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# Selective CO<sub>2</sub> reduction to HCOOH on a Pt/In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> multifunctional visible-photocatalyst†

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Selective photocatalytic reduction of CO<sub>2</sub> has been regarded as one of the most amazing ways for re-using CO<sub>2</sub>. However, its application is still limited by the low CO<sub>2</sub> conversion efficiency. This work developed a novel Pt/In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> multifunctional catalyst, which exhibited high activity and selectivity to HCOOH during photocatalytic CO<sub>2</sub> reduction under visible light irradiation owing to the synergistic effect between photocatalyst, thermocatalyst, and heterojunctions. Both In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> acted as visible photocatalysts, in which porous g-C<sub>3</sub>N<sub>4</sub> facilitated H<sub>2</sub> production from water splitting while the In<sub>2</sub>O<sub>3</sub> nanosheets embedded in g-C<sub>3</sub>N<sub>4</sub> pores favored CO<sub>2</sub> fixation and H adsorption onto the Lewis acid sites. Besides, the In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunctions could efficiently inhibit the photoelectron–hole recombination, leading to enhanced quantum efficiency. The Pt could act as a co-catalyst in H<sub>2</sub> production from photocatalytic water splitting and also accelerated electron transfer to inhibit electron–hole recombination and generated a plasma effect. More importantly, the Pt could activate H atoms and CO<sub>2</sub> molecules toward the formation of HCOOH. At normal pressure and room temperature, the TON of HCOOH in CO<sub>2</sub> conversion was 63.1 μmol g<sup>−1</sup> h<sup>−1</sup> and could reach up to 736.3 μmol g<sup>−1</sup> h<sup>−1</sup> at 40 atm.

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## 1. Introduction

CO<sub>2</sub> conversion has attracted increasing interest owing to the consideration to both reduce the green-house effect and recycle carbon resources. The key problem is the CO<sub>2</sub> fixation and activation steps, which play a critical role in determining the activity and selectivity.<sup>1,2</sup> Previously, CO<sub>2</sub> reduction was mainly driven by metal thermocatalysts,<sup>3–6</sup> but it was usually performed at high temperature due to the highly stable CO<sub>2</sub> molecule. Electrochemical CO<sub>2</sub> reduction has also been reported, but additional energy is needed and the special reactor limits large scale-production.<sup>5,6</sup> Photocatalytic CO<sub>2</sub> reduction represents a promising way for CO<sub>2</sub> conversion due to it being an energy saving and green process, which uses mild conditions, and has long durability.<sup>7–10</sup> However, the photocatalytic efficiency is still very low because of the poor CO<sub>2</sub> adsorption/activation ability and the easy photoelectron–hole recombination.<sup>11,12</sup> Moreover, such a reaction usually displays low selectivity with the formation of various products like methane, methanol, formaldehyde, formic acid, *etc.* TiO<sub>2</sub> has been frequently employed as in photocatalysis owing to its environmental friendship, easy availability, high activity, and excellent stability.<sup>13</sup> However, TiO<sub>2</sub> can only be activated by UV lights due to its large bandgap

(3.2 eV) and thus cannot sufficiently make use of sunlight.<sup>14</sup> In addition, the radical reaction steps disfavor the selectivity toward the target product. In<sub>2</sub>O<sub>3</sub> can be activated by visible light and also can easily adsorb/activate CO<sub>2</sub> molecules *via* Lewis acid sites, which greatly benefits the photocatalytic CO<sub>2</sub> reduction toward HCOOH.<sup>15,16</sup> But, pure In<sub>2</sub>O<sub>3</sub> exhibits poor activity to generate H atoms through photocatalytic water splitting. The g-C<sub>3</sub>N<sub>4</sub> is a typical visible photocatalyst for efficient water splitting,<sup>17</sup> but could effectively adsorb and activate CO<sub>2</sub> molecules. In addition, both In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> exhibit low activities due to the rapid combination between photoelectrons and holes.<sup>18</sup> Construction of heterojunction structures is frequently used in designing photocatalysts with the low photoelectron–hole recombination rate and the high photocatalytic activity in pollutant-degradation, water splitting, and CO<sub>2</sub> reduction.<sup>19,20</sup> Many efforts have been devoted to improving the photocatalytic CO<sub>2</sub> reduction efficiency.<sup>21–24</sup> Obviously, the combination of In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> could mainly overcome their individual shortcomings in photocatalytic CO<sub>2</sub> reduction. More importantly, the In<sub>2</sub>O<sub>3</sub> displays energy level matching well with the g-C<sub>3</sub>N<sub>4</sub>. Thus, In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunctions can be easily established, which can promote the photoelectron–hole separation to diminish photoelectron–hole recombination, leading to the high quantum efficiency in photocatalysis, which has applied into H<sub>2</sub> evolution, CO<sub>2</sub> reduction and pollutants degradation. Cao *et al.* reported an In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> with enhanced activity in photocatalytic H<sub>2</sub> evolution and CO<sub>2</sub> reduction owing to the heterojunctions between g-C<sub>3</sub>N<sub>4</sub> and In<sub>2</sub>O<sub>3</sub>, which promoted the transfer of photo-generated electrons and thus decreased the

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photoelectron-hole recombination.<sup>25</sup> Non-noble metal like B and S has also been induced in  $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$  to promote photocatalytic efficiency.<sup>26,27</sup> Besides, noble metals like Pt and Pd have been widely applied in catalytic  $\text{CO}_2$  reduction with high activity and selectivity.<sup>28,29</sup> Meanwhile, they could also be used as co-catalysts in photocatalysis to facilitate electron transfer owing to the excellent electric conductivity<sup>30,31</sup> and to activate reactant molecules owing to the low work function.<sup>32</sup>

Herein, we reported for the first time a  $\text{Pt}/\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$  nanocomposite and used as a multifunctional catalyst in photocatalytic  $\text{CO}_2$  reduction under visible light irradiation. The  $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$  was prepared *via* a solvothermal route, while Pt was loaded through a photo-reduced method. The unique structural assemble and the strong interaction between nanoparticle Pt, nanosheet  $\text{In}_2\text{O}_3$ , and porous  $\text{g-C}_3\text{N}_4$ . As a result, the  $\text{Pt}/\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$  exhibited high activity and selectivity to HCOOH owing to the synergetic effects. The  $\text{CO}_2$  conversion TON reached up to  $736.3 \mu\text{mol g}^{-1} \text{h}^{-1}$  at 40 atm and the catalyst exhibited excellent durability, showing good potential in the practical application.

