.% In–1TiO₂</td>
<td>3.778</td>
<td>9.436</td>
<td>134.50</td>
<td>9.50</td>
</tr>
<tr>
<td>0.3 wt.% Au–TiO₂</td>
<td>3.782</td>
<td>9.489</td>
<td>135.69</td>
<td>15.82</td>
</tr>
<tr>
<td>0.5 wt.% Au–TiO₂</td>
<td>3.777</td>
<td>9.495</td>
<td>135.50</td>
<td>16.46</td>
</tr>
<tr>
<td>0.7 wt.% Au–TiO₂</td>
<td>3.781</td>
<td>9.501</td>
<td>135.84</td>
<td>17.96</td>
</tr>
<tr>
<td>0.1 wt.% Au–3.5 wt.% In–TiO₂</td>
<td>3.768</td>
<td>9.478</td>
<td>134.30</td>
<td>9.20</td>
</tr>
<tr>
<td>0.2 wt.% Au–3.5 wt.% In–TiO₂</td>
<td>3.787</td>
<td>9.489</td>
<td>134.49</td>
<td>10.40</td>
</tr>
</tbody>
</table>

a Crystallite sizes calculated using Scherrer equation.

b Surface elemental contents calculated using EDX.

used to culminate the mole balance to 100 mol.%. The pressure inside the reactor was set to 0.40 bars and then the gases flow was turned off for batch mode study.

The products were analyzed using an on-line gas chromatograph (GC-Agilent Technologies 6890N, USA) equipped with thermal conductivity detector (TCD) and flame ionized detector (FID). Furthermore, FID detector was connected with a HP-Plot Q capillary column (Agilent, length 30 m, ID 0.53 mm, film 40 μm) for separation of C₁–C₆ paraffin and olefins hydrocarbons, alcohols and oxygenated compounds. The TCD detector was connected to
UCW982, DC-200. Porapak Q and Mol Sieve 13X columns. C1–C2, C3–C6 compounds and light gasses (H2, O2, N2, CO) were separated using Porapak Q, DC-200 and MS-13X column, respectively.

3. Results and discussion

3.1. Characterization of nanocatalysts

The XRD spectra of TiO2, In-doped TiO2, Au-doped TiO2 and Au–In co-doped TiO2 samples are presented in Fig. 3. XRD peak of un-doped TiO2 revealed pure crystalline and anatase phase TiO2. Similarly, all the peaks of the In-doped TiO2, Au-doped TiO2 and Au–In co-doped TiO2 samples confirming the formation of anatase and crystalline phase TiO2. However, all the peaks pertaining to metals and co-metals doped TiO2 were not detected, even for the sample with additional metal-contents [28]. Moreover, all the peaks become wider with increased intensities by In-doping, but no shifting in the TiO2 peaks was observed. The wider anatase TiO2 peaks were related to reduce TiO2 crystallite size by doping In-metal. Similar observations have been reported in the literature [42]. In the case of Au-doping, the crystallite size gradually increased possibly due to Au deposited over the TiO2 surface. However, the crystallite size of Au–In co-doping samples was decreased.

The Scherrer equation based on XRD (1 0 1) peaks used to calculate crystallites sizes as presented in Table 1. Using higher metals contents, lesser crystallites are obtained, perhaps due to metals controlling TiO2 crystal growth. In the previous works, similar verdicts are reported [43]. Furthermore, cell parameters and cell volumes of TiO2 and metal-doped TiO2 crystallites are summarized in Table 1. The cell parameters and cell volumes are similar to those reported in JCPDS-ICSD (89-4921) standards for anatase TiO2, i.e. \( a = b = 3.777 \text{ Å}, c = 9.501 \text{ Å}, \) and \( V = 135.54 \text{ Å}^3 ). These observations have confirmed fully developed tetragonal crystal shape of anatase TiO2. Moreover importantly, TiO2 doping with In and Au metals did not affect the lattice parameters and cell structure. The uniform and spherical TiO2 nanoparticles of mesoporous structure are obvious in Fig. 4(a). The EDX mapping analysis in Fig. 4(b) and (c) divulges the presence of Ti and O elements in TiO2. Meanwhile, it can be observed that Au and In doped TiO2 nanoparticles have smaller particle size, more mesoporous structure compared with un-doped TiO2 as shown in Fig. 4(d)–(g). However, in Au and In doped TiO2 samples, agglomerate formations can be seen. The EDX mapping analysis in Fig. 4(e) and (f) revealed uniform distribution of In-metal in the TiO2 texture. The EDX analysis of Au–In co-doped TiO2 sample is presented in Fig. 4(h) and (i), confirming the presence of Au and In metals in TiO2. Noticeably, both metals (Au and In) were evenly spread over the TiO2 surface. The elemental compositions of all the metals are presented in Table 1.

