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## Pd-Cu alloy nanoparticle supported on amine-terminated ionic liquid functional 3D graphene and its application on Suzuki cross-coupling reaction

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#### **Funding information**

Laboratory of Green Chemistry and Chemical Processes; Science and Technology Commission of Shanghai Municipality, Grant/Award Number: 18DZ1112700 Well distributed Pd-Cu bimetallic alloy nanoparticles supported on amineterminated ionic liquid functional three-dimensional graphene (3D IL-rGO/ Pd-Cu) as an efficient catalyst for Suzuki cross-coupling reaction has been prepared via a facile synthetic method. The introduction of IL-NH<sub>2</sub> cations on the surface of graphene sheets can effectively avoid the re-deposition of graphene sheets, allowing the catalyst to be reused up to 10 cycles. The addition of Cu not only saves cost but also ensures high catalytic efficiency. It is worthy to note that the catalyst 3D IL-rGO/Pd2.5Cu2.5 can efficiently catalyze the Suzuki cross-coupling reaction with the yield up to 100% in 0.25 h, almost one-fold higher than that by the pristine IL-rGO/Pd<sub>2.5</sub> catalyst (52%). The Powder X-Ray Diffraction (XRD), combining energy dispersive X-ray spectroscopy (EDS) mapping results confirm the existence and distribution of Pd and Cu in the bimetallic nanoparticles. The transmission electron microscopy (TEM) reveals the nanoparticle size with an average diameter of  $3.0 \pm 0.5$  nm. X-ray photoelectron spectroscopy (XPS) analysis proved the presence of electron transfer from Cu to Pd upon alloying. Such alloying-induced electronic modification of Pd-Cu alloy and 3D ionic liquid functional graphene with large specific surface area both accounted for the catalytic enhancement.

### KEYWORDS

amine-terminated ionic liquid, graphene, Pd-cu alloy, Suzuki, three-dimensional

## **1** | INTRODUCTION

The Suzuki cross-coupling reaction has received worldwide attention as one of the most useful and popular carbon–carbon bond forming reactions due to its tolerance of a diverse range of functional groups and its non-toxic by-products.<sup>[1]</sup> In the early stage, the Suzuki cross-coupling reaction is carried by using various phosphine ligand/palladium catalyzed complexes, which may have side effects on product and environmental quality.<sup>[2]</sup> Afterwards, ligand-free Pd catalysts play an important role in Suzuki cross-coupling reaction. Although the toxicity is greatly reduced, the separation and reusability of catalyst remains as a pressing issue which impede the development toward a greener, more friendly and more sustainable chemical industry to some extent. Hence, it is profoundly significant to develop heterogeneous catalysts with high efficiency and durability.

Many materials with high surface area, such as metal oxide, silica, activated carbon, zeolites, polymers, have been applied to support Pd metal nanoparticles in the recent years.<sup>[3]</sup> With the rise of new carbon materials, graphene is regarded as an ideal model loaded metal for catalysis attributed to its special structure, large surface

area, acid and alkali resistance, and high temperature resistance.<sup>[4]</sup> It is proved that the graphene-based catalysts not only increase the nanosized catalyst surface area for electron transport but also provide better mass transport of reactants to catalysts.<sup>[5]</sup> Recently, Yang et al. finds that the graphene support also act as both an efficient charge donor and acceptor in oxidation and reduction reaction steps of Suzuki cross-coupling reaction.<sup>[6]</sup> However, graphene also has its shortcoming as a support. Single layer of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb crystal structure may lead to its stacking via the strong van der Waals interaction consisting in graphene sheets. This would cause a series of problems such as hindered mass transfer of the catalyst and agglomeration of the active components.<sup>[7]</sup> Our precious research has introduced ionic liquids to synthesize 3D self-assembled modified Pd/graphene materials.<sup>[8]</sup> A nucleophilic ring-opening reaction between the epoxy groups of GO and the amine groups of 1-(3aminopropyl)-3-methylimidazolium bromide (IL-NH<sub>2</sub>) is easily occurred to form the IL-modified graphene. The cations of IL-NH<sub>2</sub> introduced to the surface of graphene sheets can avoid the restacking of graphene sheets efficiently. Meanwhile, the functional graphene modified by ionic liquid retains its inherent physicochemical properties and has a higher specific surface area, providing more anchor sites for the metals.

