# FULL PAPER



### Applied Organometallic Chemistry

# Photocatalytic one-pot multidirectional N-alkylation over Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>: Ti<sub>3</sub>C<sub>2</sub>-based short-range directional charge transmission

Heyan Jiang 💿 | Meilin Sheng 💿 | Yue Li 💿 | Shuzhen Kong 💿 | Fengxia Bian 💿

Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environmental and Resources, Chongqing Technology and Business University, Chongqing, China

## Correspondence

Heyan Jiang, PhD, and Fengxia Bian, Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environmental and Resources, Chongqing Technology and Business University, Chongqing 400067, China. Email: orgjiang@163.com; bianqian1201@163.com

## **Funding information**

Chongqing Key Laboratory of Catalysis and New Environmental Materials, Grant/ Award Number: KFJJ2019082; Innovation Group of New Technologies for Industrial Pollution Control of Chongqing Education Commission, Grant/Award Number: CXQT19023; Key Disciplines of Chemical Engineering and Technology in Chongqing Colleges and Universities during the 13th Five Year Plan; Ministry of Education of Chongqing, Grant/Award Number: KJQN201900811; Natural Science Foundation Project of Chongqing, Grant/Award Numbers: cstc2015jcyjBX0031, cstc2019jcyjmsxmX0641, cstc2018jcyjAX0735; Chongqing Technology and Business University, Grant/Award Number: 950119090; National Natural Science Foundation of China, Grant/Award Number: 21201184; Venture & Innovation Support Program for Chongqing Overseas Returnees, Grant/Award Number: cx2020113

Visible-light-induced one-pot, multistep, and chemoselectivity adjustable reactions highlight the economical, sustainable, and green process. Herein, we report Pt nanoparticles dispersed on S and N co-doped titanium dioxide/titanium carbide (MXene) (3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>) heterojunctions as photocatalysts for the tandem reactions between aromatic nitro compounds and alcohols to produce N-alkylated products. 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterojunction was prepared by in situ grew TiO<sub>2</sub> on Ti<sub>3</sub>C<sub>2</sub> nanosheets, S and N co-doped TiO<sub>2</sub> with thiourea, and then Pt nanoparticles with 2.9 nm average diameter well dispersed on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> showed excellent activity and chemoselectivity to N-alkyl amines in the presence of base additive K<sub>3</sub>PO<sub>4</sub> under visible-light irradiation; interestingly the chemoselectivity almost completely switched to N-benzylideneanilines in the presence of base additive KOH. In comparison, Pt nanoparticles on S and N co-doped TiO<sub>2</sub> prepared from titanium carbide (3%Pt/D-TiO<sub>2</sub>@C) showed sharply decreased activity and chemoselectivity to N-alkyl amines or N-benzylideneanilines. The enhanced performance of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> should be attributed to the improvement in photogenerated electron and hole separation efficiency by means of charge short-range directional transmission caused by the intimate contact between the  $TiO_2$  and the conductive  $Ti_3C_2$ . In situ DRIFTS spectra further verified that the substrates activation with visible-light irradiation at 25°C was much faster than heating.

## K E Y W O R D S

MXene, one-pot *N*-alkylation, photocatalysis, short-range charge transmission, titanium dioxide

# **1** | INTRODUCTION

Seeking an alternative clean, safer, and more environment-friendly technology is one of the most important goals in chemistry.<sup>[1-5]</sup> One-pot tandem/cascade reactions typically require multifunctional catalysts with different catalytically active sites in a site-isolated way to keep their independent function, provide great advantage, and spur extensive research interest by simplifying the multistep reaction catalysis process into a single synthesis operation without having to isolate the intermediate.<sup>[6-10]</sup> Two-dimensional materials have been widely investigated in different applications due to their unusual electronic, mechanical, and optical properties.<sup>[11-13]</sup> The emerging 2D transition metal carbide/carbonitride family (MXenes), with general formula  $M_{n+1}X_nT_x$  (n = 1, 2, 3;  $T_x = OH$ , O, F group), has been extensively studied during the past few years due to its excellent structure and chemical properties.<sup>[14-19]</sup> MXene's excellent electron conductivity makes it easier to transfer charge from the semiconductor to MXene, thereby improving the separation efficiency of electron and hole, thus achieving directional charge transmission.<sup>[20,21]</sup> With the above special characteristics, MXene is considered as one of the most promising catalytic material.

N-alkyl products are essential fabricating squares in the construction of agrochemicals, drugs, and bioactive molecules. Methods such as substitution, addition, cycloaddition, and cross-coupling have been developed to synthesize such intermediates.<sup>[22-28]</sup> Homogeneous Ru and Ir catalysts<sup>[24,25]</sup> along with heterogeneous metal nanoparticles have been used to N-alkylation reaction to amines.<sup>[26,27]</sup> Using light to drive chemical reactions is very attractive; various nanometal composite photocatalysts have been developed to achieve N-alkylation by photocatalytic dehydrogenation of alcohols to synthesis of aldehydes and then hydrogenation of imines in recent years.<sup>[29-35]</sup> Shiraishi et al.<sup>[29]</sup> focused on the N-alkylation of primary amines with alcohols catalyzed by Pd/TiO<sub>2</sub> under photoirradiation and discovered that the catalytic efficiency decidedly depended on the size of Pd particles. Zhang et al.<sup>[30]</sup> described Cu-Mo/TiO<sub>2</sub> catalyzed N-alkylation between amines and alcohols under UV illumination with ambient temperature, which was particularly suitable for the alkylation of anilines with halogen. Not long ago, Wang et al.<sup>[32-34]</sup> loaded metal nanoparticles onto the outside or into the pores of certain support materials to form multifunctional catalysts (Pd/ZnIn<sub>2</sub>S<sub>4</sub>, PdNPs@MIL-100 (Fe) and PdAu@MIL-100(Fe)) for visible-light-prompted N-alkyl amines synthesis from alcohols and amines with excellent catalytic activity and chemoselectivity.