## 2. Experimental

### 2.1 Sample preparation

$\text{In}_2\text{O}_3$  was prepared through a hydrothermal method. In a typical run of synthesis, 6 mmol  $\text{In}(\text{NO}_3)_3$  (Aladdin) was added into a 40 mL aqueous solution, followed by stirring for 10 min to get a clear solution. Then, 24 mmol urea (Aladdin) was added and the solution was continuously stirred for 2 h at room temperature. Subsequently, the solution was transferred into a 50 mL Teflon lined autoclave and was kept at  $140^\circ\text{C}$  for 16 h. The obtained solid product was washed thoroughly by water and ethanol, followed by drying at  $60^\circ\text{C}$  for 12 h. Finally, it was calcined at  $450^\circ\text{C}$  for 2 h to improve the crystallization degree of  $\text{In}_2\text{O}_3$  and remove impurities.

$\text{g-C}_3\text{N}_4$  was prepared by calcination of melamine (Aladdin) in a special reactor at  $500^\circ\text{C}$  for 2 h, followed by calcining at  $520^\circ\text{C}$  for another 2 h until the formation of faint yellow powder.

For preparing  $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ , a certain amount of  $\text{g-C}_3\text{N}_4$  was dispersed into 20 mL aqueous solution containing a certain amount of urea and was stirred for 2 h at room temperature. Meanwhile, a certain amount of indium nitrate was added to another 20 mL aqueous solution and was stirred until transparent. Then, the solution containing  $\text{In}(\text{NO}_3)_3$  was carefully added into the solution containing  $\text{g-C}_3\text{N}_4$  and urea. After being stirred for 2 h, the mixed solution was transferred into a 50 mL Teflon lined autoclave and kept at  $140^\circ\text{C}$  for 16 h. The obtained solid product was washed by water and ethanol, followed by drying at  $60^\circ\text{C}$  for 12 h, and finally, calcining at  $450^\circ\text{C}$  for 2 h in argon atmosphere. The as-received sample was denoted as  $x\text{INCN}$ , where  $x$  refers to the theoretical mass ratio of  $\text{In}_2\text{O}_3$  to  $\text{g-C}_3\text{N}_4$ , which is adjusted by the added amount of  $\text{g-C}_3\text{N}_4$  in mother solution. For comparison, the mechanical mixture of  $\text{In}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  was also prepared and was designated as  $\text{INCN-mix}$ .

The Pt-deposited photocatalysts were prepared by photoreduction of Pt ions. Briefly, 100 mg  $x\text{INCN}$  was dispersed in

10 mL ultra-pure water containing the desired amount of chloroplatinic acid and 1 mL TEOA (Aladdin). Then, the solution was irradiated with LED lamps for 30 min. After separation, the solid product was washed thoroughly with  $\text{H}_2\text{O}$  and ethyl alcohol, followed by drying at  $60^\circ\text{C}$  for 8 h. The as-received sample was marked as  $y\text{Pt-}x\text{INCN}$ , where  $y$  is theoretical mass ratio of Pt to  $x\text{INCN}$ .

### 2.2 Characterization

The real contents of different components in composites were determined by using Inductive Coupled Plasma Emission Spectrometer (ICP, a Jarrel-Asm Atom Scan 2000). The  $\text{N}_2$  adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 instrument in which the specific surface area ( $S_{\text{BET}}$ ) and pore volume ( $V_{\text{p}}$ ) were calculated by applying Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation at a scan rate of  $0.02^\circ \text{s}^{-1}$ . The morphologies were measured on a field emission scanning electronic micrograph (FESEM, JEOL JSM-6380LV) and transmission electronic micrograph (TEM, JEM-2010). Energy-dispersive X-ray spectroscopy (EDS) was also performed by the JSM. The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI PHI5000 VersaProbe using  $\text{Al K}\alpha$  radiation). UV-Vis diffuse reflection spectra (DRS) were obtained on a Shimadzu UV-2450 Spectrophotometer using  $\text{BaSO}_4$  as a reference. The steady-state photoluminescence (PL) spectra were obtained by a Varian Cary-Eclipse 500 fluorometer at an excitation wavelength of 350 nm. Photocurrents were measured using an electrochemical analyzer (CHI660D Instruments) containing a standard three-electrode system in 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution as the electrolyte. The as-prepared sample was used as a working electrode with an active area of  $20 \times 20 \text{ mm}^2$ . The sample was prepared by traditional technology. First, 2 mg PVDF was added into 2 mL DMF solution under ultrasonic condition. Then, 20 mg catalyst was added. The suspension was obtained and treated by ultrasound for another 5 min, followed by dropping onto a FTO piece ( $20 \times 20 \text{ mm}^2$ ), vacuum drying at  $80^\circ\text{C}$  for 8 h, and calcination at  $150^\circ\text{C}$  for 1 h. A Pt piece with an area of  $20 \times 20 \text{ mm}^2$  was used as a counter electrode and a saturated calomel electrode was used as a reference electrode. Each run of the measurements was performed by irradiating with a 300 W Xe lamp for 30 s at an interval of 30 s. Electrochemical impedance spectra (EIS) were obtained under the open-circuit potential condition, with an amplitude of 10 mV and frequency span from 10 kHz to 0.01 Hz.

### 2.3 Activity test

The photocatalytic  $\text{CO}_2$  reduction was performed in a self-made 50 mL quartz reactor. Before reaction, 20 mg catalyst was dispersed in 10 mL ultra-pure water under ultrasonication for 30 min. Then, 1 mL TEOA (Aladdin) was introduced as a sacrificial agent. The suspension was transferred onto a 50 mL quartz reactor with two vents. High purity  $\text{CO}_2$  (99.99%) was introduced into the reactor and bubbled for 0.5 h to evacuate



the air inside the reactor. Then, the reactor was sealed and filled with CO<sub>2</sub> to 1 atm. For each run of reactions, the reaction system was irradiated for 4 h by four 3 W LED lights with the wavelength of 420 nm at a constant temperature of 35 °C and stirring rate of 800 rpm. The gas products were analyzed by a gas chromatography equipped by HP-PLOT Q column connected with the FID detector and TDX-01 connected with TCD detector. The liquid products were detected by ion chromatography (Dionex DX-320) with an analytical column (Dionex IonPac AS19-4 μm Analytical Column).

