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### 1. Introduction

Methyl benzoate is an important ester compound extensively applied as a valuable intermediate in organic synthesis, solvents, and edible and chemical essentials for daily use in chemical industries.<sup>1</sup> The traditional synthesis method of methyl benzoate is *via* the esterification of benzoic acid with methanol using acids as catalysts,<sup>2</sup> but the highly corrosive nature of acid catalysts to the equipment, the harsh reaction conditions and the serious environmental pollution inhibit their applications. Besides, at present, reacting an acid halide or an acid anhydride with methanol is also a major method to synthesize methyl benzoate, but the additives required for the reaction lead to the low selectivity of the ester and a large amount of by-products.<sup>3</sup> However, alcohol is more readily available and inexpensive than benzoic acid and acid halide as the material to synthesize methyl benzoate. In addition, the transition metal-catalyzed

## The synergistic role of the support surface and Au–Cu alloys in a plasmonic Au–Cu@LDH photocatalyst for the oxidative esterification of benzyl alcohol with methanol<sup>†</sup>

Xiaoyu Wang, <sup>b</sup><sup>ab</sup> Ruiyi Wang, <sup>b</sup>\*<sup>a</sup> Jie Wang, <sup>b</sup><sup>ab</sup> Chaoyang Fan<sup>ac</sup> and Zhanfeng Zheng <sup>\*ab</sup>

Layered double hydroxide-supported Au–Cu alloy nanoparticles (NPs) were found to be highly efficient catalysts for the oxidative esterification of benzyl alcohol with methanol in the presence of molecular oxygen under visible-light irradiation to prepare methyl benzoate. Here, we report that alloying small amounts of copper into gold nanoparticles can increase the ability to activate oxygen molecules to  $O_2^{\bullet-}$  radicals and display greater charge heterogeneity to promote the cleavage of the C–H bond of benzyl alcohol molecules by reinforcing the coordination of the intermediate with unsaturated metal active sites due to the LSPR effect of alloy NPs, which is the rate-limiting step of the reaction. Besides the Au–Cu alloy NPs, the support also played a pivotal role in the catalytic process. The support with the presence of acid–base pairs, in which the basic sites served as the reactant molecule adsorption sites to provoke the intermediate formation and the acidic sites promoted the recovery of the support surface, showed better performances by affecting the overall reaction rate completely. Moreover, applying this photocatalyst in the cross-esterification of aromatic alcohols and aliphatic alcohols displayed excellent yields.

cross-coupling reaction of halogenated aromatic hydrocarbons with methanol is another direct route for the synthesis of methyl benzoate. However, the high temperature and pressure required for the reaction result in high energy consumption and environmental pollution,<sup>4</sup> which inspired us to explore greener heterogeneous catalytic processes for the oxidative esterification of benzyl alcohol to methyl benzoate. Supported Au catalysts have been reported to be efficient for the direct oxidative esterification of benzyl alcohol and other aldehydes or alcohols with methanol to give the corresponding esters.<sup>5–9</sup> However, the conversion or product selectivity is typically low and the reaction needs to be completed at a high temperature or in a long reaction time. Miyamura et al. reported that using polymerincarcerated gold nanoclusters (PI-Au) in catalyzing the aerobic oxidation of alcohols to methyl esters needed nearly 24 h to achieve a TON of 540.8 In addition, Zhao et al. reported the use of an Au/meso-y-Al<sub>2</sub>O<sub>3</sub> catalyst for the selective aerobic oxidation of alcohols at a reaction temperature of 80 °C to achieve a TOF of 145.8 h<sup>-1</sup>.<sup>10</sup> The modification of Au catalysts with other noble metals to form alloy NPs can improve the activity of the reaction.<sup>11,12</sup> For example, Wang et al. found that by alloying small amounts of palladium into gold nanoparticles, the conversion of benzyl alcohol greatly increased from 3.6% for Au/LDH and 1.5% for Pd/LDH to 91.1% for Au-Pd/LDH.<sup>13</sup> However, supported Au-Cu alloy catalysts applied in oxidation



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<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, P. R. China.

E-mail: wangruiyi@sxicc.ac.cn, zfzheng@sxicc.ac.cn

<sup>&</sup>lt;sup>b</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

<sup>&</sup>lt;sup>c</sup> Taiyuan University of Technology, Taiyuan, 030024, P. R. China

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reactions are limited as the surface Cu atoms can be easily oxidized by O214 and hence, the alloying effect is eliminated considerably. Sugano et al. found that the visible-light irradiation of Au-Cu alloy NPs during the reaction can suppress the oxidation of surface Cu atoms and successfully maintain the alloying effect<sup>15</sup> due to the localized surface plasmon resonance (LSPR) of noble metal NPs, which can strongly absorb visible light. In particular, alloying small amounts of copper into gold nanoparticles may change the electronic state of metal nanoparticles and introduce inter-metallic interactions, which can further increase the ability to activate the reactants. As is reported, the synergistic electron effect in Au-Pd alloys exists because of the electron transfer from Pd to Au atoms, which can enhance the adsorption ability of metal atoms for oxygen molecules and activate them to form  $O_2^{\bullet-}$  radicals;<sup>13</sup> thus, the supported Au–Cu alloy NP catalysts applied in the oxidative esterification of benzyl alcohol under visible-light irradiation have attracted research interest.

Moreover, the traditional supports of noble metal catalysts generally involving Al<sub>2</sub>O<sub>3</sub>,<sup>5</sup> TiO<sub>2</sub>,<sup>6</sup> SiO<sub>2</sub>,<sup>7</sup> polymers,<sup>8</sup> MOFs<sup>16</sup> and hydrotalcite<sup>9,17-19</sup> for the oxidative esterification of alcohols or aldehydes have been reported. Layered double hydroxides (LDHs) are synthetic or natural crystalline clays that consist of brucite-like (Mg(OH)<sub>2</sub>) layers of edge-sharing MO<sub>6</sub> octahedra, in which some divalent cations such as  $Mg^{2+}$  are substituted by trivalent cations; these are characterized by the presence of acid-base pairs, and these pairs can facilitate the adsorption of reactants and intermediate molecules. According to Feng and co-workers, in the MgAl-LDH-supported Au-Pd alloy NP-catalyzed benzyl alcohol oxidation reaction, the acid sites of the MgAl-LDH support were responsive toward the improvement in catalytic activity, while the basic sites give rise to high selectivity; however, this reaction needs to be conducted at 140 °C.12 Thus, the use of milder conditions for the oxidative esterification of benzyl alcohol is rarely reported.