Herein, we report Pt nanoparticles dispersed on S and N co-doped titanium dioxide/titanium carbide (MXene)

(3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>) heterojunctions as photocatalysts for the tandem reactions between aromatic nitro compounds and alcohols to synthesize N-alkylated products; 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterojunction was prepared by in situ grew TiO<sub>2</sub> on Ti<sub>3</sub>C<sub>2</sub> nanosheets, S and N co-doped TiO<sub>2</sub> with thiourea, and then Pt nanoparticles with small diameter well dispersed on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>; 3%Pt/D-TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub> showed excellent activity and chemoselectivity to N-alkyl amines in the presence of base additive K<sub>3</sub>PO<sub>4</sub> with visible-light irradiation; interestingly, the chemoselectivity almost completely switched to Nbenzylideneanilines by simply changing the base additive to KOH. In contrast, Pt nanoparticles dispersed on S and N co-doped TiO<sub>2</sub> prepared from titanium carbide (3%Pt/ D-TiO<sub>2</sub>@C) showed sharply decreased activity and chemoselectivity to N-alkyl amines or Nbenzylideneanilines. The enhanced performance of 3%Pt/ D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> was owing to the improvement in photogenerated electron and hole separation efficiency by means of a short-range directional charge transmission caused by the intimate contact between the TiO<sub>2</sub> and the conductive  $Ti_3C_2$ . This investigation established an efficient way to realize N-alkyl amines and Nbenzylideneanilines from aromatic nitro compounds, and alcohols, moreover, shed some light on the great possibility of multifunctional catalysis construction in a broad range of light-induced organic synthesis.

# 2 | RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of all prepared catalytic materials were employed to characterize the crystal phase and phase purity in Figures 1 and S1. Consistent



 $\begin{array}{lll} \textbf{FIGURE 1} & X\mbox{-ray diffraction (XRD) patterns of } TiO_2/Ti_3C_2, D\mbox{-} TiO_2/Ti_3C_2, \mbox{-} 3\%\mbox{Pt/D-TiO}_2/Ti_3C_2, D\mbox{-} TiO_2\mbox{@C and } 3\%\mbox{Pt/D-TiO}_2\mbox{@C } \end{array}$ 

with the literature,  $[^{36,37]}$  the layered TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterojunction was successfully prepared on the layered Ti<sub>3</sub>C<sub>2</sub> nanosheets by hydrothermal oxidation. The coexistence of the peak of anatase  $TiO_2$  and the peak of  $Ti_3C_2$  indipartial oxidation cated successfully of  $Ti_3C_2$ nanosheets.  $^{[36,37]}$  After  $\rm TiO_2/\rm Ti_3C_2$  was N and S doped with thiourea (D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>), the Ti<sub>3</sub>C<sub>2</sub> peak intensity in D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> was further weakened in comparison with the precursor TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>; meanwhile, the (002) diffraction peak of Ti<sub>3</sub>C<sub>2</sub> in D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> shifted to a lower angle, indicating that two-dimensional material structural expansion happened during the N and S doping.<sup>[14,38]</sup> The thiourea doping did not change the lattice morphology of anatase TiO<sub>2</sub>. Except for the diffraction peak of TiO<sub>2</sub>, there was no other impurity phase. This indicated that N and S dopant atoms were directly incorporated into the crystal lattice of TiO<sub>2</sub> and did not form related compounds or other precipitation phase.[39-42] Meanwhile, no diffraction peak of thiourea was observed, Applied Organometallic\_WILEY 3 of 12 Chemistry

has been completely indicating that thiourea decomposed.<sup>[40-42]</sup> Further loading of the metal Pt, no significant Ti<sub>3</sub>C<sub>2</sub> peak shift was observed in 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, indicating that the loading of the Pt NPs did not change the structure of D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. Meanwhile, the XRD spectrum of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> had no obvious diffraction peak of Pt, indicating the small Pt NPs were well dispersed on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. On the other hand, no characteristic peak of Ti<sub>3</sub>C<sub>2</sub> was detected in D-TiO<sub>2</sub>@C. Similar to the phenomenon in the 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> catalyst, the thiourea doping did not change the lattice morphology of anatase TiO<sub>2</sub> in D-TiO<sub>2</sub>@C and small Pt NPs were well dispersed on D-TiO<sub>2</sub>@C.

In the Fourier transform infrared (FTIR) spectrum (Figure S2), all  $Ti_3C_2T_x$  derived  $TiO_2/Ti_3C_2$ , D- $TiO_2/Ti_3C_2$ , 3%Pt/D- $TiO_2/Ti_3C_2$ , D- $TiO_2@C$ , and 3%Pt/D- $TiO_2@C$  exhibited a broad band in 400–800 cm<sup>-1</sup>, which should be owing to the characteristic of Ti–O–Ti. With the doping of  $TiO_2/Ti_3C_2$  or  $TiO_2@C$  and then the





loading of the metal Pt, the vibration of Ti–O–Ti gradually enhanced. Another absorption at 1600–1700 cm<sup>-1</sup> was the hydroxyl group bending vibrations, and the intensity of the hydroxyl group bending vibrations peak became stronger from  $TiO_2/Ti_3C_2$  to D- $TiO_2/Ti_3C_2$  and then to 3%Pt/D- $TiO_2/Ti_3C_2$  or from D- $TiO_2@C$  to 3%Pt/ D- $TiO_2@C$ . This demonstrated the doping of S and N could introduce additional hydroxyl group to the 2D catalytic material surface, which would play crucial role in the subsequent photocatalytic organic transformation.

Figure 2a is scanning electron microscope (SEM) image of  $Ti_3C_2$  with characteristics of many stacked layers. The  $TiO_2$  nanocrystals could grow on the  $Ti_3C_2$  surfaces during the oxidation process of hydrothermal treatment at 160°C (Figure 2b).<sup>[37]</sup> After hydrothermal oxidation treatment and thiourea doping, the surface of the D- $TiO_2/Ti_3C_2$  became rougher and the stacked layers became thicker (Figure S3a and S3b), indicating that 2D  $Ti_3C_2$  was

effectively encapsulated by D-TiO2. After Pt loading and reduction to nanoparticles (Figure S3c), 3%Pt/D-TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub> almost maintained the feature as observed in D- $TiO_2/Ti_3C_2$  as a consequence of the  $Ti_3C_2$  support. However, in the absence of Ti<sub>3</sub>C<sub>2</sub> support, no obvious stacked layers were observed in 3%Pt/D-TiO2@C (Figure S4). Energy dispersive X-ray spectroscopy spectra (EDS) and corresponding mapping for 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> were displayed in Figure S3d and S2e. O, S, Ti, Pt, and N could be evidently observed, and these elements exist together uniformly in the sample proving the successful doping of N and S to TiO<sub>2</sub>. The Brunauer-Emmett-Teller (BET) surface areas of Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> were 1.17, 12.60, and 9.45  $m^2 \cdot g^{-1}$ , respectively. The D- $TiO_2/Ti_3C_2$  specific surface area was more than tenfold of Ti<sub>3</sub>C<sub>2</sub> through the formation of S and N co-doped TiO<sub>2</sub> nanocrystals. After Pt NPs loading, the specific surface area obviously decreased.