## 3. Results and discussion

### 3.1 Structural characteristics

As shown in Fig. 1, the XRD patterns revealed that all the samples were present in well crystalline states of In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. The pure g-C<sub>3</sub>N<sub>4</sub> displayed two peaks around 13.1° and 27.4° characteristic of (100) and (002) facets. The In<sub>2</sub>O<sub>3</sub> was present in cubic structure (JCPDS card no. 06-0416) with the characteristic peaks at 30°, 35°, 51°, and 60°, corresponding (111), (100), (110), (622) facets, respectively. All the Pt/In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> showed typical peaks indicative of individual In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, indicating no chemical bonding formed between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. No significant diffraction peaks indicative of Pt were observed in Pt/In<sub>2</sub>O<sub>3</sub>, Pt/g-C<sub>3</sub>N<sub>4</sub>, or Pt-INCIN owing to the low Pt-loading with high dispersion of Pt nanoparticles.

The SEM and TEM images in Fig. 2 demonstrated that the In<sub>2</sub>O<sub>3</sub> was present in nanosheets with an average length of 1–2 μm and widths of 50–100 nm, while the g-C<sub>3</sub>N<sub>4</sub> was present in a lamina structure with uniform porous structure. The 10INCIN composite displayed well dispersion of In<sub>2</sub>O<sub>3</sub> nanosheets onto the g-C<sub>3</sub>N<sub>4</sub>. From 2Pt-10INCIN, we could see very tiny Pt nanoparticles uniformly distributed onto the In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> support. Interestingly, most of Pt nanoparticles were deposited onto the In<sub>2</sub>O<sub>3</sub> nanosheets. This could be easily understood since Pt ions would be more easily reduced on the In<sub>2</sub>O<sub>3</sub> than on the g-C<sub>3</sub>N<sub>4</sub> owing to the presence of Lewis acid sites which favored the adsorption of PtCl<sub>6</sub><sup>2-</sup> ions. The HRTEM image further confirmed that the Pt nanoparticles were embedded on the interface between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in 2Pt-10INCIN. Both In<sub>2</sub>O<sub>3</sub>

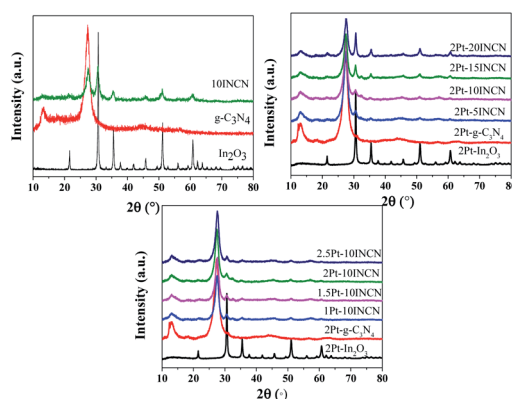


Fig. 1 XRD patterns of pure In<sub>2</sub>O<sub>3</sub>, pure g-C<sub>3</sub>N<sub>4</sub> and their corresponding composites with or without Pt-loading.

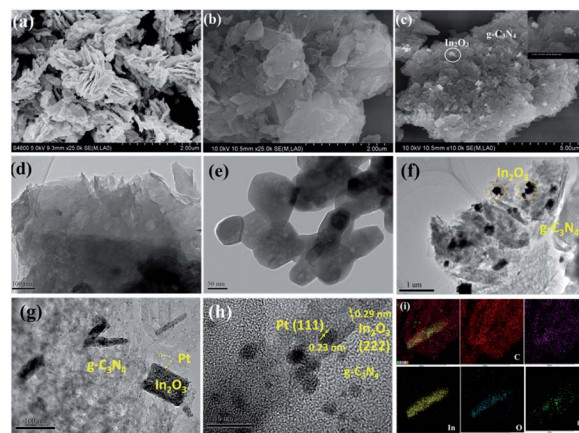


Fig. 2 SEM images of (a) In<sub>2</sub>O<sub>3</sub>, (b) g-C<sub>3</sub>N<sub>4</sub> and (c) 10INCIN. TEM images of (d) g-C<sub>3</sub>N<sub>4</sub>, (e) In<sub>2</sub>O<sub>3</sub>, (f) 10INCIN, and (g) 2Pt-10INCIN. (h) HRTEM image of 2Pt-10INCIN. (i) Mapping images of 2Pt-10INCIN.

and g-C<sub>3</sub>N<sub>4</sub> were present in well-defined crystals, in good accordance with the XRD patterns. The heterojunction was formed between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. The mapping images clarified the existence of In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in 2Pt-10INCIN, together with the uniform distribution of Pt nanoparticles.

The actual In<sub>2</sub>O<sub>3</sub>-contents and Pt-loading in the composite photocatalysts were determined by ICP and expressed in mass percentage (Table S1<sup>†</sup>), which generally matched with the theoretical contents in the mother solution. All samples displayed type-IV N<sub>2</sub> adsorption-desorption isotherms with a hysteresis loop of type H3 characteristic of porous structure (Fig. S1<sup>†</sup>). Based on the N<sub>2</sub> adsorption-desorption isotherms, the surface area, pore size, and pore volume were calculated (Table S2<sup>†</sup>). Although the similar pore volume, the In<sub>2</sub>O<sub>3</sub> exhibited higher surface area and bigger pore size than the g-C<sub>3</sub>N<sub>4</sub> owing to the porous structure constructed layer-by-layer from In<sub>2</sub>O<sub>3</sub> nanosheets. The INCIN exhibited decreased surface area and pore size due to the incorporation of In<sub>2</sub>O<sub>3</sub> nanosheets into the porous g-C<sub>3</sub>N<sub>4</sub>, leading to the close package of In<sub>2</sub>O<sub>3</sub> nanosheets. The pore volume of INCIN greatly increased in comparison with both In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, possibly owing to the formation of new micropores during the co-assembling process of In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. All the Pt-INCIN displayed lower surface area and larger pore size as well as smaller pore volume, suggesting most Pt nanoparticles were embedded into the pore channels constructed layer-by-layer from In<sub>2</sub>O<sub>3</sub> nanosheets. Some micropores were blocked by those Pt nanoparticles, which could account for the increase of average pore size and abrupt decrease of pore volume.