The TEM micrographs of TiO2, Au/TiO2 and Au–In/TiO2 nanoparticles are depicted in Fig. 5. Mesoporous and uniform sized TiO2 nanoparticles are obvious in un-doped and metal-doped TiO2 samples as depicted in Fig. 5(a)–(c). The nanoparticles have interparticle mesoporous structure, possibly due to the crystal growth. The TEM images in Fig. 5(d) corroborated with the XRD morphology of TiO2 nanoparticles, where 0.35 nm aligned anatase phase are grown along 1 0 1 directions. All the characterization results are in good agreement with previous reports [44,45].

Fig. 6 exhibits the N2 adsorption–desorption isotherms of TiO2, In/TiO2, Au/TiO2, and Au–In/TiO2 samples. All the isotherms have close resemblance with the type IV curve with obvious hysteresis loops, thus conforming mesoporous structure of TiO2 and metal-doped TiO2 samples [39]. The initial part of the isotherms (at low \( P/P_0 )\) is related to the monolayer–multilayer adsorption on the internal surface. In the upper part of isotherms at higher \( P/P_0 \), the steep increment in the adsorption volume is attributed to the capillary condensation as the pores were saturated with the liquid. On the other hand, monolayer–multilayer is more dominant in the TiO2 samples where capillary action started at \( P/P_0 \) of 0.60. Both the capillary and condensation processes are eminent in the co-doped TiO2 samples at \( P/P_0 \) of 0.55.

The surface area, pore volume and pore sizes of un-doped TiO2 and metal-doped TiO2 samples are reported in Table 2. The BET
Table 2
Summary of physicochemical characteristics of TiO2 and modified TiO2 samples.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
<th>BET surface area</th>
<th>BJH adsorption pore volume (cm³/g)</th>
<th>BJH pore diameter (nm)</th>
<th>Band values (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>43</td>
<td>52</td>
<td>0.134</td>
<td>10.33</td>
<td>3.122</td>
</tr>
<tr>
<td>2 wt.% In–TiO₂</td>
<td>61</td>
<td>69</td>
<td>0.161</td>
<td>9.34</td>
<td>3.186</td>
</tr>
<tr>
<td>3.5 wt.% In–TiO₂</td>
<td>84</td>
<td>113</td>
<td>0.22</td>
<td>7.67</td>
<td>3.195</td>
</tr>
<tr>
<td>5 wt.% In–TiO₂</td>
<td>98</td>
<td>143</td>
<td>0.28</td>
<td>7.50</td>
<td>3.217</td>
</tr>
<tr>
<td>0.3 wt.% Au–TiO₂</td>
<td>46</td>
<td>58</td>
<td>0.23</td>
<td>8.94</td>
<td>3.03</td>
</tr>
<tr>
<td>0.5 wt.% Au–TiO₂</td>
<td>47</td>
<td>74</td>
<td>0.24</td>
<td>11.35</td>
<td>2.93</td>
</tr>
<tr>
<td>0.1 wt.% Au–3.5% In–TiO₂</td>
<td>78</td>
<td>125</td>
<td>0.28</td>
<td>7.96</td>
<td>3.11</td>
</tr>
<tr>
<td>0.2 wt.% Au–3.5 wt.% In–TiO₂</td>
<td>83</td>
<td>140</td>
<td>0.25</td>
<td>8.18</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Fig. 6. N₂ adsorption–desorption isotherms of TiO₂, In-doped TiO₂, Au-doped TiO₂ and Au–In co-doped TiO₂ samples.

The surface area of TiO₂ was 43 m²/g increased to 61, 84, and 98 m²/g with 2 wt.%, 3.5 wt.%, and 5 wt.% In-doping into TiO₂, respectively. However, in the case of Au-doped-TiO₂ samples, the increase in the surface area was not significant. Similarly the surface areas of the Au–In co-doped TiO₂ samples were approximately closer to the 3.5 wt.% In-doped TiO₂ sample. It is evident that Au-doping in In/TiO₂ samples could not alter the BET surface area, confirming no significant effect on TiO₂ morphology. However, larger BJH surface area of all the metal-doped TiO₂ samples is attributed to the suppression of TiO₂ crystal growth by metal and co-metal doping. These observations agreed well with the XRD and TEM results. Similarly, BJH adsorption pore volume increased while pore diameter decreased with metal doping. Thus, the increase in pore volume with reduced pore diameter was possibly due to the controlled crystal growth in the metal-doped TiO₂ samples. Similar observations are described in earlier reports [46].