**FIGURE 3** X-ray photoelectron spectroscopy (XPS) spectra of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>: (a) full scan, (b) Pt 4f, (c) Ti 2p, (d) O 1s, (e) C 1s, (f) N 1s, and (g) S 2p

Detailed characteristics of Pt NPs on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> were analyzed by transmission electron microscopy (TEM). Figure 2c is the TEM image of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, which clearly showed that Pt nanoparticles with the average particle diameter of 2.9 nm were uniformly dispersed on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. Although the surface of most Ti<sub>3</sub>C<sub>2</sub> was covered by TiO<sub>2</sub> and Pt metal NPs after TiO<sub>2</sub> growth and Pt metal NPs loading, lattice fringes of Pt NPs (0.23 nm), TiO<sub>2</sub> (0.35 nm), and Ti<sub>3</sub>C<sub>2</sub> (0.27 nm)<sup>[14]</sup> were simultaneously observed in high resolution electron micrographs (Figure 2d). This ensured that these Pt NPs, TiO<sub>2</sub> nanocrystals, and Ti<sub>3</sub>C<sub>2</sub> would be sufficiently contacted by the reactants and acted as active centers in the photocatalytic reaction.

The X-ray photoelectron spectroscopy (XPS) characterization was employed to elucidate the nature of 3%Pt/ D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. XPS analysis identified the presence of platinum, titanium, oxygen, carbon, nitrogen, and sulfur in 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> (Figure 3a), which signified the target heterojunction successfully formed. Pt 4f were deconvoluted into two species; binding energies 71.1 and 74.5 eV were the 4f7/2 and 4f5/2 peaks of metallic Pt; 72.6 and 75.8 eV were the 4f7/2 and 4f5/2 peaks of Pt(II) (Figure 3b).<sup>[43,44]</sup> This suggested that metallic Pt was the main species along with the existence of a small amount of Pt(II), which might be brought about by the evident metal support interaction that promoted the electron transfer from Pt to TiO<sub>2</sub><sup>[44,45]</sup> The spectrum of the Ti 2p region of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> catalyst was shown in Figure 3c. The binding energy 458.8 and 464.3 eV of Ti 2p in doped catalyst shifted negatively compared with TiO<sub>2</sub>. The peak that migrated to lower binding energy might be due to that doping resulted in the formation of Ti-O-S, O-Ti-N, and O-Ti-S bands in the crystal lattice.<sup>[44,46]</sup> XPS spectrum of O 1s (Figure 3d) could be deconvoluted into two oxygen components, including 530.2 eV from Ti-O-Ti and 531.9 eV from Ti-OH.<sup>[39]</sup> C 1s in Figure 3e could be fitted to three peaks at 284.8 eV (C-C bond); 286.5 eV, which was assigned to the C-O bond<sup>[47]</sup>; and 288.2 eV, which was assigned to Ti-O-C because of the substitution of carbon atoms into titanium lattice and was also detected in some other Ti<sub>3</sub>AlC<sub>2</sub> derivative materials.<sup>[48,49]</sup> XPS spectra of N 1s in Figure 3f could be fitted to two peaks at 399.5 and 405.1 eV; 399.5 eV should be owing to the existence of lattice oxygen replaced by N atom (O-Ti-N).<sup>[50]</sup> The S 2p highresolution spectrum resulted in one peak centered at 163.8 eV (Figure 3g), which should be the  $S^{2-}$  species, comparable with the S-doping in  $TiO_2$  with  $O^{2-}$ substituted by  $S^{2-}$ .<sup>[46]</sup>

In order to clarify the intrinsic reason for the excellent performance of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, light-harvesting capability was conducted. The light absorption capacity of D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>@C, 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3% Pt/D-TiO<sub>2</sub>@C samples was characterized by ultravioletvisible (UV-vis) absorption spectroscopy in Figure 4. In general, the light absorbance of D-TiO<sub>2</sub>@C and 3%Pt/D-TiO<sub>2</sub>@C in visible-light region was weaker than D-TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub> and 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. The absorption of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> after Pt NPs loading was increased compared with material D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>; however, in comparison with D-TiO<sub>2</sub>@C, the 3%Pt/D-TiO<sub>2</sub>@C light absorption decreased. Band gaps were calculated with the Kubelka-Munk method. TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>@C, 3% Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>@C band gaps were around 2.80, 2.59, 2.95, 2.50, and 2.93 eV, respectively. Obviously, TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> formation, S and N co-doping as well as Pt nanoparticles loading were all conducive to the band gap reduction.

Photocurrent generation and electrochemical impedance spectroscopy were implemented to evaluate the charge separation and transfer efficiency of D-TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>@C, 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>@C. Figure 5a is a transient photocurrent graph of photocatalysts on ITO electrode with visible-light illumination. The photocurrent response of the  $D-TiO_2/Ti_3C_2$ , D-TiO<sub>2</sub>@C, 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>@C electrodes was rapid, stable, and repeatable during lighting on/off cycles. D-TiO2/Ti3C2 with visible light exhibited improved photocurrent than D-TiO<sub>2</sub>@C, indicating the positive synergy between  $D-TiO_2$  and  $Ti_3C_2$ . The fact Ti<sub>3</sub>C<sub>2</sub> acting as a transporter for electrons to inhibit the backward diffusion of electrons significantly improved the separation efficiency of photo-induced charge carriers<sup>[37]</sup>; 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> had higher photocurrent than that of D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, which further



**FIGURE 4** Ultraviolet–visible (UV-vis) absorption spectra of D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>@C, 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>@C



**FIGURE 5** Transient photocurrent responses (a) and electrochemical impedance spectroscopy (b) of D-TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub>, D-TiO<sub>2</sub>@C, 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, and 3%Pt/D-TiO<sub>2</sub>@C

indicated that the introduction of strong electron accepting Pt NPs to D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> could accelerate the separation efficiency of photogenerated electrons and holes. Smaller radius of the arc in the electrochemical impedance spectrum represent smaller electron transfer resistance on the surface of photoelectrode, which as a rule brings about more efficient separation of photoelectron-hole pairs as well as speedier interfacial charge transfer. In Figure 5b, the circular segment span of the electrical impedance spectroscopy (EIS) Nyquist curve of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> and 3%Pt/D-TiO<sub>2</sub>@C were smaller than the radius arc of D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> and D- $TiO_2@C$ , which represented that the resistance of the interface charge transfer from the electrode to the electrolyte molecule was in the order of 3%Pt/D-TiO<sub>2</sub>/  $Ti_3C_2 < 3\%$ Pt/D-TiO<sub>2</sub>@C < D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> < D-TiO<sub>2</sub>@C. These results of the electrochemical impedance spectroscopy echo the law of the photocurrent test.