The XPS spectra in Fig. 3 revealed that all the In species were present in In<sup>3+</sup> state, corresponding to the binding energies (BE) of 445.8 eV and 453.4 eV at In 3d<sub>5/2</sub> and 3d<sub>3/2</sub> levels.<sup>33</sup> The negative BE shift suggested the strong interaction between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, in which partial electrons transferred from g-C<sub>3</sub>N<sub>4</sub> to In<sup>3+</sup> due to the d-π feedback. Meanwhile, all the Pt species on In<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and xINCIN exhibited two principal peaks around BE of 71.4 eV and 74.5 eV in Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> energy levels (also see Fig. S2<sup>†</sup>), indicating they were all present



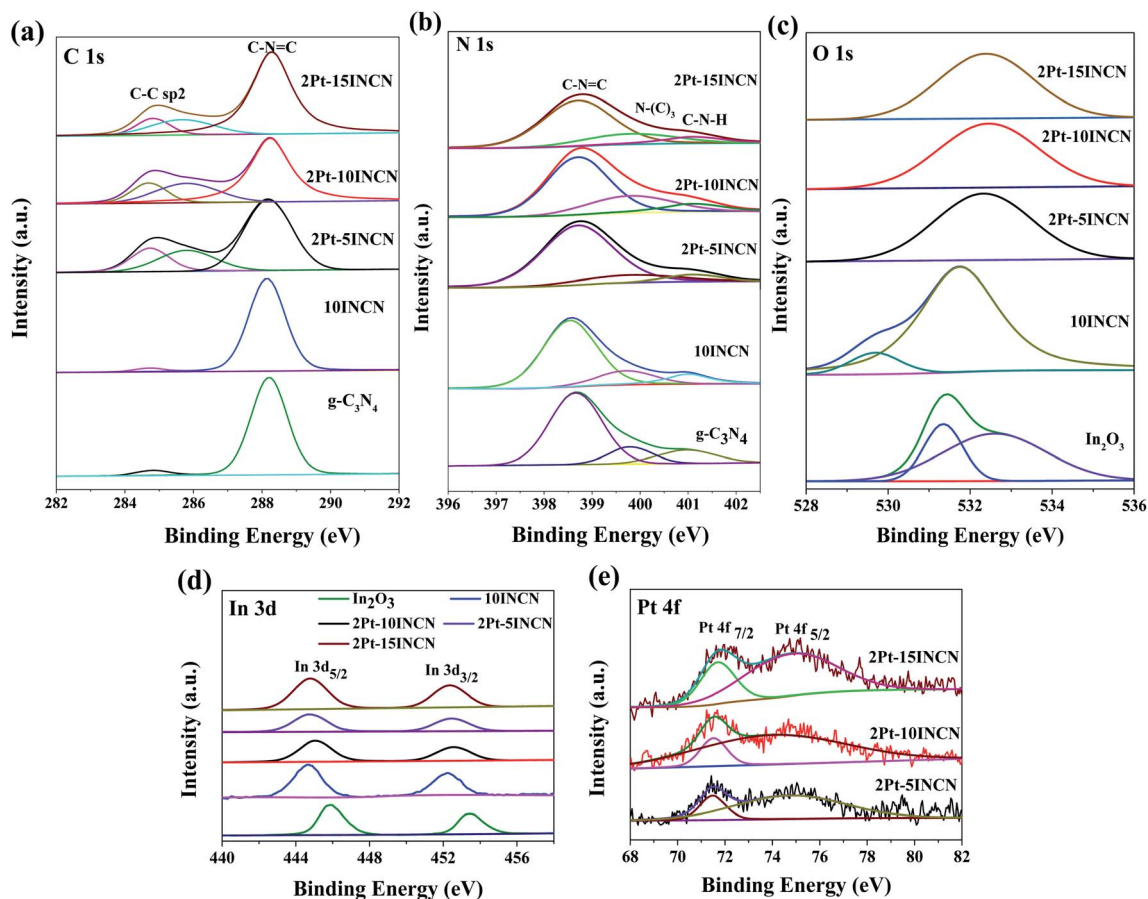


Fig. 3 XPS spectra in (a) C 1s, (b) N 1s, (c) O 1s and (d) In 3d and (e) Pt 4f levels.

in the metallic state.<sup>34</sup> The Pt/In<sub>2</sub>O<sub>3</sub> displayed negative BE shift of Pt and positive BE shift of In<sup>3+</sup>, which further confirmed that most Pt nanoparticles deposited onto In<sub>2</sub>O<sub>3</sub> nanosheets, in which partial electrons transferred from In<sup>3+</sup> to Pt owing to the strong metal-support interaction, taking into account of the higher electronegativity of Pt (2.28) than that of In<sup>3+</sup> (1.78).<sup>32</sup> All the O species were present in O<sup>2-</sup> state. The peak at 531.4 eV was assigned to lattice-oxygen and the peak at 532.5 eV was ascribed to chemisorbed oxygen.<sup>35</sup> After Pt-loading, the BE of lattice-oxygen showed a negative shift owing to the acceptance of partial electrons from metallic Pt. Besides, the well-dispersed Pt nanoparticles on the In<sub>2</sub>O<sub>3</sub> surface promoted the chemisorption of oxygen, leading to the enhanced intensity of the peak around 532.5 eV.<sup>36</sup> The C species in 10INCN were mainly presented in C-N-C coordination, corresponding to the BE at 288.2 eV in C 1s level. The weak shoulder peak at 284.5 eV was ascribed to the sp<sup>2</sup> C-C bond.<sup>37</sup> The N species displayed various states, corresponding to the different binding energies in the N 1s level. The main signal around 398.6 eV corresponded to the N in C-N-C bond, while the shoulder peak at 400.3 eV was ascribed to the N in the N-(C)<sub>3</sub> group.<sup>38</sup> No significant BE shift of either the C or the N was observed, possibly due to the symmetric structure in C-N-C bond.