Herein, we described a visible-light-driven process for the oxidative esterification of benzyl alcohol with methanol, where molecular oxygen was used as the oxidant and high conversion and product selectivity were obtained under much milder conditions over an LDH-supported Au–Cu NP photocatalyst. In this catalyst, fused Au with Cu NPs increased the ability to activate the oxygen molecules to  $O_2^{\bullet-}$  radicals and showed greater charge heterogeneity to promote the cleavage of the C–H bond of benzyl alcohol molecules due to the LSPR effect of alloy NPs; this could drive the rate-limiting step of the reaction under the premise that the support sites remained the same, and the acid–base pairs of the support played pivotal roles in the adsorption of reactant molecules to completely drive the overall reaction system.

### 2. Experimental

#### 2.1 Preparation of catalysts MgAl-LDHs

Layered double hydroxides were prepared using a sol-gel process following the established procedures and were denoted as MgAl-LDHs.<sup>20,21</sup> Then, the LDHs were calcined at 450 °C

(heating rate 10  $^{\circ}$ C min<sup>-1</sup>) in dry air for 8 h, yielding mixed oxides denoted as MgAl-LDO.

#### 2.2 Au-Cu@MgAl-LDH photocatalysts

The Au–Cu@MgAl-LDH catalyst was prepared using an impregnation–reduction method. MgAl-LDO powder (0.5 g) was placed in a beaker; then, HAuCl<sub>4</sub> (6.6 ml, 0.01 M) and Cu(NO<sub>3</sub>)<sub>2</sub> (3.3 ml, 0.01 M) aqueous solutions were added under magnetic stirring. The aqueous solution of lysine (3 ml, 0.1 M) was then added dropwise and vigorously stirred for 30 min and the pH was 8–9. Then, the freshly prepared aqueous solution of NaBH<sub>4</sub> (2 ml, 0.35 M) was added dropwise. After stirring for 24 h at room temperature, the solid was washed by deionized water (twice) and ethanol (once). Finally, the photocatalyst was obtained by centrifugation (3000 rpm) and drying at 60 °C in a vacuum oven for 12 h. All the other catalysts were prepared *via* the same method with different quantities of HAuCl<sub>4</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solutions.

#### 2.3 Characterization of catalysts

Powder X-ray diffraction (XRD) was performed on a Bruker D8 Advanced diffractometer operating with Cu Ka radiation  $(\lambda = 1.5405 \text{ Å})$ . The morphology was studied using transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained on USA Thermo ESCALAB 250 with a monochromatized Al Kα line source (200 W). The binding energy correction was referenced to C 1s peaks (284.8 eV) arising from surface hydrocarbons. The nitrogen adsorption isotherms were measured at −196 °C on a TriStar II 3020 volumetric adsorption analyzer. Prior to the measurement, all the samples were degassed under evacuation at 150 °C for 10 h. The surface area was calculated from the adsorption branch by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was obtained by desorption isotherms using the Barret-Joyner-Halender (BJH) method. Fourier transform infrared spectroscopy (FTIR) was performed using a Bruker Tensor II spectrometer with KBr pellets. The UV-vis diffuse reflectance spectra (DRS) were observed on a Hitachi UV-3900 UV-vis-NIR spectrophotometer. The actual total metal loadings and the Au/ Cu molar ratios of various Au-Cu@MgAl-LDH samples were determined by an inductively coupled plasma (ICP) spectrometer on a Thermo iCAP6300 instrument.

#### 2.4 Catalytic reactions

Typically, the photocatalytic experiments were carried out in an oxygen atmosphere at the required temperature. The reaction system consisted of a catalyst (10 mg), benzyl alcohol (0.5 mmol) in methanol (5 ml) and  $K_2CO_3$  (0.2 mmol). The incident light source used was a Xenon lamp at a UV cut-off wavelength below 420 nm. The liquid products were analyzed using Shimadzu 2014C GC equipped with a WondaCap 5 column after centrifugal separation of the catalyst. The identity of the products was established by the comparison of the retention times of authentic samples and also by NMR spectroscopy. The single-coloured LEDs (purple, blue, green and red) were also used as irradiation

sources to investigate the influence of light wavelength on the photocatalytic activity.

In order to strictly avoid the exposure of the reaction to light, the quartz reaction bottle was covered with an aluminium foil. The reaction temperature under irradiation was maintained the same as that in the dark to make sure that the comparison is meaningful.

#### 2.5 Calculation details of turnover frequency

Turnover frequency (TOF), the number of converted molecules per active site and second, is calculated on the basis of the total loadings of Au (there was no catalytic activity with monometallic Cu), *i.e.*, TOF =  $(m_{BA} \times X_{BA}/M_{BA})/(m_{cat} \times w_{Au}\% \times t/M_{Au})$ , where  $m_{BA}$  is the mass of benzyl alcohol (in g) loaded in the reactor,  $X_{BA}$  is the conversion of benzyl alcohol (%), and  $M_{BA}$  is the molar mass of benzyl alcohol;  $m_{cat}$  is the mass of the catalyst loaded (g) in the reactor,  $w_{Au}$ % is the loading mass of Au per gram LDH-supported Au–Cu alloy NP photocatalyst (%),  $M_{Au}$  is the molar mass of Au and *t* is the reaction time (h).

#### 2.6 Calculation details of apparent quantum yield (AQE)

AQE =  $[(N_{\text{light}} - N_{\text{dark}})/(\text{the number of incident photons})] \times 100\%$ , where  $N_{\text{light}}$  and  $N_{\text{dark}}$  are the numbers of products formed under irradiation and in the dark, respectively.