Although the 3D IL-rGO/Pd catalyst shows good catalytic performance and cyclability, the expensive price and low earth abundance of Pd is still a non-negligible cost issue. There is an urgent need to develop substitutes for pure Pd catalysts. Pd-based bimetallic alloy NPs catalysts, such as Pd-Rh, Pd-Ru, Pd-Cu, Pd-Co or Pd-Ni, as a kind of important catalyst attracts researchers' interests immensely.<sup>[9]</sup> Kim et al. prepared Pd/C and Pd-M/C catalysts (M = Cu, Ag, Ni) by  $\gamma$ -ray at room temperature without any reducing agent.<sup>[10]</sup> Lv et al. used NaBH<sub>4</sub> as a reducing agent to reduce the metal salts of Pd and Cu by one-step wet chemical method, a Pd-Cu nanowire (Pd-Cu NWs) bimetallic catalyst was synthesized.<sup>[11]</sup> Compared to monometallic Pd, bimetallic systems still shows superior catalytic performance because of significant synergic and cooperative interactions between the individual metal components.

Herein, we first report the successful synthesis of the ionic liquid functional 3D graphene supported Pd-Cu alloy NPs (3D IL-rGO/Pd-Cu) composite by a mild chemical reduction with ascorbic acid. Composition of Pd-Cu alloy nanoparticles can be controlled by simply tuning the ratio of metal precursors. A series of catalysts were characterized by XRD, TEM, XPS, HRTEM, ICP-AES to study the existance and interaction of Pd and Cu. The experimental results show that the catalyst 3D IL-rGO/  $Pd_{2.5}Cu_{2.5}$  has the superior catalytic activity with high stability and low cost.

# 2 | GENERAL EXPERIMENTAL DETAILS

### 2.1 | Materials

Graphite powder (1200 mesh), Sulfuric acid ( $H_2SO_4$ ), Potassium permanganate (KMnO<sub>4</sub>), hydrogen peroxide ( $H_2O_2$ ), Sodium tetrachlopalladate (Na<sub>2</sub>PdCl<sub>4</sub>, 98%), Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, AR), KOH (AR) and Na<sub>2</sub>CO<sub>3</sub> (AR) are purchased from Aladdin Reagent Co., Ltd. 1-(3-aminopropyl)-3-methylimidazolium bromide (NH<sub>2</sub>-IL, 97%) is acquired from Shanghai Cheng Jie Chemical Co., Ltd. L-ascorbic acid is obtained from Sinopharm Chemical Reagent Co., Ltd. All the organic substrates are supplied from Sinopharm Chemical Reagent Co., Ltd and Aladdin Reagent Co., Ltd. The remaining materials are available from local suppliers. All chemicals in this work were used as received. Deionized water was used for the preparation of various solutions throughout the entire study.

### 2.2 | Instrumentation

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were monitored with a Thermo Scientific iCAP 6300 instrument. The Powder X-Ray Diffraction (XRD) patterns were collected using a Bruker AXS D8 diffractometers (Cu K $\alpha$ ,  $\lambda = 0.15406$  nm) by scanning over the range of  $10^{\circ}$  to  $80^{\circ}$  in  $2\theta$  at a scanning speed of 15°·min<sup>-1</sup>. Raman Spectroscopy was tested on Thermo DXR with 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) results were measured on a Versaprobe Phi 5000 ULVAC-PHI spectrometer with an Al Ka (1486.6 eV) radiator. Infrared spectra results were collected on a NEXUS 670 Fourier transform infrared (FTIR) spectrometer. Transmission electron microscopy (TEM), Xray energy dispersive spectroscopy (EDS), and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) were all conducted on a JEM-2100F transmission electron microscope coupled with an energy dispersive X-ray spectrometer with an accelerating voltage of 200 kV and applied Mo grid as the substrate.

## 2.3 | Preparation of graphene oxide (GO)

GO was synthesized from natural graphite powder according to a modified Hummers' method.<sup>[12]</sup> Briefly, It required three stages. Stage I: Firstly, graphite powder

(5 g, 1200 mesh),  $K_2S_2O_8$  (2.5 g) and  $P_2O_5$  (2.5 g) were added into concentrated sulfuric acid (100 ml) under stirring at 80 °C about 6 h. Afterwards, the pre-oxidation product was washed with deionized water until the pH value is close to neutral. Then the product was drying under 50 °C for 12 h and was added to concentrated  $H_2SO_4$  (115 ml). KMnO<sub>4</sub> (15 g) was added slowly under stirring in an ice bath to keep the temperature of the suspension lower than 20 °C. Stage II: The reaction system was transferred to a 35 °C oil bath and stirred vigorously for 2 h. Then a dark green suspension formed. Subsequently, deionized water (800 ml) was added with a peristaltic pump (gathering speed slowly from 1 rpm to 70 rpm for 3 h) while the diluted suspension was further stirred. Stage III: H<sub>2</sub>O<sub>2</sub> (30 wt% 12.5 ml) was added into the mixture and the color of the solution turns bright yellow. The obtained product was centrifuged and washed with hydrochloric acid and deionized water several times. Finally, the aqueous suspension was dialysis for 7 days to remove metal ions and ultrasonicated for 30 min to form GO.