The chemical states of the component elements of the Au–In co-doped TiO₂ sample were analyzed by X-ray photoelectron spectroscopy (XPS). The Ti 2p spectrum in Fig. 7(a) shows the peaks with binding energies (BE) located at ~458.60 eV (2p₃/₂) and 464.3 eV (2p₁/₂), both of which attributed to Ti⁴⁺/⁴ oxidation state. The XPS spectrum of Au 4f is shown in Fig. 7(b). The binding energy of the Au 4f₃/₂ peak is 83.89 eV and the binding energy of Au 4f₅/₂ is 89.20 eV, which confirmed the metallic state of Au in Au–In/TiO₂ sample. Fig. 7(c) shows the In-3d spectrum peaks of In 3d₅/₂ and In 3d₃/₂ with BE region centered at ~444.30 and 450.69 eV, respectively, indicates indium in In³⁺ species or In₂O₃. The spectrum of O 1s shown in Fig. 7(d) reveals three peaks centered at 529.95, and 532.20 eV. The BE value of 529.95 eV is attributed to the lattice oxygen O²⁻ in TiO₂, and In₂O₃ which is in agreement with the reported values [47]. The oxygen peak at around 532.20 eV is due to H₂O or the free hydroxyl group (O–H) on the surface. The C 1s spectrum of all the carbon peaks is shown in Fig. 7(e). The peak with binding energy located at ~284.60 eV is assigned to elemental carbon (C–C) while, the one at 586.64 eV corresponds to C–O. The presence of carbon may be recognized as the carbon from carbon tape used for analysis of sample.

The optical properties of pure TiO₂, In-doped TiO₂, Au-doped TiO₂ and Au–In co-doped TiO₂ samples were studied using UV–vis absorption measurements of wavelength 200–800 nm as presented in Fig. 8(a). All the samples have higher absorbance intensities than the un-doped TiO₂. A blue shift in the absorbance spectra was observed in all the In-doped TiO₂ samples, which is in agreement with our previous observations [24,39]. The presence of Au metal improves the absorbance spectra toward red shift due to their optical absorption spectra dominated by two peaks ranging between 400 and 420 and 450–700 nm, with the former being associated with surface plasmon resonance absorption peak. These results confirmed that Au-metal could enhance TiO₂ photoactivity in the visible region due to plasmonic response [30]. The band gap energies were determined using Tauc plot, i.e. (αhν)² versus (hν) (where α is the absorbance, h is Planks constant and ν is light frequency), by extrapolating the linear region of the plot to the intercept of the photon energy axis (Fig. 8(b)). The obtained band gap energy values of TiO₂ and metal doped TiO₂ samples are reported in Table 2. The band gap energy of un-doped TiO₂ was 3.12 eV, shifted to 3.19, 3.20, 3.22 and 3.24 eV with 2 wt.%, 3.5 wt.%, 5 wt.% and 7 wt.% In-doping, respectively. The increase in the band gap energy was due to the higher In₂O₃ band gap energy (E₉g = 3.7 eV). The shift in TiO₂ band gap energy toward UV regions is reported in the literatures for In-doped TiO₂ nanoparticles [48,49]. The band gap energies of 3.03 and 2.93 eV for 0.3 wt.% and 0.5 wt.% Au-doped TiO₂ samples were obtained. On the other hand, the band gap energy of Au–In/TiO₂ samples was higher than Au/TiO₂ samples but lower than In/TiO₂ samples. This infers Au impurity level is beneficial for extending the absorption spectra toward the visible light region.

The photoluminescence (PL) spectra of TiO₂, In-doped TiO₂, Au-doped TiO₂ and Au–In co-doped TiO₂ samples are shown in Fig. 9. The fluorescence peaks of metals doped TiO₂ were in the range of 450–550 nm using excitation wavelength of 350 nm. The emitted peaks of pure TiO₂ and metals-doped TiO₂ samples exhibit wide and strong PL signals in the identical regions. The existence of PL is attributed to the recombination of e⁻/h⁺ pairs. Moreover, a decline in PL intensity was observed for different metals-doped TiO₂ samples compared to un-doped TiO₂. The lower intensities of metal-doped TiO₂ revealed the decrease in recombinating rates of electron–hole pairs on the metal-doped TiO₂ samples. The positively charged plasmas of Au-doped TiO₂ attracted electrons in the conductance band of TiO₂ and then increased the capability of e⁻/h⁺ separations. Accordingly, a significant reduction in PL intensity could be seen in Au-doped and Au–In co-doped TiO₂ samples, obviously due to efficient electron trapping by these metals. From
Fig. 7. XPS spectra of Au–In co-doped TiO₂ catalyst; (a) Ti 2p, (b) Au 4f, (c) In 3d (d) O 1s, and (e) C 1s.