### 3. Results and discussion

#### 3.1 Photocatalytic performance

LDH-supported Au-Cu alloy NP photocatalysts with various Au/ Cu ratios were synthesized (Au1Cu@Mg3Al-LDHs, Au2Cu@ Mg<sub>3</sub>Al-LDHs, and Au<sub>3</sub>Cu@Mg<sub>3</sub>Al-LDHs) (Table 1, entries 1-3) to probe their catalytic activities in the oxidative esterification of benzyl alcohol with methanol to give methyl benzoate in the presence and absence of light. It was indicated that the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH catalyst (entry 1) exhibited optimal catalytic activity with 97.0% conversion of benzyl alcohol, 99.4% selectivity to methyl benzoate and a turnover frequency (TOF) of 172.8  $h^{-1}$ at 30 °C for 3 h under visible-light irradiation, which were much higher than those in the dark. The catalytic activities of the monometallic Au catalyst and the mixture of monometallic Au and Cu catalysts (entries 4 and 6) were obviously lower than that of the alloy NP catalyst, and there was no catalytic activity while using monometallic Cu and supports (Mg<sub>3</sub>Al-RE, Mg<sub>3</sub>Al-LDHs and Mg<sub>3</sub>Al-LDO; entries 5, 7-9) as the catalysts. It was concluded that alloying the two metals could further enhance the catalytic activity. Due to the excellent performance, Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs were chosen as the primary materials for the following study. Then, the activation energies of light-driven and thermal-driven reactions were calculated according to the Arrhenius equation

| Table 1 | Table 1         Photocatalytic oxidative esterification of benzyl alcohol with methanol <sup>a</sup> |                                   |   |                                       |              |                       |   |  |  |  |
|---------|--|-----------------------------------|---|---------------------------------------|--------------|-----------------------|---|--|--|--|
|         | CH <sub>2</sub> C  | РН<br>+ CH <sub>3</sub> OH —<br>К | Photocatalyst/hv<br>22CO3, O2, 30 °C, 3 | • OCH <sub>3</sub> + H <sub>2</sub> O |              |                       |   |  |  |  |
|         |  |                                   |   |                                       |              |                       |   |  |  |  |
| Entry   | Catalyst   | Au                                | Cu                                      | Light source                          | Conv. (%)    | Sel. <sup>c</sup> (%) | $\operatorname{TOF}^{d}\left(\mathrm{h}^{-1} ight)$ |  |  |  |
| 1       | Au2Cu@Mg3Al-LDHs   | 1.89                              | 0.27                                    | Visible                               | 97.0         | 99.4                  | 172.8   |  |  |  |
| 2       | Au <sub>1</sub> Cu@Mg <sub>3</sub> Al-LDHs   | 0.62                              | 0.21                                    | Visible                               | 61.3<br>17.4 | 97.0<br>73.2          | 93.6  |  |  |  |
| 3       | Au <sub>3</sub> Cu@Mg <sub>3</sub> Al-LDHs   | 2.32                              | 0.25                                    | Dark<br>Visible                       | 14.5<br>74.8 | 63.1<br>98.6          | 75.6<br>100.8                                       |  |  |  |
| 4       | Au@Mg <sub>3</sub> Al-LDHs   | 1.78                              | _                                       | Dark<br>Visible                       | 42.7<br>43.8 | 94.2<br>91.3          | 57.6<br>79.2  |  |  |  |
| 5       | Cu@Mg <sub>3</sub> Al-LDHs   | _                                 | 0.24                                    | Dark<br>Visible                       | 25.8         | 81.3<br>0             | $\begin{array}{c} 46.8 \\ 0 \end{array}$            |  |  |  |
| 6       | Au@Mg <sub>3</sub> Al-LDHs + Cu@Mg <sub>3</sub> Al-LDHs <sup>e</sup>                                 | _                                 | _                                       | Dark<br>Visible                       | 0<br>7.9     | 0<br>38.2             | _0  |  |  |  |
| 7       | Mg <sub>3</sub> Al-LDO-RE <sup>f</sup>   | _                                 | _                                       | Dark<br>Visible                       | 9.5<br>0     | 32.8<br>0             | _   |  |  |  |
| 8       | Mg <sub>3</sub> Al-LDHs  | _                                 | _                                       | Dark<br>Visible                       | 0<br>0       | 0<br>0                | _   |  |  |  |
| 9       | Mg <sub>3</sub> Al-LDO   | _                                 | _                                       | Dark<br>Visible                       | 0<br>0       | 0<br>0                | _   |  |  |  |
| 10      | Au2Cu@Mg3Al-LDHsg  | 1.89                              | 0.27                                    | Dark<br>Visible                       | 0<br>90.2    | 0<br>98.4             | _   |  |  |  |
| 11      | h  | _                                 | _                                       | Dark<br>Visible                       | 58.4<br>4.6  | 93.8<br>0             | _   |  |  |  |
|         |  |                                   |   | Dark                                  | 3.6          | 0                     |   |  |  |  |

<sup>*a*</sup> Reaction conditions: photocatalyst, 10 mg; benzyl alcohol, 0.5 mmol; methanol, 5 ml;  $K_2CO_3$ , 0.2 mmol;  $O_2$ , atmospheric pressure; reaction temperature, 30 °C; reaction time, 3 h; light intensity (cut-off wavelength of 420 nm of Xe lamp), 0.5 W cm<sup>-2</sup>. The conversion and selectivity were calculated from the reactant converted and the product formed, as measured by gas chromatography (GC). <sup>*b*</sup> ICP analysis results. <sup>*c*</sup> The <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra of the product (methyl benzoate) are shown in Fig. S3 and S4 (ESI), respectively; it was separated by the distillation of the reaction solution. <sup>*d*</sup> Turnover frequency (TOF), the number of benzyl alcohol molecules converted to methyl benzoate per active site and second, is estimated on the basis of total Au atoms (ESI). <sup>*e*</sup> Au@Mg<sub>3</sub>Al-LDHs and Cu@Mg<sub>3</sub>Al-LDHs were mechanically mixed in a mortar according to  $n(Au): n(Cu) = 1:1.^{f}$  Reconstruction of Mg<sub>3</sub>Al-LDHs. <sup>*g*</sup> Without K<sub>2</sub>CO<sub>3</sub>, reaction temperature, 55 °C; reaction time, 18 h. <sup>*h*</sup> No catalyst, only K<sub>2</sub>CO<sub>3</sub> was added; reaction temperature, 55 °C; reaction time, 18 h.