## 2.4 | Preparation of 3D IL-rGO/Pd-cu alloy aerogels

The 3D IL-rGO/Pd-Cu alloy aerogels was prepared using metal and GO co-reduction method. In a typical procedure, 20 mg GO was dissolved in 10 ml of deionized water, and sonicated for 30 min to assist dissolution. 32 mg IL-NH2 and 200 µL KOH (0.2 g/ml) were added into the GO solution. The result mixture was sonicated for less 30 min and kept at under 25 °C until a homogeneous and transparent solution formed. Next, both Na<sub>2</sub>PdCl<sub>4</sub> (10 mg/ml) and CuCl<sub>2</sub> (10 mg/ml) were added to the above solution and sonicated for 0.5 h followed with stirring overnight at the room temperature. (Different qualities of Pd-Cu were prepared by only changing the amount of metal solution. For example, Pd<sub>2.5</sub>Cu<sub>2.5</sub> (Pd 2.5 wt% Cu 2.5 wt%) were synthesized by using 84  $\mu$ L Na<sub>2</sub>PdCl<sub>4</sub> solution and 202  $\mu$ L CuCl<sub>2</sub> solution) And then 0.1 g L-ascorbic acid was added into the mixture and stirred for 30 min at room temperature. Afterwards, the mixture was kept at 90 °C for 3 h. Large amount of deionized water were used to wash the catalyst to remove the residual impurity. Last, the sample was freeze-dried into an aerogel for further use.

## 2.5 | Catalytic performance for Suzuki cross-coupling reactions

We have found that  $K_2CO_3$  exerts most effectively for the Suzuki cross-coupling reaction, superior to  $Na_2CO_3$ ,

KOH, CsCO<sub>3</sub> and other bases in our previous work.<sup>[8]</sup> Therefore, we adopted K<sub>2</sub>CO<sub>3</sub> as base for the Suzuki cross-coupling reaction. In a typical procedure, the Suzuki cross-coupling reactions are carried out in a 25 ml round-bottom flask under an air atmosphere. Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), as-synthesized 3D IL-rGO/Pd-Cu catalyst (10 mg) were well-dispersed in 25 ml EtOH-H<sub>2</sub>O (v/v = 4: 1, 25 ml) solution. Then the mixture was heated up to 80 °C in an oil bath for 15 min under stirring. After the reaction, the catalyst can be easily separated, then washed with ethanol and water, and finally freeze-dried for the next run. The product was extracted with ethyl acetate and dehydrated using anhydrous MgSO<sub>4</sub>. The reaction yield is analyzed by using a gas chromatograph (GC-2014, Shimadzu), which was calculated based on using n-dodecane as an internal standard.

## **3** | **RESULT AND DISSCUTION**

### 3.1 | Catalyst characterization

The crystal structures of 3D IL-rGO/Pd, 3D IL-rGO/Cu and 3D IL-rGO/Pd-Cu with different Pd Cu mass ratio were determined by XRD. As shown in Figure 1, no sharp and strong (0 0 2) diffraction peak at 10.8° demonstrated that pure graphene oxide has been deoxygenated via chemical reduction.<sup>[13]</sup>The appearance of broad diffractions at 24° (corresponding to d-spacing of 0.37) indicated the presence of more disordered stacking, less agglomeration of graphene sheets attributed to the insert of IL-NH<sub>2</sub> molecules.<sup>[14]</sup> The XRD peak corresponding to the (1 1 1),



**FIGURE 1** The XRD pattern of (a) 3D IL-rGO/Pd, (b) 3D IL-rGO/Pd<sub>4</sub>Cu<sub>1</sub>, (c) 3D IL-rGO/Pd<sub>3</sub>Cu<sub>2</sub>, (d) 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub>, (e) 3D IL-rGO/Pd<sub>2</sub>Cu<sub>3</sub>, (f) 3D IL-rGO/Pd<sub>1</sub>Cu<sub>4</sub> and (g) 3D IL-rGO/Cu.