Due to the In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> are both indirect band semiconductors.<sup>39–42</sup> It is reasonable that  $(\alpha h\nu)^{0.5}$  vs. photon energy

plot was used to estimate band-gap energy of them. From UV-Vis DRS spectra and their corresponding plots of  $(\alpha h\nu)^{1/2}$  vs. photon energy ( $h\nu$ ) (Fig. 4a and S3<sup>†</sup>), together with the calculated energy bandgaps and light absorbance edge wavelength (Table S3<sup>†</sup>), we could see that both In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> could be activated by visible lights. The 5INCN displayed a broader adsorption area with an obvious red-shift in comparison with the pure In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, which could be understood by considering the appearance of some intermediate energy bands owing to the formation of heterojunctions between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. Further increase in the ratio of In<sub>2</sub>O<sub>3</sub> to g-C<sub>3</sub>N<sub>4</sub> (from 5INCN to 20INCN) had no significant influence on the light absorbance edge, suggesting no more heterojunctions formed. Meanwhile, both Pt/In<sub>2</sub>O<sub>3</sub> and Pt/g-C<sub>3</sub>N<sub>4</sub> exhibited red-shift comparing to pure In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, obviously owing to plasma effect from Pt nanoparticles, which could also account for the red-shift of light absorbance by loading Pt onto INCN. However, the change of Pt-loading from 1 wt% to 2 wt% had a very limited effect on the light adsorption edge, suggesting the similar size of Pt nanoparticles, and thus, the increased Pt-loading could only enhance the light adsorption intensity. However, 2.5Pt-10INCN displayed a blue-shift of light absorbance wavelength due to the gathering of Pt nanoparticles, which reduced the plasma effect. All the increasing ratio of In<sub>2</sub>O<sub>3</sub> to g-C<sub>3</sub>N<sub>4</sub> had almost on effect on the light absorbance



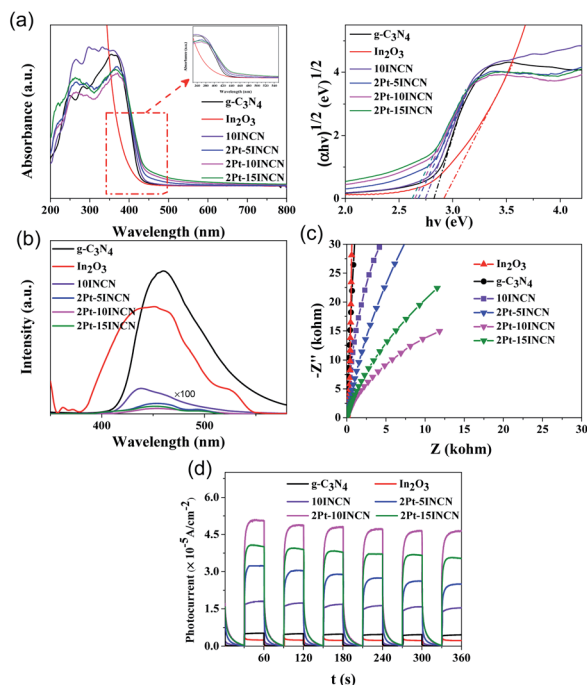


Fig. 4 (a) UV-Vis DRS spectra and their corresponding plots of  $(\alpha h\nu)^{1/2}$  vs. photon energy, (b) steady-state PL spectra at  $\lambda_{\text{ex}}$  of 350 nm, (c) electrochemical impedances, and (d) photocurrent response spectra obtained under irradiation of a 300 W Xe lamp.

wavelength in INCN, it caused remarkable red-shift in 2Pt- $x$ INCN. This could be ascribed to the enhanced plasma effect from Pt nanoparticles at high-content  $\text{In}_2\text{O}_3$  since the above TEM images demonstrated that the Pt ions were preferentially reduced and deposited onto  $\text{In}_2\text{O}_3$  rather than  $g\text{-C}_3\text{N}_4$ .

The steady-state PL spectra obtained at an excited wavelength of 350 nm (Fig. 4b and S4†) displayed an emission peak around 450 nm indicative of the recombination between photoelectrons and holes. The 10INCN exhibited lower intensity compared to  $\text{In}_2\text{O}_3$  and  $g\text{-C}_3\text{N}_4$ , implying the lowest photoelectron-hole combination rate, which could be attributed to the rapid charge transfer through the  $\text{In}_2\text{O}_3\text{-C}_3\text{N}_4$  heterojunctions. With the increase of the  $\text{In}_2\text{O}_3/\text{C}_3\text{N}_4$  ratio up to 10INCN, the PL peak intensity decreased gradually owing to the formation of more  $\text{In}_2\text{O}_3\text{-C}_3\text{N}_4$  heterojunctions, corresponding to the reduced photoelectron-hole combination rate. However, further increase in the  $\text{In}_2\text{O}_3/\text{C}_3\text{N}_4$  ratio resulted in the increasing PL peak intensity due to the presence of more free  $\text{In}_2\text{O}_3$  nanosheets, leading to the enhanced photoelectron-hole combination rate. Loading Pt could greatly decrease the PL peak intensity, corresponding to the efficient inhibition of photoelectron-hole combination, obviously owing to the rapid electron transfer through Pt nanoparticles to separate from holes. The 2Pt-10INCN showed the lowest photoelectron-hole combination rate. This could be further by the electrochemical impedance spectra (Fig. 4c and S5†). The loading of Pt nanoparticles onto  $\text{In}_2\text{O}_3$ ,  $\text{C}_3\text{N}_4$ , and INCN resulted in a significant decrease of arc radius, corresponding to the reduced electric resistance owing to the excellent electric conductivity of

metallic Pt. The 2Pt-10INCN displayed the smallest arc radius, corresponding to the lowest electric resistance. Further increase in the Pt-loading caused an enlarged arc radius corresponding to the enhanced electric resistance, which could attribute to the gathering of Pt nanoparticles.