Fig. 1 (a) Spectrum showing photocatalytic action for the oxidative esterification of benzyl alcohol using Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH photocatalyst under singlecoloured LED lights. The light-absorption spectrum (left axis) is the DR-UV/vis spectrum of the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH catalyst (black curve). (b) Dependence of the catalytic activity of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH photocatalyst for the oxidative esterification of benzyl alcohol with methanol on the intensity of irradiation. The light contribution =  $[(Y_{light} - Y_{dark})/Y_{light}] \times 100\%$ , where  $Y_{light}$  and  $Y_{dark}$  are the product yields under irradiation and in the dark, respectively. Reaction conditions: photocatalyst, 10 mg; benzyl alcohol, 0.5 mmol; methanol, 5 ml; K<sub>2</sub>CO<sub>3</sub>, 0.2 mmol; O<sub>2</sub>, atmospheric pressure; reaction temperature, 30 °C; reaction time, 3 h.

shown in Fig. S1 (ESI<sup>†</sup>); the values were found to be 105.9 and 115.1 kJ mol<sup>-1</sup>, respectively. This means that light energy can facilitate the reaction by reducing the activation energy. The catalyst activity of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs remained stable (Fig. S2a, ESI<sup>†</sup>) and a slight decline in activity during the cycling experiment may be due to the oxidation of a small amount of Cu during the catalytic cycle process (Fig. S2f, ESI<sup>†</sup>). No obvious agglomeration of the alloy NPs appeared (Fig. S2b and c, ESI<sup>†</sup>); the Cu content and the structure showed no obvious change (Fig. S2d and e, ESI<sup>†</sup>) after being reused for five cycles.

In the control experiment, the dependence of photocatalytic activity on wavelengths with the irradiation intensity maintained constant was studied (Fig. 1a). The apparent quantum yield (AQE) of the reaction is closely related to the irradiation wavelength. Moreover, the highest yield is achieved under irradiation at the wavelength where alloy NPs have the most intense absorption (527 nm). It can be deduced that the LSPR effect of the alloy NPs makes a primary contribution to photooxidative esterification. Moreover, the relationship between the photocatalytic activity and the incident light intensity was studied, as shown in Fig. 1b. When the irradiance was  $0.2 \text{ W cm}^{-2}$ , the light contribution to the reaction was only 6.7% and when the irradiance increased to 0.5 W cm<sup>-2</sup>, a 35% yield of methyl benzoate was obtained. Hence, it was concluded that the methyl benzoate yield increased with the increase in the irradiation intensity, and the contribution of irradiation to the overall reaction rate was greater at a higher intensity; this indicates that a higher irradiation intensity can provide more light-excited electrons to drive the reaction by facilitating the cleavage of the C-H bond of the reactant molecules in a photocatalytic process, which is the rate-limiting step of the reaction.<sup>11,22–24</sup>

#### 3.2 Alloy effect

To confirm the formation of Au–Cu alloy NPs, transmission electron microscopy (TEM) images of the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH



Fig. 2 (a) TEM image of the  $Au_2Cu@Mg_3Al-LDH$  sample. (b) Particle size distribution of the NPs based on the statistical analysis of TEM images. (c) HR-TEM image of an alloy particle. (d) XPS profiles of Au and Cu species in  $Au_2Cu@Mg_3Al-LDH$  sample.

sample were obtained. It was shown that the alloy NPs were distributed evenly on the LDH surface (Fig. 2a), and the mean size of the alloy NPs was approximately 3-4 nm (Fig. 2b). The high-resolution TEM (HR-TEM) images reveal the atomic lattices of Au-Cu alloy NPs (Fig. 2c). The lattice fringe spacing of 0.22 nm corresponds to the interplanar distance of the (111) planes of the Au-Cu alloy.<sup>25</sup> The characterization results confirmed the formation of Au-Cu alloy NPs. The light absorption characterization of the Au2Cu@Mg3Al-LDH sample provided by the UV-vis spectra (Fig. S5, ESI<sup>†</sup>) also proved alloying because a red shift in the band at 527 nm due to the LSPR effect was observed for the Au-Cu alloy NP sample compared to that for the monometallic Au NP sample (Au<sub>2</sub>@Mg<sub>3</sub>Al-LDHs, 509 nm).<sup>26</sup> Besides, the Mg<sub>3</sub>Al-LDH support itself could not contribute to the photocatalytic activity because it exhibited weak absorption at visible light wavelengths above 400 nm, as shown in Fig. S5 (ESI<sup>+</sup>). In contrast, the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH sample displayed strong absorption in the visible region of the spectrum, indicating that Au2Cu@MgAl-LDHs could utilize most of the irradiation energy delivered by the solar spectrum. To further characterize the electronic state of Au-Cu alloy NPs on the support, X-ray photoelectron spectroscopy (XPS) measurements of the Au<sub>2</sub>Cu@ Mg<sub>3</sub>Al-LDH sample were obtained (Fig. 2d), which also evinced the incorporation of the Au-Cu alloy units onto the surface of the Mg<sub>3</sub>Al-LDH support. It was revealed that the appearance of the Au 4f peaks at around 83.4 eV and 87.1 eV could be mainly attributed to the Au<sup>0</sup> state. The binding energies of Cu 2p<sub>1/2</sub> at around 952.0 eV and Cu 2p<sub>3/2</sub> at 932.5 eV could be attributed to the Cu<sup>0</sup> state.25 Although the challenge for the supported Cu NP catalysts in the aerobic oxidation reaction still existed, i.e., O2 could oxidize

surface Cu atoms<sup>14</sup> and eliminate the alloving effects, the visiblelight irradiation of Au-Cu alloy NPs during the reaction could suppress the oxidation of the surface Cu atoms and successfully maintain the alloying effect.<sup>15</sup> Besides, as shown in Fig. S6a (ESI<sup> $\dagger$ </sup>), the peaks of Au 4f<sub>7/2</sub> show a positive shift from 83.1 eV for Au@Mg<sub>3</sub>Al-LDHs to 83.4 eV for Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs and the peaks of Au 4f<sub>5/2</sub> shift from 86.6 eV for Au@Mg<sub>3</sub>Al-LDHs to 87.1 eV for Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs, suggesting that the electron cloud density of Au species decreases in Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs. In contrast, as shown in Fig. S6b (ESI<sup> $\dagger$ </sup>), the Cu 2p<sub>3/2</sub> peaks show a negative shift from 932.8 eV for Cu@Mg<sub>3</sub>Al-LDHs to 932.5 eV for Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs and the Cu 2p<sub>1/2</sub> peaks shift from 952.5 eV for Cu@Mg<sub>3</sub>Al-LDHs to 952.0 eV for Au<sub>2</sub>Cu@ Mg<sub>3</sub>Al-LDHs, indicating that the electron cloud density of the Cu species in Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs increases. It was revealed that the fusion of Au with Cu led to electrons preferentially transferring from Au to Cu atoms, which also suggested that the e<sup>-</sup> transfer from Au atoms facilitated the successful reduction of the oxidized surface Cu. This electron transfer was also confirmed by Wang et al.;13 the peaks of Pd 3d<sub>5/2</sub> showed a positive shift and the Au  $4f_{7/2}$  peaks showed a negative shift compared to that for the corresponding monometallic catalysts, which revealed that the fusion of Au with Pd led to charge transfer from Pd to Au. Besides, the XRD patterns show that the Au-Cu@Mg<sub>3</sub>Al-LDH samples exhibit both a hydrotalcite-like structure and the corresponding oxide structure after loading Au-Cu alloy NPs because of the memory effect of hydrotalcite (Fig. S7a, ESI<sup>+</sup>), which is in good agreement with the FT-IR spectrum results (Fig. S7b, ESI<sup>+</sup>). The surface area of the samples was maintained stable (Table S1, ESI<sup>+</sup>).