The as-prepared 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> catalyst was used for one-pot hydrogenation and N-alkylation of nitro compounds and alcohols with visible light. Nitrobenzene and benzyl alcohol were chosen as the substrates to test the catalytic performance in Table 1. No product was detected in the absence of catalyst or without metal Pt (Table 1, entries 1 and 2). In the absence of base additive, hydrogenation and N-alkylation of nitrobenzene were only converted 36.0% with 9.0% chemoselectivity to Nbenzylideneaniline (D1) and 10.0% chemoselectivity to Nbenzylaniline (E1) (Table 1, entry 3). In the presence of base additive K<sub>3</sub>PO<sub>4</sub>, hydrogenation and N-alkylation reaction could reach 100% conversion with up to 93.0% chemoselectivity to E1 (Table 1, entry 4). When  $H_2$  was substituted by N<sub>2</sub>, hydrogenation and N-alkylation reaction could also be carried out, but the catalytic activity decreased (Table 1, entry 5). This should be attributed to the fact that dissociated hydrogen could be easily formed on the surface of Pt NPs with H<sub>2</sub> to accelerate the reduction reaction. The one-pot hydrogenation and Nalkylation reaction could not be carried out without visible-light irradiation (Table 1, entry 6). Because K<sub>3</sub>PO<sub>4</sub> played an important role to promote the reaction, we

further investigated the promotion of catalytic reactions by other bases or salts (Table 1, entries 7-13). With the carbonate additive, the chemoselectivity to E1 was sharply decreased accompany with moderate activity; interestingly, with the alkali metal hydroxide additive, the chemoselectivity almost completely switched to D1 with good to excellent catalytic activity; moreover, with other additives like CH<sub>3</sub>COONa or CaCl<sub>2</sub>, both the activity and the chemoselectivity were rather low. Considering catalytic activity and chemoselectivity were always very sensitive to the solvent used in heterogeneous catalysis,[51-53] different solvents were investigated (Table 1, entries 14-16). Only aniline was detected with DMF instead of acetonitrile, just 9% E1 was obtained when acetonitrile was replaced with H<sub>2</sub>O. The chemoselectivity to E1 was substantially maintained with significantly reduced reactivity when benzyl alcohol displaced acetonitrile.

In order to acquire a deeper understanding of the role of light in the reaction, we investigated the effect of wavelength on one-pot hydrogenation and N-alkylation. The catalytic activity was generally maintained with the irradiation of UV, white or green LEDs (Table 1, entries 17-19). However, the chemoselectivity of E1 was significantly decreased to 46.3% with UV. The catalytic reaction gave 82.2% E1 chemoselectivity under the irradiation of green LED. In comparison with 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C, 3% Pt/D-TiO<sub>2</sub>@C exhibited lower photocatalytic activity accompanied with decreased chemoselectivity (60.0%) to E1 with K<sub>3</sub>PO<sub>4</sub> and 75.5% chemoselectivity to D1 with KOH (Table 1, entries 20 and 21). The above results indicated that the combination of Ti<sub>3</sub>C, TiO<sub>2</sub>, and Pt NPs together to form heterojunction, with Ti<sub>3</sub>C acting as a transporter for electrons to inhibit the backward diffusion of electrons, significantly improved nitrobenzene and benzyl alcohol one-pot hydrogenation and N-alkylation. The 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> catalyst could be recovered by simple centrifugation and acetonitrile washing followed by vacuum drying. No significant photocatalytic activity and chemoselectivity decrease was observed after recycling for five times in Figure 6. Additionally, no Pt

		· · · · · · · · · · · · · · · · · · ·	+	↓ + +		
	A1 B1	C1	D1	E1	F	
Entry	Catalyst	A1 conv. (%)	C1 sel. (%)	D1 sel. (%)	E1 sel. (%)	F (µmol)
1	-	-	-	-	-	-
2	D-TiO <sub>2</sub> /Ti <sub>3</sub> C	-	-	-	-	-
3 <sup>a</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	36.0	81.0	9.0	10.0	51
4	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	100.0	0.1	6.9	93.0 <sup>b</sup>	95
5 <sup>c</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	30.6	6.6	17.4	76.0	117
6 <sup>d</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	-	-	-	-	-
7 <sup>e</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	70.2	23.1	12.0	35.1	75
$8^{\mathrm{f}}$	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	75.0	16.2	72.0	11.8	85
9 <sup>g</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	96.7	1.2	95.0 <sup>h</sup>	3.8	86
$10^{i}$	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	81.0	5.4	89.5	5.1	80
$11^{j}$	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	29.0	0.5	13.6	15.0	78
$12^k$	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	17.6	25.0	68.2	6.8	62
13 <sup>1</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	7.2	6.2	0.3	0.7	29
14 <sup>m</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	100.0	100.0	-	-	64
15 <sup>n</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	100.0	91.0	-	9.0	91
16 <sup>o</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	12.4	-	15.4	84.6	153
17 <sup>p</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	95.5	34.9	18.8	46.3	97
18 <sup>q</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	90.0	5.5	12.3	82.2	86
19 <sup>r</sup>	3%Pt/D-TiO <sub>2</sub> /Ti <sub>3</sub> C	83.6	10.8	18.2	71.0	90
20	3%Pt/D-TiO2@C	75.5	14.2	25.8	60.0	89
21 <sup>g</sup>	3%Pt/D-TiO <sub>2</sub> @C	80.2	-	75.5	24.5	93

**TABLE 1** Visible-light-induced catalytic performance for one-pot hydrogenation and *N*-alkylation of nitrobenzene with benzyl alcohol over Pt nanoparticles on N and S co-doped  $TiO_2/MX$ ene  $Ti_3C_2$  heterojunctions

*Note*: Reaction conditions: nitrobenzene (0.5 mmol),  $K_3PO_4$  (0.5 mmol), and solvent (benzyl alcohol 1 ml, acetonitrile 4 ml) were stirred magnetically under  $H_2$  (1 atm) in a reaction tube in the presence of Pt NPs on N, S co-doped TiO<sub>2</sub>/MXene Ti<sub>3</sub>C<sub>2</sub> heterojunctions catalysts (substrate: Pt = 300) for 24 h, TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>: the the doping, 0.75 W cm<sup>-2</sup> blue LED (460 nm), "-" = no product or negligible product.