The photocurrent response spectra (Fig. 4d and S6†) clearly demonstrated that the INCN exhibited higher photocurrent than either the pure  $\text{In}_2\text{O}_3$  or the pure  $g\text{-C}_3\text{N}_4$ , which could attribute to the enhanced light absorbance and decreased photoelectron-hole recombination rate as discussed above. Increasing the  $\text{In}_2\text{O}_3/g\text{-C}_3\text{N}_4$  ratio from 5 to 10 wt% resulted in the enhanced photocurrent intensity. A possible reason was the rapid electron transfer from  $g\text{-C}_3\text{N}_4$  to  $\text{In}_2\text{O}_3$  since  $\text{In}_2\text{O}_3$  was present in well-defined crystals with better electric conductivity than  $g\text{-C}_3\text{N}_4$  in poor crystallization, which might decrease the photoelectron-hole recombination. Further increasing the  $\text{In}_2\text{O}_3/g\text{-C}_3\text{N}_4$  ratio to 15 wt% caused a decrease in photocurrent intensity due to the presence of more free  $\text{In}_2\text{O}_3$  nanosheets. Those free  $\text{In}_2\text{O}_3$  displayed higher photoelectron-hole recombination rate than the  $\text{In}_2\text{O}_3/g\text{-C}_3\text{N}_4$  nanocomposite due to the absence of heterojunctions (Fig. S4a†).<sup>43</sup> Meanwhile, the Pt-INCN showed a higher photocurrent than the INCN owing to the enhanced light absorbance and decreased photoelectron-hole recombination rate as discussed above. The highest photocurrent was observed on the 2Pt-10INCN, corresponding to the highest light absorbance and the lowest photoelectron-hole recombination rate.

### 3.2 Catalytic performances

Controlled experiments (Fig. S7†) demonstrated that only trace  $\text{HCOOH}$  and  $\text{CH}_4$  obtained during  $\text{CO}_2$  reduction on 2Pt-10INCN without light irradiation or  $\text{CO}_2$ , suggesting the  $\text{CO}_2$  reduction was mainly driven by photocatalysis. The addition of  $\text{K}_2\text{Cr}_2\text{O}_7$  as an electron capture agent resulted in an abrupt decrease in  $\text{CO}_2$  conversion efficiency, showing the photoelectrons played a key role in photocatalytic  $\text{CO}_2$  reduction. Meanwhile, it was also found that the  $\text{HCOOH}$  yield greatly decreased without adding TEOA in the reaction system. TEOA was frequently used as a hole capturing agent in photocatalysis,<sup>44</sup> which could consume photo-induced holes from the photocatalyst through its oxidation (see Scheme S1†) and thus could inhibit their recombination with photoelectrons. Therefore, TEOA was a necessary sacrifice agent in the present photocatalytic  $\text{CO}_2$  reduction.

Under UV light irradiation, the 2Pt-10INCN exhibited higher  $\text{HCOOH}$  and  $\text{CH}_4$  yields than that under visible light irradiation (Fig. S8a†) since the UV light could generate more photoelectrons and holes. Taking into account that the sunlight contained only less than 5% UV lights, we still employed the visible light irradiation for driving the photocatalysis to simulate the natural photosynthesis. The 2Pt-10INCN exhibited extremely high selectivity to  $\text{HCOOH}$  in photocatalytic  $\text{CO}_2$ . Only very little  $\text{CH}_4$  could be obtained and no other side-products were detected. With the increase of reaction time to 4 h, the  $\text{HCOOH}$  yield increased rapidly and an only slight increase in  $\text{CH}_4$  yield was observed. However, further increase in the reaction time had no



significant influence on the CO<sub>2</sub> reduction efficiency (Fig. S8b†), indicating the reaction arrived equilibrium point. So, 4 h was used as the reaction time in the following activity tests. Meanwhile, the increase of CO<sub>2</sub> pressure could also greatly promote photocatalytic CO<sub>2</sub> reduction toward HCOOH (see Fig. S8c†). The HCOOH yield could reach up to 736.3 μmol g<sup>-1</sup> h<sup>-1</sup> at 4.0 MPa, which represented a high level in CO<sub>2</sub> conversion in photosynthesis. However, the increasing CO<sub>2</sub> pressure resulted in a rapid increase of the CH<sub>4</sub> yield (see Fig. S8d†), the high cost, and the difficult operation. Thus, we employed the normal CO<sub>2</sub> pressure (1 atm) in the following tests to meet the requirement of industrial production.

Fig. 5 demonstrated that both In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> could be activated by visible lights. Although the In<sub>2</sub>O<sub>3</sub> contained sufficient Lewis acid sites to adsorb CO<sub>2</sub> molecules, it showed very low activity due to its high CB potential (-0.62 V vs. NHE) which could not efficiently generate H atoms by photocatalytic water splitting. The g-C<sub>3</sub>N<sub>4</sub> was active to produce H atoms