Generally, there are negligible effects on the structural and textural properties of Mg<sub>3</sub>Al-LDHs after loading Au–Cu alloy NPs.

Molecular oxygen is activated by plasmonic metals. The ESR spectra of the catalyst dispersion solutions confirm the formation of O<sub>2</sub><sup>•-</sup> radicals during the photocatalytic reaction, as shown in Fig. S8 (ESI<sup>†</sup>). The typical signals of DMPO-O<sub>2</sub><sup>•-</sup> appeared for both the Au2Cu@Mg3Al-LDH and Au@Mg3Al-LDH dispersion solutions under irradiation in the presence of 5.5-dimethyl-1pyrroline N-oxide (DMPO) as a trapping agent.<sup>13</sup> No  $O_2^{\bullet-}$  signal was detected in the dark and for the support Mg<sub>3</sub>Al-LDO-RE solution, which indicated that the plasmon-activated electrons on the surface metal sites activated the oxygen molecules  $(O_2)$ . Moreover, the  $O_2^{\bullet-}$  radical signal was significantly more intense for Au2Cu@Mg3Al-LDHs than for the monometallic Au catalyst (Au@Mg<sub>3</sub>Al-LDHs), indicating more efficient electron transfer to O<sub>2</sub> in case of alloying the two metals.<sup>27</sup> This is because the alloy NP surface has greater charge heterogeneity than the pure metal NP surface, resulting in a longer lifetime of light-excited electrons, which increases the ability to activate oxygen.<sup>11</sup>

#### 3.3 Role of support

The crucial role of the support in supported metal catalysts was considered. Au–Cu nanoparticles were immobilized on commercial MgO and  $Al_2O_3$  as comparable samples for the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH catalyst. As shown in Fig. 3a and Table S2 (ESI†), the support of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs has a cooperative role for the acid–base pairs to achieve excellent catalytic results (entry 1); because the supports MgO and Mg<sub>3</sub>Al-LDHs contain basic surface sites and Al<sub>2</sub>O<sub>3</sub> has acidic surface sites, all of them exhibit lower activity under irradiation and in the dark than Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs



**Fig. 3** (a) Photocatalytic oxidative esterification of benzyl alcohol with methanol over Au–Cu alloy NPs with varied supports. Reaction conditions: photocatalyst, 10 mg; benzyl alcohol, 0.5 mmol; methanol, 5 ml;  $K_2CO_3$ , 0.2 mmol;  $O_2$ , atmospheric pressure; reaction temperature, 30 °C; reaction time, 3 h; light intensity (cut-off wavelength of 420 nm of Xe lamp), 0.5 W cm<sup>-2</sup>. (\*a: Au<sub>2</sub>Cu@MgO and Au<sub>2</sub>Cu@Al<sub>2</sub>O<sub>3</sub> were mechanically mixed in a mortar according to n(Mg) : n(Al) = 3 : 1; \*b: direct loading of Au–Cu alloy NPs onto HT; \*c: reaction time, 6 h and light source, full-spectrum Xe lamp (0.5 W cm<sup>-2</sup>); \*d: reaction time, 6 h; \*e: the reaction was conducted in the dark using the catalyst, which has been irradiated under full-spectrum Xe lamp for 6 h). (b) The amount of surface basic and acidic sites of varied supports determined by CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD profiles because the recovery of LDHs by memory effect is not reliable in the process of TPD measurement due to the release of CO<sub>2</sub> and H<sub>2</sub>O as the reaction temperature rises; so, we can only compare the TPD profiles for different LDOs. The specific reasons are as follows: MgAl-LDHs were calcined at 450 °C in dry air for 8 h to release H<sub>2</sub>O, CO<sub>3</sub><sup>2-</sup>, Al–OH and Mg–OH, yielding MgAl-LDO and then, the Au–Cu alloy was supported on the MgAl-LDO in the HAuCl<sub>4</sub> (0.01 M) and Cu(NO<sub>3</sub>)<sub>2</sub> (0.01 M) aqueous solutions by the reduction of NaBH<sub>4</sub>; meanwhile, the MgAl-LDO recovered the surface hydroxyl groups by water absorption and the layered structure of hydrotalcite was restored. Thus, the trend of total acidity and alkalinity of MgAl-LDO can reflect the trend of total acidity and alkalinity of layered hydrotalcite recovered by memory effect when the synthesis conditions are consistent.

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(entries 2, 3, 5 and Fig. 3b). Besides, the mechanically mixed Au2Cu@MgO and Au2Cu@Al2O3 photocatalysts also exhibited low activity (entry 4), which also proved the crucial role of acidbase pairs in the support of Au<sub>2</sub>Cu(a)Mg<sub>3</sub>Al-LDHs.<sup>28,29</sup> As shown in Fig. 3a and Table S2 (ESI<sup>+</sup>), the photocatalyst supports with varied Mg/Al ratios were synthesized and various Mg/Al ratios were determined by ICP, as shown in Table S3 (ESI<sup>†</sup>) (Au<sub>2</sub>Cu<sub>(a)</sub> Mg<sub>2</sub>Al-LDHs, Au<sub>2</sub>Cu@Mg<sub>2</sub>Al-LDHs and Au<sub>2</sub>Cu@Mg<sub>1</sub>Al-LDHs); the catalytic performance also agreed with the above results (entries 1, 6, 7). The support of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs having the maximum amount of basic and acidic sites exhibited the best catalytic performance (Fig. 3b),<sup>30</sup> as reflected by the TPD profile trends of different LDOs (the details are given in the caption of Fig. 3). Besides, the physical properties of the catalysts are shown in Table S1 (ESI<sup>+</sup>). Obviously, the surface area is not the decisive factor for the performance as the optimal catalyst has a relatively small specific surface area. In addition, the particle size distributions of the Au-Cu alloy NPs with varied support samples are shown in Fig. S9a-e (ESI<sup>+</sup>). There was a little effect of supports on the alloy particle sizes as the mean sizes of the alloy NPs were approximately similar between 2 and 4 nm. It is concluded that the Mg<sub>2</sub>Al-LDH support containing acid-base pairs plays an important role in this catalytic system.