<sup>a</sup>No K<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup>TOF based on 10 h yield was 13.5  $h^{-1}$ .

<sup>c</sup>N<sub>2</sub> instead of H<sub>2</sub>.

<sup>d</sup>Dark.

<sup>e</sup>K<sub>2</sub>CO<sub>3</sub> instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>f</sup>Cs<sub>2</sub>CO<sub>3</sub> instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>g</sup>KOH instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>h</sup>TOF based on 10 h yield was 19.8  $h^{-1}$ .

<sup>i</sup>NaOH instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>j</sup>LiOH instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>k</sup>CH<sub>3</sub>COONa instead of K<sub>3</sub>PO<sub>4</sub>. <sup>l</sup>CaCl<sub>2</sub> instead of K<sub>3</sub>PO<sub>4</sub>.

<sup>m</sup>DMF instead of acetonitrile.

<sup>n</sup>H<sub>2</sub>O instead of acetonitrile.

<sup>o</sup>Benzyl alcohol instead of acetonitrile.

<sup>p</sup>UV LED (400 nm).

<sup>q</sup>White LED.

<sup>r</sup>Green LED (517 nm).



**FIGURE 6** Cycling visible-light-induced one-pot hydrogenation and *N*-alkylation of nitrobenzene with benzyl alcohol over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> in the presence of K<sub>3</sub>PO<sub>4</sub> or KOH. The reaction conditions were the same as in Table 1, K<sub>3</sub>PO<sub>4</sub> for the synthesis of E1, KOH for the synthesis of D1

loss was detected with inductively coupled plasma optical emission spectrometry (ICP-OES). Many excellent studies have been reported on alcohols *N*-alkylation, and it is necessary to compare our work with these reports (Table S1). When compared with traditional thermal catalysis (Table S1, entries 1–2), photocatalytic *N*alkylation could achieve high catalytic activity under mild conditions (Table S1, entries 3–6). Recently, the reaction substrate could be extended from aniline to nitrobenzene (Table S1, entries 5–6). Furthermore, the *N*alkylation chemoselectivity could be easily switched by adjust the base additive in this study.

In the visible-light-induced 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C catalytic system, the tandem reaction of aromatic nitro compounds with alcohols to form N-alkylamines or Nbenzylideneanilines could also be extended to various substrates (Table 2). Aromatic nitro compounds having different substituents could be reacted with benzyl alcohol to prepare N-alkylamines or N-benzylideneanilines on the irradiated 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C with good to excellent activity and chemoselectivity. In comparison with nitrobenzene, aromatic nitro compounds with different substituents generally had a good catalytic activity; the electron-donating group on the aromatic nitro compound was more favorable for catalytic activity than the electron-withdrawing group (Table 2, entries 3-12 vs. 13-18). When the aromatic nitro compounds had methyl substituent (Table 2, entries 3-8), the reactivity order, onitrotoluene < *m*-nitrotoluene < *p*-nitrotoluene, should be owing to the steric hindrance effect. Nitroanisole with stronger electron-donating effect than nitrotoluene exhibited higher catalytic activity (Table 2, entries 9-12). For the electron-withdrawing group substituted nitrobenzene, the steric hindrance on the aromatic ring also had a significant effect on the catalytic activity (Table 2, entries 13and 14 vs. 15 and 16). Similar to the law of catalytic reactivity, substrates with electron-donating groups tended to be lower than substrates with electronwithdrawing groups in the chemoselectivity of one-pot hydrogenation and N-alkylation (Table 2, entries 13-16). On the other hand, the steric hindrance had a significant effect on the chemoselectivity, and the ortho-substituted nitrobenzenes had overall lower chemoselectivity to corresponding N-alkylamines or N-benzylideneanilines (Table 2, entries 3 and 4, 9 and 10, and 13 and 14). Various benzyl alcohols could react with nitrobenzene synthesis corresponding N-alkylamines or Nto benzylideneanilines with good to excellent catalytic performance over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C (Table 2, entries 19-24). The one-pot hydrogenation and N-alkylation activity of the substituted benzyl alcohols was universally maintained, but the chemoselectivity was generally decreased (Table 2, entries 19-24). It is worth mentioning that 91.0% chemoselectivity to N-alkylamine and 93.4% chemoselectivity to N-benzylideneaniline were achieved with *p*-methylbenzyl alcohol (Table 2, entries 21 and 22). When 2-phenylethyl alcohol and 1-phenylethyl alcohol were used as substrates, the activity and chemoselectivity of the catalytic reaction could also be well maintained (Table 2, entries 25, 27, 28, and 30). One-pot hydrogenation and N-alkylation could also be carried out using nitrobenzene and butanol as the substrate with moderate to good catalytic activity and chemoselectivity (Table 2, entries 31 and 32).

In order to gain insight view about how the catalytic system achieved highly efficient activation under the visible-light irradiation, we employed the in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to dynamically observe and analyze the primary difference in activation of the catalytic system over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> and 3%Pt/D-TiO<sub>2</sub>@C with visiblelight irradiation or heating (Figure 7). The baseline spectrum was tested before light irradiation or heating. The following characteristic peaks weakening were obviously observed in the DRIFTS between light irradiation and heating, such as the absorption of the telescopic vibration of the C–O bond in benzyl alcohol at about  $1000 \text{ cm}^{-1}$ , the absorption of the in-plane deformation vibration of hydroxyl group benzyl alcohol around 1200 cm<sup>-1</sup>, and the absorption peak of the symmetrical stretching vibration as well as asymmetric stretching vibration of nitro group in nitrobenzene around 1500 and 1620  $\text{cm}^{-1}$ , respectively.<sup>[54,55]</sup> Meanwhile, the absorption between 3000 and 3700  $\text{cm}^{-1}$  was a telescopic vibration of the hydroxyl group. In the presence of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>

**TABLE 2** Visible-light-induced catalytic performance for one-pot hydrogenation and *N*-alkylation of aromatic nitro compounds with alcohols over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C