photocatalytic water splitting owing to its low CB potential (-1.1 V vs. NHE). However, its adsorption for CO<sub>2</sub> molecules was very poor due to the lack of active sites together with the low surface area, leading to the poor activity of photocatalytic CO<sub>2</sub> reduction. The INCN exhibited higher activity than either the In<sub>2</sub>O<sub>3</sub> or g-C<sub>3</sub>N<sub>4</sub> owing to the cooperation between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> to adsorb CO<sub>2</sub> molecules and produce H atoms. Meanwhile, the INCN contained narrow energy bandgap owing to the presence of intermediate energy bands and thus could be more easily and effectively activated by visible lights. More importantly, the INCN contained enriched heterojunctions between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, which facilitated the electron transfer from the CB of g-C<sub>3</sub>N<sub>4</sub> to that of In<sub>2</sub>O<sub>3</sub>, leading to the lower photoelectron-hole recombination rate. Although the pure In<sub>2</sub>O<sub>3</sub> exhibited very poor activity in photocatalytic CO<sub>2</sub> reduction, the Pt/In<sub>2</sub>O<sub>3</sub> exhibited remarkable enhancement on the activity since the metallic Pt could act as a co-catalyst to produce H atoms by collecting electrons from In<sub>2</sub>O<sub>3</sub> semiconductor and plasma during photocatalytic water splitting.<sup>45</sup> More importantly, the Pt/In<sub>2</sub>O<sub>3</sub> displayed much higher selectivity to HCOOH than the pure In<sub>2</sub>O<sub>3</sub>, which could be understood based on a plausible reaction pathway in photocatalytic CO<sub>2</sub> reduction (Scheme S1†). The noble-metal Pt was a typical metal catalyst with low work function to activate H atoms while the In<sub>2</sub>O<sub>3</sub> could efficiently adsorb CO<sub>2</sub> molecules owing to the presence of enriched Lewis acid sites.<sup>46,47</sup> The Lewis acid sites also enhanced the interaction between Pt and In<sub>2</sub>O<sub>3</sub>, which induced the unique bridged co-adsorption model of the CO<sub>2</sub> molecule on Pt and In<sub>2</sub>O<sub>3</sub>. Such co-adsorbed CO<sub>2</sub> molecules favored the reaction with active H atoms to HCOO\*,<sup>48-50</sup> which was a key intermediate in determining the selectivity to HCOOH.<sup>16</sup> Besides, the metallic Pt nanoparticles also promoted the activation of In<sub>2</sub>O<sub>3</sub> by visible lights owing to the plasma effect and facilitated the electron transfer to diminish photoelectron-hole recombination, which could further promote the photocatalytic CO<sub>2</sub> reduction. Similarly, the Pt/g-C<sub>3</sub>N<sub>4</sub> also exhibited higher activity and selectivity than the g-C<sub>3</sub>N<sub>4</sub>, which could also be explained based on the above discussions. It was noted that the Pt-loading exhibited much weaker promoting effect on the HCOOH production in g-C<sub>3</sub>N<sub>4</sub> than that in In<sub>2</sub>O<sub>3</sub>. A possible reason was that the g-C<sub>3</sub>N<sub>4</sub> could not effectively adsorb CO<sub>2</sub> molecules due to the absence of Lewis acid sites. Although the presence of Pt could greatly enhance the production of H atoms, no enough adsorbed CO<sub>2</sub> molecules could be activated and subsequently reacted with those H atoms. Meanwhile, the Pt/g-C<sub>3</sub>N<sub>4</sub> displayed poor interaction between Pt and g-C<sub>3</sub>N<sub>4</sub> due to the absence of Lewis acid sites, leading to the low number of bridge-coadsorbed CO<sub>2</sub> molecules on both Pt and g-C<sub>3</sub>N<sub>4</sub>, which could account for the lower selectivity to HCOOH in comparison with the Pt/In<sub>2</sub>O<sub>3</sub>.

As expected, the Pt-loading onto INCN also greatly enhanced the activity and selectivity in photocatalytic CO<sub>2</sub> reduction, which could also be accounted by considering various Pt-functions discussed above. Interestingly, the Pt-INCN exhibited a much stronger promoting effect than either the Pt/In<sub>2</sub>O<sub>3</sub> or Pt/g-C<sub>3</sub>N<sub>4</sub> possibly owing to the enhanced role of heterojunctions. The presence of metallic Pt nanoparticles facilitated

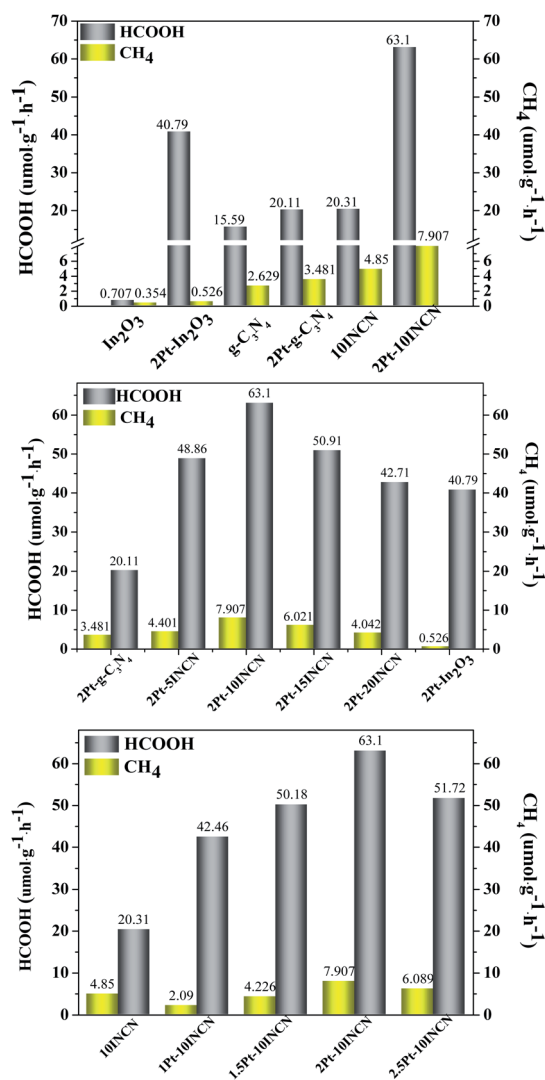


Fig. 5 HCOOH and CH<sub>4</sub> yields on different catalysts. Reaction conditions: Four 3 W LED (420 nm), 1 atm CO<sub>2</sub>, 20 mg catalyst, 10 mL H<sub>2</sub>O, 1 mL TEOA, 35 °C, 4 h.