In addition, considering that illumination may affect the surface functional groups of the support and then affect the reaction eventually, another support, *i.e.*, Zn<sub>2</sub>Al-LDHs (Zn<sub>2</sub>Al-LDO-RE) that can exhibit light absorption in the spectrum range of a fullspectrum Xe lamp (350-880 nm) (Fig. S10a and b, ESI<sup>+</sup>) was chosen to further investigate the specific action of the support in the oxidative esterification of benzyl alcohol. This was because the Mg<sub>3</sub>Al-LDH (Mg<sub>3</sub>Al-LDO-RE) support showed no light absorption in the UV-vis spectrum (the mean size of alloy NPs on the Zn<sub>2</sub>Al-LDH support was also approximately between 2 and 4 nm, as shown in Fig. S9f (ESI<sup>+</sup>), which excluded the effect of alloy particle size). It was distinctively shown that the yield of methyl benzoate declined to 17.7% under irradiation (full-spectrum Xe lamp) compared to the yield of 35.9% in the dark (Fig. 3a and Table S2 entry 8, ESI<sup>+</sup>). When a cut-off wavelength of 420 nm of the Xe lamp (420-880 nm) was used, the yield of methyl benzoate was up to 53.3% (entry 9). Then, the Au<sub>2</sub>Cu@Zn<sub>2</sub>Al-LDH photocatalyst was irradiated with the full-spectrum Xe lamp for 6 h before the reaction was conducted in the dark; the yield of methyl benzoate (14.9%) was almost equal to that of the reaction under irradiation (17.7%). It was concluded that the Zn<sub>2</sub>Al-LDH support absorbed light in the spectrum range of 350-420 nm to have a negative effect on the catalytic process. In addition, as shown in the FT-IR spectra of Au<sub>2</sub>Cu@Zn<sub>2</sub>Al-LDHs before and after irradiation with the full-spectrum Xe lamp (Fig. 4a and b), the intensity of the band for hydroxyl groups at around 3460 cm<sup>-1</sup> increases obviously after irradiation under the Xe lamp. This indicated that the amount of hydroxyl groups on the surface of the Zn<sub>2</sub>Al-LDH support changed greatly after irradiation, which ultimately affected the adsorption of the reactant molecules on the support; this was proven by the in situ FT-IR spectra of Au<sub>2</sub>Cu@Zn<sub>2</sub>Al-LDHs after the co-adsorption of benzyl alcohol and methanol,



**Fig. 4** (a) FT-IR spectra of Au<sub>2</sub>Cu@Zn<sub>2</sub>Al-LDHs before and after irradiation under full-spectrum Xe lamp. (b) FT-IR subtraction spectra of Au<sub>2</sub>Cu@ Zn<sub>2</sub>Al-LDHs before and after irradiation under full-spectrum Xe lamp. (c) *In situ* FT-IR spectra of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs after co-adsorption of benzyl alcohol and methanol (\*a: dropping the reaction solution of 0.5 mmol benzyl alcohol, methanol as solvent; \*b: after argon purge for 30 min; \*c: pass in oxygen and start to heat up). (d) *In situ* FT-IR spectra of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs after co-adsorption of benzyl alcohol and methanol (deduction of IR spectra of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs).

as shown in Fig. S11 (ESI<sup>+</sup>).<sup>31</sup> The new band intensity of Zn–O=C (452 cm<sup>-1</sup>) was apparently stronger for the photocatalyst system without irradiation compared to that for the photocatalyst system after irradiation under the full-spectrum Xe lamp. This indicated that the increase in the surface hydroxyl groups after irradiation inhibited the adsorption of alcohol molecules due to the fact that the increase in the hydroxyl groups suggests that the distance between the hydroxyl groups becomes smaller, which may inhibit the adsorption of alcohol molecules due to the steric hindrance effect, ultimately resulting in the decrease in activity (detailed explanation shown in the ESI<sup>+</sup>).

Besides, as shown in Fig. 4c and Fig. S12 (ESI†), the intensity of the vibrational mode band of Mg–OH at 459  $\text{cm}^{-1}$  decreases, indicating the dehydroxylation of Mg-OH of the Mg<sub>3</sub>Al-LDH support<sup>32</sup> during the reaction. Meanwhile, a new vibrational mode band of Mg–O at 488 cm<sup>-1</sup> appeared, and it exhibited increase in intensity during the reaction and a blue frequency shift compared to the IR spectra of Mg-OH in the Mg<sub>3</sub>Al-LDH support; this indicated the formation of Mg-O=C after the dehydroxylation of Mg-OH due to the adsorption of alcohol molecules on the basic sites of the support by oxygen. Then, the intermediate aldehyde species was formed because of the dehydrogenation of alcohols during the reaction. Moreover, as shown in Fig. S11 (ESI<sup>+</sup>), the same results are achieved in the in situ FT-IR spectra of Au2Cu@Zn2Al-LDHs after the co-adsorption of benzyl alcohol and methanol. In addition, the silane coupling agent EPTMS ( $\gamma$ -(2,3-epoxypropoxy)propytrimethoxysilane) that has a negligible effect on the reaction was chosen, and the

Au<sub>2</sub>Cu@MgAl-LDH catalyst was silanized to cover the surface hydroxyl groups of the support. It was found that the yield of methyl benzoate decreased significantly from 96.4% to 43.9% under visible-light irradiation and from 59.4% to 20.4% in the dark (Fig. 3a), indicating that the alcohol molecules were adsorbed on the surface of the support through hydroxyl groups because the adsorption of alcohol molecules will be inhibited if the surface hydroxyl groups of the support are covered.

On the basis of the above-mentioned results, it was concluded that both the support and the metal contributed to high activity. The support with acid-base pairs affected the adsorption of reactant molecules, in which the alcohol molecules were adsorbed on the basic sites of the support (Mg–OH<sup> $\delta$ -</sup>); this could promote the cleavage of the O–H bond to give an alkoxide intermediate at the surface and form a water molecule during the reaction. Then, the formed water molecule was adsorbed on the acidic site of the support (Al–OH<sup> $\delta$ +</sup>) to promote the recovery of hydroxyl groups on the catalyst surface to determine the overall reaction rate completely.