Fig. 8. (a) UV–vis diffuse reflectance absorbance spectra of TiO₂, In/TiO₂, Au/TiO₂ and Au–In/TiO₂ samples and (b) band gap energy calculation of corresponding samples.
of CO production, a significant amount of hydrocarbons namely CH4, C2H4, C2H6, C3H6, and C3H8 were also observed over In-doped Au-doped TiO2 and Au–In co-doped monolithic catalysts. Significantly higher TiO2 photoactivity in the presence of Au-metal was obviously due to the plasmonic effect of Au-doped TiO2 catalyst and the hindered recombination of charges over the TiO2 surface. The different rates of e−/h+ formations and recombinations in the TiO2 has been expected to occur due to plasmonic response of Au-metal to increase the efficiency of CO2 reduction to fuels [28].

From the above discussion, it is obvious that gold is the most active metal to enhance TiO2 photoactivity. According to thermodynamics, the electrons being trapped by metal (Mʷ⁺) within the photocatalyst (e.g. TiO2) are more feasible if the reduction potential of metal (Mʷ⁺) is more positive than the TiO2 conduction band (CB). The potential redox values of Au⁺, and Au²⁺ are given in Eqs. (1) and (2). As the Au has the highest positive potential redox value than the CB of TiO2 (−0.50 V) [15], thus Au doped into TiO2 would perform as an efficient electron trap to hinder electron–hole pair recombination:

\[
\text{Au}^{2+} + e^- \rightarrow \text{Au}^+ \quad (E^0 = +1.80 \text{V}) \tag{1}
\]

\[
\text{Au}^+ + e^- \rightarrow \text{Au} \quad (E^0 = +1.69 \text{V}) \tag{2}
\]

Fig. 11 illustrates the dependency of CO2/H2 molar ratios on the photo-activity of Au and In-doped TiO2 catalyst for the CO2 photo-reduction through RWGS reaction. As presented in Fig. 10(A), CO was the main product with a smaller amount of CH4 production at all the CO2/H2 mole ratios. However, the CO yield increased rapidly with increasing CO2 concentration up to 30 mol.% of CO2 at a fixed H2 concentration of 20 mol.%. Therefore, the CO2/H2 mole ratio of 1.5 was optimum. Thus, it is inferred that the amount of adsorbed CO2 increased with an increase in the initial CO2 concentration, resulting in higher CO production. This phenomenon is likely due to adsorption competition between CO2 and H2 molecules to the catalyst active sites during photo-reduction process. At lower CO2 concentrations, large amount of H2 could adsorb over the catalyst surface, thus CO2 has to compete with H2, resulting in lesser CO2 reduction. On the other hand, at higher CO2 concentration, supposedly maximum active sites were covered and H2 would have to compete with CO2 for the active sites leading in reduced reaction rate. Therefore, an optimum concentration of both reactants would

The effects of Au and In co-doping into TiO2 was investigated to evaluate the TiO2 photoactivity as illustrated in Fig. 10(C). Compared with TiO2, In/TiO2, Au/TiO2, Au doped in In/TiO2 exhibited a significant increase in CO production rate. It was found that 0.2 wt.% Au content was the optimum in 3.5 wt.% In-doped TiO2. In addition

the PL results it can be envisaged that Au-doped and co-metals doped TiO2 catalysts would be more capable to enhance TiO2 photoactivity for CO2 reduction applications.

3.2. Photocatalytic CO2 reduction with H2

Preliminary investigation of photocatalytic CO2 reduction with H2 as a reducing agent at 100 °C in the presence of UV-irradiations in a monolith photocatalyst reactor was performed for the cases of (a) uncoated monoliths + helium, (b) catalyst coated monoliths + helium, and (c) H2 + helium + catalyst coated monoliths. In any case carbon containing compounds were not produced. This confirmed catalysts and monoliths did not degrade and carbon containing compounds were not produced from organic residues in the catalyst if any. Therefore, any carbon containing compounds produced were derived from CO2 through photocatalysis. The photoactivity of TiO2, In-doped TiO2, Au-doped TiO2 and Au–In co-doped TiO2 nanocatalysts in a monolith photoreactor was evaluated by measuring the production rate of CO and hydrocarbons under UV-light irradiations.

The effects of metal and co-metal doping on the TiO2 photoactivity for photocatalytic CO2 reduction with H2 in a monolith photoreactor is illustrated in Fig. 10. Fig. 10(A) reveals un-doped TiO2 promotes CO and CH4 production, but poor photoactivity is registered. This can be attributed to higher electron–hole pair’s recombination rate over the TiO2 surface. By doping In-metal into TiO2, there was a substantial increase in CO2 reduction with CO as the major reduction product. The yield of CO was increased up to an optimum 3.5 wt.% In-content, and then gradually decreased. On the other hand, the performance of Au-metal on TiO2 photoactivity for CO2 reduction with H2 is depicted in Fig. 10(B). Significantly higher amount of CO production with appreciable amount of hydrocarbons could be seen in Au-doped TiO2 samples. A 0.5 wt.% Au-doped TiO2 catalyst was optimum, then the yield rates decreased with higher Au-doping.