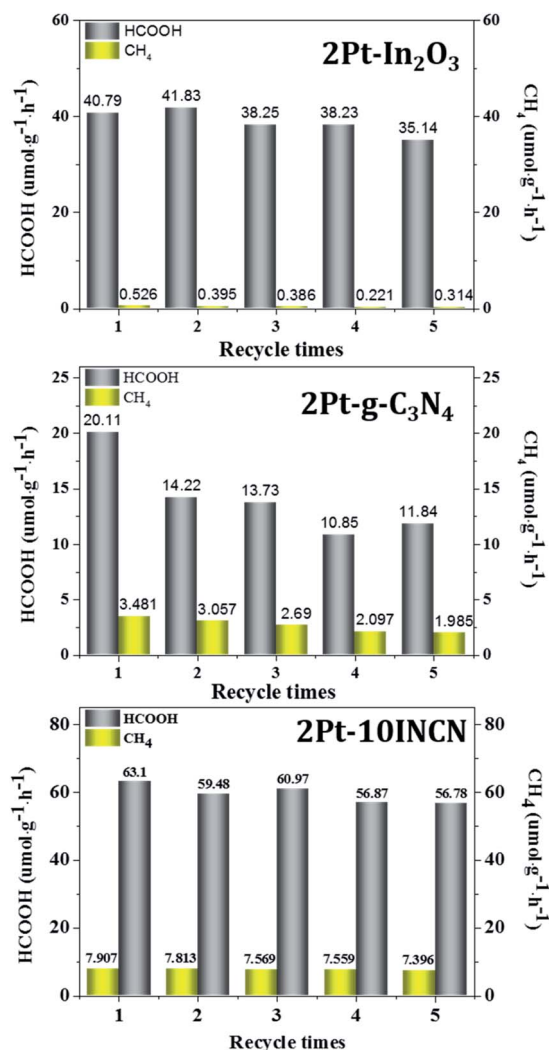


Fig. 6 Recycling test of 2Pt-In<sub>2</sub>O<sub>3</sub>, 2Pt-g-C<sub>3</sub>N<sub>4</sub> and 2Pt-10INCN. Reaction conditions are given in Fig. 5.

electron-transfer from In<sub>2</sub>O<sub>3</sub> to g-C<sub>3</sub>N<sub>4</sub> and hole-transfer from g-C<sub>3</sub>N<sub>4</sub> to In<sub>2</sub>O<sub>3</sub>, which could greatly diminish photoelectron-hole recombination (see Scheme S1†). By fixing the Pt-loading at 2 wt%, the Pt-INCN showed a rapid increase in HCOOH yield while only very slight increase in CH<sub>4</sub> yield with the increasing ratio of In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> up to 10 wt%. This could be ascribed to the enhanced adsorption of CO<sub>2</sub> molecules by In<sub>2</sub>O<sub>3</sub>. Besides, the increase of heterojunctions played a key role in promoting the photocatalytic CO<sub>2</sub> reduction by inhibiting photoelectron-hole recombination. However, further increase of the In<sub>2</sub>O<sub>3</sub>-content caused slight decrease in the HCOOH yield due to the appearance of free In<sub>2</sub>O<sub>3</sub> nanosheets. Such a free In<sub>2</sub>O<sub>3</sub> displayed higher photoelectron-hole recombination rate than the In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite due to the absence of heterojunctions.<sup>51</sup> In addition, since the In<sub>2</sub>O<sub>3</sub> favored the photocatalytic reduction of PtCl<sub>6</sub><sup>2+</sup>, some of Pt nanoparticles would deposit onto the free In<sub>2</sub>O<sub>3</sub> nanosheets, leading to the reduced promoting effect on the role of heterojunctions between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

By fixing the In<sub>2</sub>O<sub>3</sub>-content at 10 wt%, the Pt-10INCN exhibited increasing HCOOH yield and CH<sub>4</sub> yield with the increase of Pt-loading up to 2 wt% since more Pt nanoparticles would enhance the plasma effect, the activity for activating H atoms and CO<sub>2</sub> molecules, the electron transfer ability to inhibit photoelectron-hole recombination. However, further increase in the Pt-loading caused slight decrease in either the HCOOH yield or the CH<sub>4</sub> yield due to the gathering of Pt nanoparticles to reduce above promoting effects. Besides, the large Pt nanoparticles may also block the pore channels, leading to an abrupt decrease in surface area (see Table S2†). The 2Pt-10INCN exhibited the highest HCOOH yield (63.1 μmol g<sup>-1</sup> h<sup>-1</sup>) at the normal pressure of CO<sub>2</sub> and room temperature. In addition, the 2Pt-10INCN exhibited much higher activity than the 2Pt-10INCN-mix obtained by mechanical mixing In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> (see Fig. S7†), obviously due to the absence of heterojunctions and the synergetic effect between In<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

The lifetime is also a key parameter to determine the practical application of a photocatalyst. As shown in Fig. 6, both 2Pt-10INCN and 2Pt-In<sub>2</sub>O<sub>3</sub> could be used repetitively for more than 5 times without a significant decrease in their activities. The slight decrease might be caused by the loss of photocatalysts during separation and wash processes. However, the 2Pt-g-C<sub>3</sub>N<sub>4</sub> showed a rapid decrease in photocatalytic activity during the recycling test. The XRD patterns (Fig. S9†) revealed that, similar to 2Pt-In<sub>2</sub>O<sub>3</sub> and 2Pt-g-C<sub>3</sub>N<sub>4</sub>, no significant change in the structure of 2Pt-10INCN was observed, indicating the excellent stability during the reaction process. Meanwhile, ICP analysis demonstrated no significant Pt leaching occurred on either 2Pt-10INCN or 2Pt-In<sub>2</sub>O<sub>3</sub> occurred during the reaction, which could be attributed to the strong adsorption of Pt nanoparticles onto In<sub>2</sub>O<sub>3</sub> owing to the presence of Lewis acid sites. However, the 2Pt-g-C<sub>3</sub>N<sub>4</sub> showed Pt leaching during the reaction process, leading to a decrease in photocatalytic activity.

## 4. Conclusions

We developed a Pt/In<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> multifunctional catalyst by controlling the assembling method. This catalyst exhibited high activity and selectivity to HCOOH during visible-light-driven photocatalytic CO<sub>2</sub> reduction owing to the synergetic effects in producing H atoms *via* water splitting, adsorbing/activating CO<sub>2</sub> molecules, and inhibiting photoelectron-hole recombination by accelerating electron transfer and forming heterojunctions. Besides, it also displayed a long lifetime owing to the high structural stability and the strong interaction to inhibit Pt leaching. This work supplied a promising way for designing new catalysts with multiple functions for photocatalytic CO<sub>2</sub> reduction at normal pressure and room temperature with a high yield of target products.

## Conflicts of interest

There are no conflicts to declare.



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