#### 3.4 Role of K<sub>2</sub>CO<sub>3</sub>

It was found that equivalent activities can be achieved when the reaction temperature and time were increased to 55 °C and 18 h, respectively, in the absence of  $K_2CO_3$  (Table 1, entry 10). When only  $K_2CO_3$  was added, slight activity was achieved both under irradiation and in the dark (Table 1, entry 11), which proved that the role of  $K_2CO_3$  in this photocatalytic system is that of a co-catalyst to facilitate the dehydrogenation of alcohol because of its basic property as equivalent results were also obtained by increasing the reaction temperature under alkaline-free conditions.

#### 3.5 Monitoring the surface reaction

To understand the activation process of the reactants on the catalyst surface, the evolution of the products during the time course of the oxidative esterification of benzyl alcohol over the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH photocatalyst under irradiation and in the dark was conducted (Fig. S13, ESI<sup>+</sup>). It is a remarkable fact that formaldehyde was not detected by methanol oxidation, and benzaldehyde was the only intermediate during the reaction course both under light irradiation and in the dark. This demonstrates that benzyl alcohol oxidation is easier than methanol oxidation over this photocatalyst, with the implication that the energy of the Au<sub>2</sub>Cu(a)Mg<sub>3</sub>Al-LDH photocatalyst is not enough to activate the methanol molecules to dehydrogenate under this reaction condition. It is concluded that benzyl alcohol is first oxidized to benzaldehyde during the photocatalysis process; then, benzaldehyde further reacts with methanol molecules to achieve methyl benzoate on the surface of the catalyst.

In addition, *in situ* FT-IR spectra after the coadsorption of benzyl alcohol and methanol on Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs were recorded (Fig. 4d and Fig. S14, ESI†) to further investigate the activation of reactants (detailed explanation shown in the ESI†). The decrease in the intensity of the O–H stretching vibration band of benzyl alcohol and methanol at 3643 cm<sup>-1</sup> indicates that the hydroxyl groups of benzyl alcohol and methanol have been dehydrogenated by the cleavage of the O–H bonds.<sup>33</sup> The gradual decrease in the intensity of the carbon–carbon double bond and C–H bond deformation vibrations of the aromatic ring of benzyl alcohol at 1620 cm<sup>-1</sup>, 1538 cm<sup>-1</sup> and 1313 cm<sup>-134</sup> indicates that some benzyl alcohol molecules have been desorbed after the reaction process.<sup>35</sup> The appearance and increase in the intensity of the –C==O– bond stretching vibrations of



Scheme 1 Schematic diagram of the proposed reaction mechanism.

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benzaldehyde at  $1715 \text{ cm}^{-1}$  with the increase in reaction time from 0 min to 90 min indicate that the intermediate benzaldehyde is first generated.<sup>36</sup> The blue frequency shift of this band compared to the IR spectra of neat benzaldehyde  $(1710-1630 \text{ cm}^{-1})$  indicates that the carbonyl oxygen atoms of benzaldehyde are associated with the basic sites of the support because the coordination of C-H of benzaldehyde with unsaturated Au-Cu alloy NP active sites to form a metal-H bond can result in a decrease in the C=O bond length of benzaldehyde. This provides another favourable evidence that the benzyl alcohol molecules are associated with the basic sites of the support of Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs at the beginning of the catalytic reaction rather than being associated with the Au-Cu alloy NP active sites; this is because a red shift for the C=O bond is expected with respect to neat benzaldehyde when benzyl alcohol molecules are associated with the Au-Cu alloy NP active sites as the coordination of the carbonyl oxygen atoms with metal atoms can result in an increase in the bond length. The proportional decrease in the intensity of the C-H stretching vibration band at 2939 cm<sup>-1</sup> and 2833 cm<sup>-1</sup> indicates the cleavage of the C-H bond of methylene of benzyl alcohol during the catalytic process. Then, the appearance and increase in the intensity of the -C-O- bond and -COO- bond stretching vibrations of methyl benzoate at 1749 cm<sup>-1</sup> and 1422 cm<sup>-1</sup>, respectively,<sup>37</sup> with the increase in reaction time from 90 min to 400 min indicate that methyl benzoate is then generated after nucleophilic attack at the carbonyl carbon of intermediate benzaldehyde by the methoxy group of methanol. The blue frequency shift of the -C=Obond compared to the IR spectra of neat methyl benzoate (1730- $1725 \text{ cm}^{-1}$ ) indicates that the carbonyl oxygen atoms of methyl benzoate are associated with the basic sites of the support. Meanwhile, the blue frequency shift of the C-H stretching vibration band at 2939 cm<sup>-1</sup> and 2833 cm<sup>-1</sup> indicates that the inductive effect of the C-OCH<sub>3</sub> band is generated due to the nucleophilic addition of the methoxy group of methanol with the carbonyl carbon, which can result in a decrease in the bond length.

#### 3.6 Proposed mechanism

On the basis of the above-mentioned analysis, we proposed a possible mechanism for the oxidative esterification of benzyl alcohol, illustrating that the Au-Cu alloy NPs as the light absorption sites (Scheme 1) determined the rate-limiting step of the reaction when the support sites were identical, and the Mg<sub>3</sub>Al-LDH support as the reactant molecule adsorption sites could drive the overall reaction rate. The reaction proceeds through the synergistic effect between the Au-Cu alloy NPs and the base-acid sites on the surface of the Mg<sub>3</sub>Al-LDH support. First, benzyl alcohol adsorbed on the basic sites of the MgAl-LDH support (Mg–OH $^{\delta-}$ ) promotes the cleavage of the O–H bond of benzyl alcohol to give an alkoxide intermediate at the surface and form a water molecule (I, II). Second, the intermediate undergoes coordination with the unsaturated metal active sites due to the LSPR effect of alloy NPs to form a metal-H bond to afford unsteady metal-alcoholate-LDH species (III). Then, the lightexcited electrons can promote hydrogen abstraction from α-H of the metal-alcoholate-LDH species to generate aldehyde species

(IV). Third, the alloy site activates  $O_2$  and produces  $O_2^{\bullet^-}$  radicals; the formed aldehyde can condense with methanol to form a hemiacetal intermediate.<sup>38-40</sup> Then, methyl benzoate and a water molecule are achieved by the oxidative dehydrogenation of the hemiacetal intermediate (V). Finally, the rapid oxidation of metal hydride by the  $O_2^{\bullet^-}$  radicals forms one molecule of water promoted by the acidic sites of the support while recovering the initial metal active sites and hydroxyl groups on the support surface for another reaction cycle (VI, VII). Besides, it is noted that the carbon balance of the reaction is satisfied within the experimental error (Table S4, ESI<sup>†</sup>).