The effects of Au and In co-doping into TiO2 was investigated to evaluate the TiO2 photoactivity as illustrated in Fig. 10(C). Compared with TiO2, In/TiO2, Au/TiO2, Au doped in In/TiO2 exhibited a significant increase in CO production rate. It was found that 0.2 wt.% Au content was the optimum in 3.5 wt.% In-doped TiO2. In addition
be favorable for higher CO₂ conversion. Similar findings have been reported in literature during photocatalytic CO₂ with H₂O vapors using various TiO₂ based photocatalysts [50].

Fig. 11(b) portrays the production of hydrocarbons over Au–In/TiO₂ monoliths at different initial CO₂/H₂ molar ratios. The hydrocarbons observed were C₂H₄, C₂H₆, C₃H₆ and C₃H₈ at CO₂/H₂ mole ratios of 0.5, 1.0, 1.5 and 2.0. Apparently, much higher C₂H₆ yield was observed at CO₂/H₂ feed ratio of 0.5 and 1.0, then, reduced radically at higher initial CO₂/H₂ molar ratios. Besides, C₂H₆ is the second largest yield followed by the trace distribution of C₂H₄ and C₃H₆ for all the initial feed ratios. The much higher C₂H₄ and C₂H₆ production at a lower CO₂/H₂ feed ratio was possibly due to more adsorption of H₂ over the catalyst surface, resulting in superfluous production of higher hydrocarbons.

The effect of irradiation times on the yield of CO over un-doped TiO₂, In-doped TiO₂ Au-doped TiO₂ and Au–In co-doped TiO₂ catalysts at irradiation times of 0–8 h is presented in Fig. 12. Using un-doped TiO₂ smaller amount of CO produced, which increased significantly with In-doping. A much higher CO production could be seen using Au-doped TiO₂ compared to In-doped TiO₂. On the other hand, Au and In co-doped TiO₂ performed more efficiently than Au-doped TiO₂ catalyst. The amount of CO produced over Au–In/TiO₂ was 8982 μmol g-catal⁻¹ h⁻¹, a 1.3 fold higher than Au/TiO₂, 4.39 fold higher than In/TiO₂ and 76 fold higher than TiO₂ catalyst.

The conversion yield rates and selectivity of different products over various types of catalysts in a monolith photoreactor during CO₂ photoreduction with H₂ is presented in Table 3. The products observed were CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ over TiO₂, In/TiO₂, Au/TiO₂ and Au–In/TiO₂ catalysts. Among all the products, CO was the main CO₂ reduction products and was higher in the order of Au–In/TiO₂ > Au/TiO₂ > In/TiO₂ > TiO₂. The photocatalysts activity for CO₂ reduction to CH₄ as the second largest product was in the order of Au–In/TiO₂ > Au/TiO₂ > In/TiO₂ > TiO₂. Among the hydrocarbons, C₂H₆ production was highest and was in order of Au–In/TiO₂ > Au/TiO₂ > In/TiO₂ > TiO₂. These products can be understood by comparing the conduction band energies of TiO₂ with the reduction potential of CO₂ for the three reduction products CO, CH₄ and C₂H₆. Since, the conduction band of TiO₂ lies above the reduction potential of CO₂/CO, thus CO is the most favorable CO₂ reduction product. In general, Au doped TiO₂ and Au–In co–doped TiO₂ catalysts efficiency was evidently higher for CO production through RWGS reaction with appreciable amounts of C₁–C₃ hydrocarbons. The significant increase in CO production was probably due to the effective production of electrons–holes pairs and inhibited their recombination rate over metal and co-metal doped TiO₂ catalyst coated inside monolith channels.

Besides, in the case of gold doped TiO₂, the higher photocactivity was also due to the surface plasmon resonance of gold nanoparticles as explained in the UV–vis analysis. The electrons were efficiently transferred from the TiO₂ conductance band to Au-nanoparticles due to the lower Fermi level and intensified local electromagnetic fields created by the surface plasmons of Au-nanoparticles. The intense electromagnetic fields also enhanced electron–hole pairs separation and transferred toward CO₂, resulting in higher photocatalytic activity [31,51].