$R^{1}-NO_{2} + R^{2}$ OH $\longrightarrow$ $R^{1}-NH_{2} + R^{2}$ $N$ $R^{1} + R^{2}$ $N$ $R^{1} + R^{2}$ CHO										
	A B	с	D	E F						
Entry	Substrates A/B	A conv. (%)	C sel. (%)	D sel. (%)	E sel. (%)	F (µmol)				
1	Nitrobenzene/benzyl alcohol	100.0	0.1	6.9	93.0	95				
2 <sup>a</sup>	Nitrobenzene/benzyl alcohol	96.7	1.2	95.0	3.8	86				
3	o-Nitrotoluene/benzyl alcohol	98.1	16.6	12.1	71.3	110				
4 <sup>a</sup>	o-Nitrotoluene/benzyl alcohol	85.0	-	81.0	19.0	109				
5	<i>m</i> -Nitrotoluene/benzyl alcohol	99.5	-	10.0	90.0	93				
6 <sup>a</sup>	<i>m</i> -Nitrotoluene/benzyl alcohol	97.2	0.2	97.7	2.1	105				
7	<i>p</i> -Nitrotoluene/benzyl alcohol	100.0	-	9.0	91.0	90				
8 <sup>a</sup>	p-Nitrotoluene/benzyl alcohol	100.0	-	90.0	10.0	99				
9	2-Nitroanisole/benzyl alcohol	99.5	19.6	12.6	67.8	89				
10 <sup>a</sup>	2-Nitroanisole/benzyl alcohol	86.1	2.0	80.0	18.0	95				
11	4-Nitroanisole/benzyl alcohol	100.0	-	5.0	95.0	96				
12 <sup>a</sup>	4-Nitroanisole/benzyl alcohol	100.0	-	92.2	7.8	100				
13	o-Chloronitrobenzene/benzyl alcohol	83.0	21.7	20.5	57.8	81				
14 <sup>a</sup>	o-Chloronitrobenzene/benzyl alcohol	95.1	1.0	85.5	13.5	98				
15	p-Chloronitrobenzene/benzyl alcohol	93.5	-	20.0	80.0	85				
16 <sup>a</sup>	p-Chloronitrobenzene/benzyl alcohol	99.5	-	97.5	2.5	99				
17	p-Fluoronitrobenzene/benzyl alcohol	98.1	16.6	12.1	71.3	93				
$18^{\mathrm{a}}$	p-Fluoronitrobenzene/benzyl alcohol	90.9	0.5	80.0	19.5	101				
19	Nitrobenzene/o-methylbenzyl alcohol	98.0	8.3	10.0	81.7	89				
$20^{a}$	Nitrobenzene/o-methylbenzyl alcohol	96.0	0.2	77.2	22.6	96				
21	Nitrobenzene/p-methylbenzyl alcohol	99.0	1.0	8.0	91.0	85				
22 <sup>a</sup>	Nitrobenzene/p-methylbenzyl alcohol	98.1	3.0	93.4	3.6	89				
23	Nitrobenzene/p-methoxybenzyl alcohol	99.0	1.0	6.0	93.0	90				
24 <sup>a</sup>	Nitrobenzene/p-methoxybenzyl alcohol	96.3	5.6	60.3	34.1	108				
25	Nitrobenzene/2-phenylethyl alcohol	100.0	-	12.0	88.0	51				
26 <sup>a</sup>	Nitrobenzene/2-phenylethyl alcohol	100.0	0.6	99.0	0.4	66				
27	Nitrobenzene/1-phenylethyl alcohol	100.0	3.0	16.0	81.0	69				
28 <sup>a</sup>	Nitrobenzene/1-phenylethyl alcohol	93.0	6.0	90.0	4.0	72				
29	Nitrobenzene/N-butanol	78.0	5.5	16.5	78.0	19				
30 <sup>a</sup>	Nitrobenzene/N-butanol	100.0	22.7	76.3	1.0	36				

*Note*: The reaction conditions were the same as in Table 1, entry 4.  ${}^{a}$ KOH instead of K<sub>3</sub>PO<sub>4</sub>.

catalyst at 50°C, telescopic vibration of the C–O bond, the in-plane deformation vibration of hydroxyl group, the stretching vibration of nitro group, and the telescopic vibration of hydroxyl group gradually decreased with the increase of heating time, which should be related to the

substrate catalytic activation. On the other hand, the decrease in the C–O bond telescopic vibration, hydroxyl group in-plane deformation vibration, nitro group stretching vibration, and hydroxyl group telescopic vibration with visible-light irradiation at  $25^{\circ}$ C was much



10 of 12

FIGURE 7 In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra for one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> and 3%Pt/D-TiO<sub>2</sub>@C under visible-light irradiation or heating

faster than heating. When comparing the visible-light illumination with heating in the catalyst system, the activation efficiency of visible-light irradiation promotion in either the benzyl alcohol dehydrogenation or the nitro group reduction was much faster than that of heating, which should also be the key reason for the evident selective N-alkylation catalytic efficiency improvement under visible-light irradiation; 3%Pt/D-TiO2@C catalyst was also tested under similar conditions. Without the Ti<sub>3</sub>C electron transporter, some difference in substrate activation was observed. Such as, the decrease in symmetrical stretching vibration of nitro group in nitrobenzene became not that obvious accompany with the hydroxyl group telescopic vibration frequency reduction, which indicated the decrease in the nitro group reduction activation.

Up on above observations, photo-induced one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol over 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> was proposed (Scheme 1). D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> could be excited to generate electrons and holes under visible-light irradiation. Charge short-range directional transmission construction with the assistance of electron transporter Ti<sub>3</sub>C along with metal NPs supported on  $D-TiO_2/Ti_3C_2$  could lead to efficient electron transfer from excited D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> to metal NPs.<sup>[37,56]</sup> The formation of electron-rich Pt specie was achieved by the transfer of photogenerated electrons to Pt nanoparticles after visible-light irradiation of 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> (①); conversion of benzyl alcohol to benzaldehyde undergone electron transfer from benzyl alcohol to the D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> along with benzyl alcohol activation (2) follow up with oxidant-free C-H bond cleavage to form benzaldehyde (3). Hydrogen from both



SCHEME 1 Proposed mechanism for visible-light-induced catalytic performance of one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol over 3%Pt/D-TiO2/Ti3C

benzyl alcohol and the H-H bond cleavage (④) was transferred to electron-rich Pt to form Pt hydride, and then the selective hydrogenation of nitro was achieved (③). Imine was formed through the condensation between in situ generated benzaldehyde and aniline (6). Imine could be further hydrogenated to N-alkyl amine with Pt hydride (⑦). The interesting chemoselectivity switch to imine or N-alkyl amine with KOH or K<sub>3</sub>PO<sub>4</sub> base additive might be related to the Pt hydride hydrogenation ability adjusted by the basicity of photocatalytic system.