 $(2\ 0\ 0)$  and  $(2\ 2\ 0)$  planes of the typical face-centered cubic (f c c) Pd lattices, respectively for 3D IL-rGO/Pd were seen at 40°, 46° and 68°.(JCPDS no. 05-0681) And the peak corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes of the typical face-centered cubic (f c c) Cu lattices for 3D IL-rGO/Cu were seen at 43.3°, 50.5° and 74.2°. (JCPDS no. 04-0836) (Figure 1 (a) and(g)) The series of 3D IL-rGO/Pd-Cu composites has only a single diffraction peak, located between the face centered cubic Pd (1 1 1) crystal plane. It presented that the 3D IL-rGO/Pd-Cu catalyst forms a solid-solution (alloy) structure.<sup>[15]</sup> It is worth mentioning that the diffraction angles are observed to be shifted toward the peak of the Cu (1 1 1) crystal plane of Cu gradually with the increase of Cu. (Figure 1 (b)-(f)) Moreover, the XRD data also clearly reflected the nanoparticle size increased with the addition of copper since Pd NPs had smaller dimensions of crystal than Cu.<sup>[16]</sup> According to the Debye-Scherrer formula the average crystallite sizes of nanoparticles supported on each catalyst can be calculated. From (a) to (g), the sizes were about 2.5 nm, 3.22 nm, 3.45 nm, 3.58 nm, 3.64 nm, 4.49 nm and 5.53 nm, which were consistent with the TEM results.

A transmission electron microscopy (TEM) image of the as-prepared 3D IL-rGO/Pd and 3D IL-rGO/Pd-Cu with different mass ratio is shown in Figure 2. It is easily discerned that graphene modified by ionic liquids can form a transparent layer structure with very few curling and agglomeration. From Figure 2(a)-(f), TEM with different magnification with different Pd Cu ratio all showed that metals can be evenly dispersed on the surface of the carrier with no significant difference. It indicated that the introduction of Cu did not lead to the agglomeration of metal particles. Meanwhile, the interaction of metal ions with defect points on IL-functionalized graphene provided favorable conditions for nucleation of metal nanoparticles, and this effect also effectively reduces the surface mobility of metal particles, enabling the metal to be uniformly supported on the carrier.<sup>[17]</sup> According to particle size analysis, average particle diameter from (a) to (f) were 2.56 nm, 2.67 nm, 2.78 nm, 3.0 nm, 3.57 nm and 4.16 nm. It was found that metal particles gradually increased respectively, which was due to the gradual introduction of Cu. The HRTEM image of 3D IL-rGO/ Pd, 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub>. and 3D IL-rGO/Cu were shown in Figure 3. The interplanar spacing of the single metal palladium catalyst 3D IL-rGO/Pd was 0.224 nm, which was consistent with the (1 1 1) crystal plane of the face centered cubic Pd. The interplanar spacing of the single metal copper catalyst 3D IL-rGO/Cu is 0.208 nm, which was corresponded to the (1 1 1) crystal plane of face-centered cubic Cu.<sup>[18]</sup> The interplanar spacing of the alloy catalyst rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> is 0.218 nm,

which is located between the interplanar spacing of the single metal palladium catalyst and the single metal copper catalyst, indicating that the lattice of the palladium copper alloying shrinks.<sup>[19]</sup>