The results of this study are compared to the work reported by various researchers. Teramura et al. [52] investigated CO₂ reduction with H₂ over MgO and 2.9 μmol of CO was produced after 6 h irradiation time. When TiO₂ and ZrO₂ catalysts were tested for CO₂ + H₂ + H₂O and CO₂ + H₂ reduction under UV light irradiation, CH₄ and CO were produced at rates of 4.1 and 0.65 μmol g-catal⁻¹ h⁻¹, respectively [53]. Similarly, photocatalysis of CO₂ with H₂ as a reductant over β-Ga₂O₃ photocatalysts produced CO of 0.76 μmol g-catal⁻¹ h⁻¹ [11], CO of 0.56 μmol g-catal⁻¹ h⁻¹ over ZrO₂ [54], and CO of 1.6 μmol g-catal⁻¹ h⁻¹ over MgO [55]. Although, in all the above reports, CO was the main product during CO₂ reduction, the yield rates and process efficiency were lower. A comparison study between previous reports and current study revealed that monolith geometry and doped metals into TiO₂ facilitated in improving yield rates. In general, higher production rate of CO was obviously due to larger illuminated surface area inside monolith channels and to efficient trapping of electrons in the presence of Au and In-metals.

Fig. 13 compares conversion and selectivity over various monolithic catalysts. CO₂ conversion over Au–In/TiO₂ was 9.5%, a 1.22 times higher than Au/TiO₂. 1.92 times more than In/TiO₂ and 6.78 times higher than TiO₂, while the catalysts efficiencies for H₂ conversion was higher in the order of Au–In/TiO₂ (18.8%) > Au/TiO₂.
Fig. 11. Effects of CO₂/H₂ feed ratio on the photoactivity of 0.2 wt.% Au–3.5 wt.% In/TiO₂ monoliths at irradiation time 2 h: (a) production of CO and CH₄ and (b) production of C₁–C₃ hydrocarbons.

Fig. 12. Effects of irradiation time on the photoactivity of TiO₂ and metal-doped TiO₂ monoliths for CO₂ reduction with H₂ to CO at CO₂/H₂ mole ratio 1.5 at 100 °C.

Table 3
Summary of the products over un-doped and doped TiO₂ nanocatalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion(d) (%)</th>
<th>Production rate (µmol g-catal⁻¹ h⁻¹)</th>
<th>Selectivity(e) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>1.4</td>
<td>CO 120  CH₄ 68  C₂H₂ 0.09  C₂H₆ 1.20  C₃H₄ 0.03  C₃H₈ 0.05</td>
<td>CO 63.37  CH₄ 35.91</td>
</tr>
<tr>
<td>In₃/TiO₂</td>
<td>4.9</td>
<td>2045  31  0.48  1.94  0.19  0.18</td>
<td>98.37  1.49</td>
</tr>
<tr>
<td>Au–In–TiO₂</td>
<td>7.8</td>
<td>6963  54.5  0.345  2.745  1.13  0.152</td>
<td>99.16  0.78</td>
</tr>
<tr>
<td>Au–In₃–TiO₂</td>
<td>9.5</td>
<td>8982  82.65  1.057  5.975  0.527  0.7425</td>
<td>99.00  0.91</td>
</tr>
</tbody>
</table>

a In = 3.5 wt.%

b Au = 0.5 wt.%

c Au = 0.2 wt.%, product rates were calculated on 8 h irradiation basis at CO₂/H₂ molar ratio 1.5 and 100 °C.

d Conversion of CO₂ or H₂ (%) = ([moles of CO₂ or H₂ in feed-moles of CO₂ or H₂ in product]/[moles of CO₂ or H₂ in feed]) × 100.

e Selectivity of product Ci (%) = ([moles of C in product mixture]/[Total moles of C produced]) × 100, Ci is the mole of carbon specie i (CO, CH₄, C₂H₆, C₂H₄, C₃H₆, and C₃H₈) in the products mixture and C is the mole of total carbon compounds produced.
It is remarkable to note conversion of H$_2$ was much higher. According to the stoichiometric reactions in Eqs. (3) and (4), one and four moles of H$_2$ are required to produce one mole of CO and one mole of CH$_4$ respectively:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 \overset{\text{light,} \text{Au-In/TiO}_2}{\rightarrow} \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 \overset{\text{light,} \text{Au-In/TiO}_2}{\rightarrow} \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

(3) (4)

As the selectivity of CO is about to 99% (Table 3), thus Eq. (3) is more favorable, indicating consumption of H$_2$ and CO$_2$ would be approximately much closer. Thus, conversion of H$_2$ should be approximately closer to CO$_2$ conversion. As illustrated by XPS results, Au was presented over TiO$_2$ in metal state. Therefore, a much higher H$_2$ conversion was registered possibly due to higher consumption of protons by Au metal during its reduction as described in Eqs. (5)–(7)[56,57]:

\[
\begin{align*}
\text{Au} + \frac{\text{h}^+}{2\text{h}^+} & \rightarrow \text{Au}^{+} \\
\text{Au}^{+} + \frac{2\text{e}^-}{2\text{e}^-} & \rightarrow \text{Au} \\
\text{AuO} + \text{H}_2 \overset{\text{UV-light}}{\rightarrow} & \text{Au} + \text{H}_2\text{O}
\end{align*}
\]