#### CONCLUSIONS 3

Two-dimensional transition metal carbide/carbonitridederived 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterojunction was prepared by in situ grew TiO<sub>2</sub> on Ti<sub>3</sub>C<sub>2</sub> nanosheets, S and N codoped TiO<sub>2</sub> with thiourea, and then Pt nanoparticles with small diameter well dispersed on D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>; 3%Pt/D-TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> showed excellent photocatalytic activity and chemoselectivity in the tandem reactions between aromatic nitro compounds and alcohols. Interestingly, the chemoselectivity to N-alkyl amines Nor benzylideneanilines could be easily switched by adjust the Pt hydride hydrogenation ability through the base additive change from K<sub>3</sub>PO<sub>4</sub> to KOH under visible-light irradiation. In contrast, 3%Pt/D-TiO2@C exhibited sharply decreased activity and chemoselectivity to Nalkyl amines or N-benzylideneanilines. The photocatalytic performance difference was owing to the improvement in photogenerated electron and hole

separation efficiency by means of short-range directional charge transmission caused by the intimate contact between the  $TiO_2$  and the conductive  $Ti_3C_2$ . This work established a highly efficient way to realize both *N*-alkyl amines and *N*-benzylideneanilines via a successful coupling of the 2D transition metal carbide/carbonitride-based photocatalysis,  $Ti_3C_2$  based short-range directional charge transmission, metal NP-based multistep hydrogenation, and base additive-based Pt hydride hydrogenation ability adjustment. In situ DRIFTS spectra further verified that the substrates activation with visible-light irradiation at 25°C was much faster than heating in one-pot hydrogenation and *N*-alkylation reaction.

## ACKNOWLEDGMENTS

This work was financially supported by Natural Science Foundation Project of Chongqing (No. cstc2018jcyjAX0735, cstc2019jcyj-msxmX0641, cstc2015jcyjBX0031), Venture & Innovation Support Program for Chongqing Overseas Returnees (No. cx2020113), National Natural Science Foundation of China (No. 21201184), Ministry of Education of Chongqing (No. KJQN201900811), Chongqing Technology and Business University (950119090) and Chongqing Key Laboratory of Catalysis and New Environmental Materials (KFJJ2019082), Key Disciplines of Chemical Engineering and Technology in Chongqing Colleges and Universities during the 13th Five Year Plan and Innovation Group of New Technologies for Industrial Pollution Control of Chongqing Education Commission (CXQT19023).

## AUTHOR CONTRIBUTIONS

**Heyan Jiang:** Conceptualization; data curation; funding acquisition; supervision. **Meilin Sheng:** Formal analysis; methodology; software; validation. **Yue Li:** Formal analysis; investigation; software; validation. **Shuzhen Kong:** Funding acquisition; supervision. **Fengxia Bian:** Funding acquisition; supervision.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## ORCID

Heyan Jiang https://orcid.org/0000-0003-1239-7861 Meilin Sheng https://orcid.org/0000-0001-9394-5713 Yue Li https://orcid.org/0000-0002-4318-8037 Shuzhen Kong https://orcid.org/0000-0002-7512-8119 Fengxia Bian https://orcid.org/0000-0001-9328-648X

## REFERENCES

C. J. Clarke, W. C. Tu, O. Levers, A. Bröhl, J. P. Hallett, *Chem. Rev.* 2018, 118, 747.

- [2] B. M. Trost, Science 1991, 254, 1471.
- [3] M. Zhaleh, A. Zangeneh, S. Goorani, N. Seydi, M. M. Zangeneh, R. Tahvilian, E. Pirabbasi, *Appl. Organomet. Chem.* 2019, 33, e5015.
- [4] H. Jiang, J. Xu, S. Zhang, H. Cheng, C. Zang, F. Bian, *Catal. Sci. Technol.* 2021, 11, 219. https://doi.org/10.1039/D0CY01881C
- [5] H. Jiang, J. Xu, B. Sun, Appl. Organomet. Chem. 2018, 32, e4260.
- [6] P. Kalck, M. Urrutigoïty, Chem. Rev. 2018, 118, 3833.
- [7] S. Abednatanzi, P. G. Derakhshandeh, H. Depauw, F. X. Coudert, H. Vrielinck, P. Van Der Voort, K. Leus, *Chem. Soc. Rev.* 2019, 48, 2535.
- [8] X. F. Yuan, Z. J. Wan, J. J. Ning, Q. Zhang, J. Luo, Appl. Organomet. Chem. 2020, 34, e5897.
- [9] R. Sarkar, A. Gupta, R. Jamatia, A. K. Pal, Appl. Organomet. Chem. 2020, 34, e5646.
- [10] S. Zhang, J. Xu, H. Cheng, C. Zang, B. Sun, H. Jiang, F. Bian, *Appl. Catal. A* **2020**, *596*, 117536.
- [11] D. Rhodes, S. H. Chae, R. Ribeiro-Palau, J. Hone, Nat. Mater. 2019, 18, 541.
- [12] Q. Peng, J. Guo, Q. Zhang, J. Xiang, B. Liu, A. Zhou, R. Liu, Y. Tian, J. Am. Chem.Soc. 2014, 136, 4113.
- [13] J. Zhang, K. H. Cao, X. Zhang, Q. T. Zhang, Appl. Organomet. Chem. 2020, 34, e5377.
- [14] M. Ming, Y. Ren, M. Hu, Y. Zhang, T. Sun, Y. Ma, X. Li, W. Jiang, D. Gao, J. Bi, G. Fan, *Appl. Catal. B* 2017, 210, 462.
- [15] S. Shi, B. Qian, X. Wu, H. Sun, H. Wang, H. Zhang, Z. Yu, T. P. Russell, Angew. Chem., Int. Ed. 2019, 58, 18171.
- [16] F. Hajlaoui, N. Audebrand, T. Roisnel, N. Zouari, Appl. Organomet. Chem. 2020, 34, e5293.
- [17] H. Jiang, C. Zang, Y. Zhang, W. Wang, C. Yang, B. Sun, Y. Shen, F. Bian, *Catal. Sci. Technol.* **2020**, *10*, 5964.
- [18] G. Y. Fan, X. J. Li, C. L. Xu, W. D. Jiang, Y. Zhang, D. J. Gao, J. Bi, Y. Wang, *Nanomaterials* **2018**, *8*, 141.
- [19] B. Anasori, M. R. Lukatskaya, Y. Gogotsi, Nat. Rev. Mater. 2017, 2, 16098.
- [20] X. Chia, M. Pumera, Nat. Catal. 2018, 1, 909.
- [21] T. Su, R. Peng, Z. D. Hood, M. Naguib, I. N. Ivanov, J. K. Keum, Z. Qin, Z. Guo, Z. Wu, *ChemSusChem* 2018, *11*, 688.
- [22] Z. Nasresfahani, M. Z. Kassaee, Appl. Organomet. Chem. 2020, 34, e6032.
- [23] M. Ghanimati, M. A. Senejani, T. M. Isfahani, M. A. Bodaghifard, Appl. Organomet. Chem. 2018, 32, e4591.
- [24] Q. Yang, Q. F. Wang, Z. K. Yu, Chem. Soc. Rev. 2015, 44, 2305.
- [25] A. Bartoszewicz, G. G. Miera, R. Marcos, P. O. Norrby, B. Martín-Matute, ACS Catal. 2015, 5, 3704.
- [26] M. C. Bryan, P. J. Dunn, D. Entwistle, F. Gallou, S. G. Koenig, J. D. Hayler, M. R. Hickey, S. Hughes, M. E. Kopach, G. Moine, P. Richardson, F. Roschangar, A. Steven, F. J. Weiberth, *Green Chem.* **2018**, *20*, 5082.
- [27] T. Irrgang, R. Kempe, Chem. Rev. 2019, 119, 2524.
- [28] H. Cheng, X. Long, F. Bian, C. Yang, X. Liu, H. Jiang, J. Catal. 2020, 389, 121.
- [29] Y. Shiraishi, K. Fujiwara, Y. Sugano, S. Ichikawa, T. Hirai, ACS Catal. 2013, 3, 312.
- [30] L. N. Zhang, Y. Zhang, Y. Q. Deng, F. Shi, Catal. Sci. Technol. 2015, 5, 3226.
- [31] D. Stíbal, J. Jacinto Sá, J. A. V. Bokhoven, *Catal. Sci. Technol.* 2013, *3*, 94.