X-ray photoelectron spectroscopy (XPS) measurements were used on 3D IL-rGO/Pd<sub>2</sub> <sub>5</sub>Cu<sub>2</sub> <sub>5</sub> catalysts to study their surface elemental composition and to investigate the chemical state of the Pd and Cu metals (Figure 4). In the wide energy spectrum of catalysts, three peaks at 286.7 eV, 401.6 eV and 542.3 eV are found obviously, which were attributed to C1s, N1 s and O1s, respectively. Other two peaks at 335.8 eV and 933.3 eV corresponded to Pd 3d and Cu 2p. From Figure 4(b), it can be seen that the C-C bonding of C1s peak (284.6 eV) was dominant, while the peak value of C(C=O, C (epoxy/ether)) was significantly reduced. The new peak at 285.9 eV is newly produced corresponded to C-N bonding. Moreover, the N1 s band is centered at 401.7 eV and the lower binding energy is 399.9 eV from Figure 4(c). These results were caused by the success of NH<sub>2</sub>-IL grafted graphene sheets.<sup>[20]</sup> From Figure 4(d), it was concluded by the detailed examination of the deconvoluted XPS spectra that Pd was found all in the metallic state ((336.2 eV, Pd  $3d_{5/2}$ ) and (341.5 eV, Pd  $3d_{3/2}$ )). It is believed that the bimetallic catalyst had a stronger antioxidant capacity than the monometallic catalyst compared to the reference data (more than one chemical state of Pd).<sup>[21]</sup> From Figure 4(e), Cu is mainly in the zero valent state ((952.2 eV, Cu  $2p_{1/2}$ ) and (932.1 eV, Cu  $2p_{3/2}$ )). But there were also a small amount of CuO detected in the sample, which were corresponded with peaks ((953.2 eV, CuO 2p1/2) and (933.2 eV, CuO 2p3/ <sub>2</sub>)).<sup>[22]</sup> Meanwhile, a negative shift of the Pd  $3d_{5/2}$  peak (336.2 eV) and a positive shift of Cu 2p<sub>3/2</sub> peak (932.1 eV) was observed compared to the reference data (Pd<sup>0</sup> 336.9 eV Cu<sup>0</sup> 932.5 eV).<sup>[23]</sup> As Cu has a lower reduction potential than the Pd, the synergistic effect of the Pd and Cu via alloving can transfer electrons from Cu to Pd. The such electron transfer essentially changed the electronic states of Pd or Cu atoms, leading Pd to zero oxidation state (electron rich state), which are beneficial to the oxidative addition of aryl halides in the Suzuki coupling process.<sup>[24]</sup> While The Cu/Pd atomic ratio at the catalyst surface was measured to be 1/0.86, which was consistent with the alloy composition determined by ICP-AES (Table 1). In addition, it can be seen from the Table 1 that the actual loading of Pd-Cu in this series of 3D IL-rGO/Pd-Cu is almost the same as the theoretical load. This indicated that Pd-Cu bimetal alloy can also be well loaded on ionic liquid functionalized graphene.

In order to determine the distribution of Pd and Cu in IL-RGO catalyst, we collected the HAADF-STEM images and elemental mappings and EDS line scanning profiles (Figure 5). Noticeably, Pd and Cu were uniformly



**FIGURE 2** TEM images (left) and the particle size distribution (right) of (a) 3D IL-rGO/Pd<sub>4</sub>Cu<sub>1</sub>, (b) 3D IL-rGO/Pd<sub>3</sub>Cu<sub>2</sub>, (c) 3D IL-rGO/Pd<sub>2</sub>Cu<sub>2</sub>, (c) 3D IL-rGO/Pd<sub>1</sub>Cu<sub>4</sub> and (f) 3D IL-rGO/Cu



FIGURE 3 The HRTEM image of (a) 3D IL-rGO/Pd, (b) 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> and (c) 3D IL-rGO/Cu



**FIGURE 4** (a) XPS survey spectra, (b) deconvoluted high-resolution XPS spectrum of C 1s, (c) deconvoluted high-resolution XPS spectrum of N 1s, (d) deconvoluted high-resolution XPS spectrum of Pd 3d, and (e) deconvoluted high-resolution XPS spectrum of Cu 2p for 3D IL-RGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> catalysts

TABLE 1 The experimental metal loadings in the catalysts were determined using ICP-AES

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Catalyst	Pd <sub>4</sub> Cu <sub>1</sub>	Pd <sub>3</sub> Cu <sub>2</sub>	Pd <sub>2.5</sub> Cu <sub>2.5</sub>	Pd <sub>2</sub> Cu <sub>3</sub>	Pd <sub>1</sub> Cu <sub>4</sub>	Cu <sub>5</sub>
Pd wt%	3.109	2.2	1.86	1.294	0.63	0
Cu wt%	0.958	1.887	2.401	2.917	3.894	4.206

distributed across the nanoparticles in Figure 5(a)-(d). Moreover, the corresponding line scanning profiles confirmed their homogeneous distribution once again, providing another piece of evidence for the successful formation of Pd-Cu alloy.<sup>[23a]</sup> Then, the EDS surface scan spectrum, which showed the peaks corresponding to C, O, Pd and Cu elements in further confirmed bimetallic Pd-Cu nanoparticles on the surface of IL-reduced graphene. And the atomic ratio of Pd to Cu in 3D ILrGO/Pd-Cu catalyst was roughly 1:1. The observations matched well with the results of line scanning profiles, indicating the effective reduction of the Pd and Cu precursors.