(5) (6) (7)

During photocatalytic CO$_2$ reduction with H$_2$ over Au/TiO$_2$ and Au–In/TiO$_2$ catalysts, the generation of Au ions occurred through the oxidation of Au metal by photo-generated holes. Therefore, Au species could be oxidized to Au$^+$ by ions of H$^+$ and/or O$_2$ present in the system (Eq. (5)). Eq. (6) illustrates the redox cycle of Au$^{2+}$/Au$^+$ over the TiO$_2$ matrix. Eq. (7) presents the reduction of AuO with H$_2$ to produce Au. Due to rapid transfer of excited electrons to the Au particles, the separations between electron and hole pairs enhanced the photocatalytic activity for CO$_2$ reduction through RWGS reaction.

### 3.3. Performance analysis of CO$_2$ reduction in monolith photo reactor

The efficiency of a photoreactor is usually evaluated based on quantum efficiency. The quantum efficiency was calculated for each experiment, as the ratio of the product rate (mol/s) with photonic flux (mol/s). Two electrons are needed to transform CO$_2$ into CO. If one electron–hole pair is to be generated by one photon activation, then the quantum efficiency of CO$_2$ photoreduction to CO and CH$_4$ can be defined as the ratio of production rate (mol/s) with photonic flux (mol/s) as shown in Eqs. (8) and (9)[58]:

Quantum efficiency of CO ($\%$)

\[
\frac{2 \times \text{moles of CO production rate (mol/s)}}{\text{moles of photon flux (mol/s)}} \times 100
\]

(8)

Quantum efficiency of CH$_4$ ($\%$)

\[
\frac{8 \times \text{moles of CH}_4 \text{ production rate (mol/s)}}{\text{moles of photon flux (mol/s)}} \times 100
\]

(9)

The quantum efficiency can be estimated by the CO and CH$_4$ production rate and moles of photon input energy from the UV-light. Table 4 highlights operating parameters used in TiO$_2$ and metal modified TiO$_2$ catalysts to calculate quantum efficiency. Over the Au–In/TiO$_2$ catalyst, the quantum efficiency of CO production was 0.79%, a 1.51 times higher than Au/TiO$_2$, 5.6 times higher than In-doped TiO$_2$ and a 105 times higher than a pure TiO$_2$ based monolithic catalyst. Besides, quantum efficiencies for CH$_4$ production were 0.0042%, 0.0022%, 0.0041% and 0.0072% for TiO$_2$, In/TiO$_2$, Au/TiO$_2$ and Au–In/TiO$_2$ monolithic catalysts, respectively. Tahir and Amin[39] worked on photocatalytic CO$_2$ reduction with H$_2$O vapors in a monolith photoreactor using In/TiO$_2$ catalyst and the quantum efficiency for CO production was 0.10%, 7.9 times lower than the quantum efficiency of CO production through RWGS reaction over Au–In/TiO$_2$ monoliths in the present study.

This infers that efficiency of photocatalysis process depends on the type of reducing agent and photocatalyst. Liou et al. [35] reported quantum efficiency of internally illuminated monolith photo-reactor for CH$_3$OH production during CO$_2$ reduction with H$_2$O vapors which was 0.012%, a 66 times lower than the value reported in this study for CO production over Au–In/TiO$_2$. The much higher quantum efficiency attributed to higher photonic efficiency inside the monolith channels due to larger illuminated active surface area and inhibited recombination of charges. These results confirmed reducing agent and metal-doping to TiO$_2$ contributed significantly to enhance photoreactor performance.

In order to investigate the stability of doped and co-doped monolithic catalysts, all the experiments were repeated three times under identical conditions on the recycled catalyst-coated monoliths. The stability test of photocatalytic CO$_2$ reduction with H$_2$ to
CO for all three catalysts is presented in Fig. 14. After each cycle, the monolith was removed from the reactor and placed in open air for 24 h before starting the next run. Apparently, the CO yield did not differ much in the first and second runs, but was significantly reduced in the third run. The loss of photoactivity was obviously due to catalyst deactivation after prolonged reaction time in monolith photocatalyst.