## 12 of 12 WILEY Organometallic Chemistry

- [32] D. Wang, Z. Li, J. Catal. 2016, 342, 151.
- [33] D. Wang, Y. Pan, L. Xu, Z. Li, J. Catal. 2018, 361, 248.
- [34] B. Wang, Z. Deng, X. Fu, C. Xu, Z. Li, Appl. Catal. B 2018, 237, 970.
- [35] B. Chen, L. Wang, S. Gao, ACS Catal. 2015, 5, 5851.
- [36] C. Peng, X. F. Yang, Y. H. Li, H. Yu, H. J. Wang, F. Peng, ACS Appl. Mater. Inter. 2016, 8, 6051.
- [37] Y. Xu, S. Wang, J. Yang, B. Han, R. Nie, J. Wang, J. Wang, H. Jing, Nano Energy 2018, 51, 442.
- [38] G. Y. Fan, X. J. Li, Y. L. Ma, Y. Zhang, J. T. Wu, B. Xu, T. Sun, D. J. Gao, J. Bi, *New J. Chem.* **2017**, *41*, 2793.
- [39] Q. Liu, L. Ai, J. Jiang, J. Mater. Chem. A 2018, 6, 4102.
- [40] T. Umebayashi, T. Yamaki, H. Itoh, K. Asa, Appl. Phys. Lett. 2002, 81, 454.
- [41] Q. Yang, C. Xie, Z. Xu, Z. Gao, Y. Du, J. Phys. Chem. B 2005, 109, 5554.
- [42] K. Takeshita, A. Yamakata, T. Ishibashi, H. Onishi, K. Nishijima, T. Ohno, J. Photoch. Photobio. A 2006, 177, 269.
- [43] J. I. Chen, E. Loso, N. Ebrahim, G. A. Ozin, J. Am. Chem. Soc. 2008, 130, 5420.
- [44] B. Y. Xia, B. Wang, H. B. Wu, Z. Liu, X. Wang, X. W. Lou, J. Mater. Chem. 2012, 22, 16499.
- [45] Y. Wei, J. Jiao, Z. Zhao, W. Zhong, J. Li, J. Liu, G. Jiang, A. Duan, J. Mater. Chem. A 2015, 3, 11074.
- [46] D. Ma, Y. Xin, M. Gao, J. Wu, Appl. Catal. B 2014, 147, 49.
- [47] Z. Huang, Z. Gao, S. Gao, Q. Wang, Z. Wang, B. Huang, Y. Dai, *Chinese J. Catal.* 2017, 38, 821.
- [48] P. Dhanasekaran, S. V. Selvaganesh, S. D. Bhat, J. Power, Sources 2016, 304, 360.

- [49] W. Yuan, L. Cheng, Y. Zhang, H. Wu, S. Lv, L. Chai, X. Guo, L. Zheng, Adv. Mater. Interfaces 2017, 4, 1700577.
- [50] S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. D. Valentin, G. Pacchioni, J. Am. Chem. Soc. 2006, 128, 15666.
- [51] H. Jiang, C. Yang, C. Li, H. Fu, H. Chen, R. Li, X. Li, Angew. Chem., Int. Ed. 2008, 47, 9240.
- [52] J. Xu, S. Zhang, X. Liu, F. Bian, H. Jiang, Catal. Sci. Technol. 2019, 9, 6938.
- [53] H. Jiang, X. Zheng, Catal. Sci. Technol. 2015, 5, 3728.
- [54] R. Cano, M. Yus, D. J. Ramón, Tetrahedron 2011, 67, 8079.
- [55] S. Zhang, J. Xu, H. Cheng, C. Zang, F. Bian, B. Sun, Y. Shen, H. Jiang, *ChemSusChem* **2020**, *13*, 5264.
- [56] D. R. Sun, W. J. Liu, Y. H. Fu, Z. X. Fang, F. X. Sun, X. Z. Fu, Y. F. Zhang, Z. H. Li, *Chem. – Eur. J.* **2014**, *20*, 4780.

## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: H. Jiang, M. Sheng, Y. Li, S. Kong, F. Bian, *Appl Organomet Chem* **2021**, e6291. https://doi.org/10.1002/aoc.6291