 Table 2
 Photocatalytic selective oxidative esterification of aromatic alcohols with aliphatic alcohols<sup>a</sup>

|                       | $R_{\underline{u}}^{\underline{n}} \rightarrow OH_{+} R_{-}$ | $DH \frac{Au_2Cu@Mg_3Al-LDHs/}{K_2CO_3, O_2}$ | $r \to R \frac{f}{U}$         | Ŕ                   |
|-----------------------|--|---|-------------------------------|---------------------|
|                       | Ŕ-OH= aliphatic alcol  | hol   |                               |                     |
| Ent                   | ry Reactant  | Product                                       | Yield <sup><i>i</i></sup> (%) | $T(^{\circ}C)/t(h)$ |
| $1^b$                 | ОН   | C C   | 96.4 (59.4)                   | 30/3                |
| 2 <sup>b</sup>        | CI   | CI  | 97.9 (78.8)                   | 30/24               |
| 3 <sup>b</sup>        | O <sub>2</sub> N OH  | O2N O   | 87.6 (68.5)                   | 30/24               |
| $4^b$                 | ОН ОСН3  | OCH3  | 53.0 (26.3)                   | 30/24               |
| 5 <sup>c</sup>        | ОН   |   | 44.6 (23.9)                   | 30/24               |
| 6 <sup><i>d</i></sup> | ОН   |   | 32.7 (10.4)                   | 50/24               |
| 7 <sup>e</sup>        | ОН   |   | 66.6 (25.2)                   | 60/24               |
| 8 <sup>f</sup>        | ОН   |   | 40.2 (14.0)                   | 60/24               |
| 9 <sup>g</sup>        | ОН   |   | 58.7 (30.7)                   | 50/30               |
| $10^h$                | ОН   |   | 90.3 (51.7)                   | 40/5                |

<sup>*a*</sup> Reaction conditions: photocatalyst, 10 mg; aromatic alcohols, 0.5 mmol; solvent, 5 ml; K<sub>2</sub>CO<sub>3</sub>, 0.2 mmol; O<sub>2</sub>, atmospheric pressure; light intensity (cut-off wavelength of 420 nm of Xe lamp), 0.5 W cm<sup>-2</sup>. <sup>*b*</sup> Methanol as solvent. <sup>*c*</sup> Ethanol as solvent. <sup>*d*</sup> 1-Propanol as solvent. <sup>*e*</sup> 1-Hexyl alcohol as solvent. <sup>*f*</sup> 1-Octanol as solvent. <sup>*g*</sup> 1-Heptane as solvent. <sup>*h*</sup> Methanol as solvent, photocatalyst, 100 mg; benzyl alcohol, 5 mmol; K<sub>2</sub>CO<sub>3</sub>, 2 mmol; methanol, 50 ml. <sup>*i*</sup> The values in parentheses are the results in the dark.

#### 3.7 Synthesis of different aromatic esters

To investigate the universality of the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH photocatalyst in other oxidative esterifications (Table 2), the chlorine and nitro groups were situated in the para-position of benzyl alcohol; the ester yields of up to 97.9% and 87.6% were achieved (entries 2 and 3) under visible-light irradiation. When the methoxy group was situated in the *ortho*-position of benzyl alcohol, the ester yield declined to 53.0% (entry 4) due to the steric hindrance effect of the substituent. Besides, the oxidative esterifications of benzyl alcohol with ethanol and 1-propanol were investigated, which produced the corresponding aryl esters in 44.6% and 32.7% yields by using the Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDH catalyst under visible-light irradiation (entries 5 and 6). Here, it is worth noting that we could also achieve the yields of 66.6% and 40.2% by using visible-light irradiation in esterification with long-chain aliphatic 1-hexyl alcohol and 1-octanol (entries 7 and 8), respectively, which are more challengeable because the uniform dispersion of the catalyst in the reaction solution will be inhibited and the dehydrogenation of aliphatic alcohols will become harder; this is because the more the carbon atoms, the greater the viscosity and the greater the ability to donate electrons. Furthermore, the self-esterification of benzyl alcohol afforded the corresponding ester with an excellent yield of up to 58.7% under visible-light irradiation (entry 9). Although the selective oxidative esterifications always require high reaction temperatures and high oxygen pressures, as reported in the literature,<sup>41,42</sup> the milder conditions in the present study for oxidative esterification reactions are rarely reported. In a word, excellent universality of this photocatalyst in other oxidative esterifications was achieved. In addition, we performed an expanded 10-fold reaction system (0.5 g scale) for the oxidative esterification of benzyl alcohol with methanol to demonstrate the catalytic utility of our catalyst, as shown in Table 2, entry 10; the previous yield was verified up to 90.3% under visible-light irradiation.

### 4. Conclusions

In summary, Au<sub>2</sub>Cu@Mg<sub>3</sub>Al-LDHs were prepared by utilizing the "memory effect" of LDHs. Also, the impregnation-reduction of gold and copper salts was found to afford an efficient photocatalyst for the oxidative esterification of benzyl alcohol with methanol under visible-light irradiation. The excellent photocatalytic performance could be attributed to the synergistic effects of two factors: (1) the interaction of light-excited electrons from the alloy NPs with the intermediate molecules afforded metal-alcoholate-LDH species to promote the cleavage of the C-H bond of the reactant molecules, which could drive the ratelimiting step of the reaction under the premise that the support sites appeared identical. (2) The acid-base pairs of Mg<sub>3</sub>Al-LDHs could facilitate the adsorption of the reactant molecules. The basic sites adsorbed benzyl alcohol molecules to provoke the cleavage of the O-H bond, the acidic sites promoted the formation of water molecules and the recovery of hydroxyl groups on the catalyst surface at the end of the reaction especially promoted the

overall reaction system completely. This simple, cost-effective, and environmentally benign catalytic process exhibits a great potential in the oxidative esterification of aromatic alcohols.

### Conflicts of interest

There are no conflicts to declare.

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