3.4. Mechanism of CO2 photoreduction through RWGS reaction

Photocatalytic CO2 reduction is a multi-electron process, which involves photo-excited electron ($e^-$) and hole ($h^+$) generation over the semiconductor surface with light energy as well as transfer of charges, O—C—O bonds breaking, and formation of C—O, C—H and O—H bonds. Thermodynamically, CO2 molecules needs 2, 8, 12, 14, 18 and 20 electrons ($e^{-1}$) to be converted into CO, CH4, C2H4, C2H6, C1H6, and C3H8, respectively. The proposed reaction mechanism for photocatalytic CO2 reduction with H2 as reducing agent over Au–In co-doped TiO2 is illustrated in Eqs. (10)–(21) [24]:

$$\text{TiO}_2 + h^+ \rightarrow e^+ + h^+ \text{(electron–hole pair)}$$  \hspace{1cm} (10)

$$[\text{Ti}^{3+} + \text{O}^{2-}] \rightarrow e^+ + h^+ + [\text{Ti}^{2+} - \text{O}^{-}]^+$$  \hspace{1cm} (11)

$$\ln^{3+} + e^- \rightarrow \ln^{3+} - (e^-)$$  \hspace{1cm} (12)

$$\frac{Au^+ + e^-}{2e^-} \rightarrow \frac{Au^{2+} - e^-}{2e^-}$$  \hspace{1cm} (13)

$$\text{CO}_2 + e^- \rightarrow \text{O}^- + \text{C} + \text{O}^-$$ \hspace{1cm} (14)

$$\text{H}_2 + 2h^+ \rightarrow \text{H}^+ + \text{H}^+$$ \hspace{1cm} (15)

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$$ \hspace{1cm} (16)

$$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$$ \hspace{1cm} (17)

$$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$$ \hspace{1cm} (18)

$$2\text{CO}_2 + 14\text{H}^+ + 14e^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$$ \hspace{1cm} (19)

$$3\text{CO}_2 + 18\text{H}^+ + 18e^- \rightarrow \text{C}_3\text{H}_8 + 6\text{H}_2\text{O}$$ \hspace{1cm} (20)

$$3\text{CO}_2 + 20\text{H}^+ + 20e^- \rightarrow \text{C}_3\text{H}_8 + 6\text{H}_2\text{O}$$ \hspace{1cm} (21)

The schematic representation of photocatalytic CO2 reduction through RWGS reaction over Au–In co-doped TiO2 catalyst is illustrated in Fig. 15. In Fig. 15(a), the electrons transformed from the excited TiO2 to Au-nanoparticles under UV-light were due to the lower Fermi level of Au than that of TiO2. Thus, more electrons assembled in the Fermi level of the metal, and brought better reductive power in TiO2. Due to the localized surface plasma resonance of Au-nanoparticles, incident light induced an electric field in the metal nanoparticles, thus positively and negatively charged plasmas were separated [59]. Eqs. (10)–(13) reveal photo-excited electron–hole pair production and their efficient trapping by Au and
In metals, thus increasing the lifetime of charges to precede oxidation and reduction processes. CO₂ reduction by electrons and H₂ oxidation with holes is illustrated in Eqs. (14) and (15), respectively. Reactions in Eqs. (16)–(21) divulge reduction of CO₂ to CO, CH₄, C₂H₄, C₃H₆, and C₄H₁₀ through utilization of H⁺ ions and electrons (Fig. 15(b)). The evolution of CO was much higher which confirmed efficient reverse water gas shift reaction in the presence of Au–In co-doped TiO₂ monolithic catalysts. However, appreciable amounts of CH₄ and C₂–C₃ hydrocarbons were also produced over Au/TiO₂ and Au–In/TiO₂ samples. This was apparently due to higher mobility of charges and their hindered recombination rate in the presence of Au metal ions and higher quantum efficiency inside the monolith photoreactor (Fig. 15(c)).

**4. Conclusions**

The gold and indium co-doped TiO₂ catalysts were tested for CO₂ reduction through RWGS reaction in a monolith photoreactor. The parameters investigated were metal-doping into TiO₂, CO₂/H₂ feed ratios and irradiation time. CO was observed as the main product over all types of photocatalysts. The other products observed were CH₄, C₂H₄, C₂H₆, and C₃H₆. Over the Au–In/TiO₂ catalyst, the quantum efficiency of CO production was 0.79%, 1.5 times higher than Au/TiO₂. 5.64 times higher than In-doped TiO₂ and 105 times higher than un-doped TiO₂ catalyst. The higher proficiency of the monolith photoreactor was apparently due to the larger illuminated surface area, higher photon energy consumption and better reactor volume utilization. Thus, the monolith photoreactor is appropriate for efficient photocatalytic CO₂ reduction applications while gold and In metals doped into TiO₂ are decidedly effective for enhancing CO yield rates and selectivity through RWGS reaction. The stability test revealed prolonged activity of the photocatalysts supported over monolith channels.

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**References**

Bharadwaj, age.