## 3.2 | Catalytic performance

To explore the influence of mass ratio of metal Pd and Cu, a series of catalysts were prepared for Suzuki crosscoupling reaction while maintaining the total metal loading. The effect of the catalyst was tested by the conversion of reactants when the reaction was at 1/4 h, as shown in Table 2. The loading amount of Pd decreased from 4% to 2.5%, while the amount of Cu gradually increased from1% to 2.5%, the yield of diphenyl still remain 100%. As the Pd loading continued to decrease and the Cu loading continued to increase, the yield of biphenyl began to decrease gradually. Meanwhile, the yield of reactants using with

**TABLE 2** The catalytic activity of catalysts with different qualities of Pd and Cu on Suzuki cross-coupling reactions

composition	Time (h)	Yield <sup>a,b</sup> (%)
$Pd_4Cu_1$	1/4	100
Pd <sub>3</sub> Cu <sub>2</sub>	1/4	100
Pd <sub>2.5</sub> Cu <sub>2.5</sub>	1/4	100
Pd <sub>2</sub> Cu <sub>3</sub>	1/4	92
$Pd_1Cu_4$	1/4	38
Cu <sub>5</sub>	1/4	trace
3D rGO/Pd <sub>2.5</sub> Cu <sub>2.5</sub>	1/4	72
Pd <sub>2.5</sub>	1/4	59

<sup>a</sup>Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.5 mmol),  $K_2CO_3$  (2 mmol) and EtOH-H<sub>2</sub>O ( $\nu/\nu = 4$ : 1, 25 ml) at 80 °C under air. <sup>b</sup>GC yield.



**FIGURE 5** (a)The HAADF-STEM image of 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub>; (b) the overlap of Pd and Cu EDS mapping; (c) and (d) the HAADF-STEM-EDS mapping images of Pd and Cu elements, respectively; (e) the EDS line scanning profiles of a PdCu nanocapsule in 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> and (f) the EDS spectrum of 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub>

3D rGO/Pd<sub>2</sub> <sub>5</sub>Cu<sub>2</sub> <sub>5</sub> and Pd<sub>2</sub> <sub>5</sub> catalysts was also showed in Table 2. With the same content of Pd, the catalytic effect of Pd-Cu alloy NPs whether supported on 3D rGO or 3D IL-rGO is better than Pd NPs due to the significant synergic and cooperative interactions between Cu and Pd. The conversion of reactants with 3D IL-rGO/Pd25Cu25 is larger than 3D rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> catalyst, which means the ionic liquid-modified graphene can promote the Suzuki cross-coupling reaction to some extent. We speculated that the interaction of graphene and ionic liquid synergistically may stimulate the redox reaction step of the Suzuki reaction.<sup>[6]</sup> All the result demonstrated that under the premise of minimizing Pd content and ensuring catalytic activity 3D IL-rGO/Pd2.5Cu2.5 composite should be the optimized catalyst and used for further coupling reactions.

To further verify that the catalytic performance of 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub>, the Suzuki cross-coupling reactions of various aryl halides with phenylboronic acid were investigated and the result were depicted in Table 3. The Suzuki cross-couplings of aryl iodides with phenylboronic acid were tested and all the products were obtained by yields higher than 90% in 15 min (Table 3 entry 1–6) This may be attributed to the abundant and uniformly dispersed active nanoparticles on the surface of the catalyst.<sup>[5]</sup> It is well known that the coupling reaction of aryl bromide is

**TABLE 3** The Suzuki cross-coupling reactions of phenylboronicacid and functionalized aryl halides catalyzed by 3D IL-rGO/Pd2.5Cu2.5

R		→B(OH) <sub>2</sub> →	$\frac{\text{IL-rGO/Pd}_{2.5}\text{Cu}_{2.5} (0.5 \text{ mol}\%)}{\text{EtOH-H}_2\text{O} (v/v = 4:1)}$ $K_2\text{CO}_3, 80^{\circ}\text{C}$	
Entry	R	Х	Time (h)	Yield <sup>a,b</sup> (%)
1	Н	Ι	1/4	100
2	$4-NH_2$	Ι	1/4	93
3	4-OH	Ι	1/4	93
4	4-NO <sub>2</sub>	Ι	1/4	96
5	4-CH <sub>3</sub>	Ι	1/4	95
6	$2-NH_2$	Ι	1/4	90
7	Н	Br	1	94
8	4-OH	Br	2	83
9	4-CH <sub>3</sub>	Br	2	86
10	$4-NH_2$	Br	2	91
11	4-NO <sub>2</sub>	Br	2	93
12	$2-NH_2$	Br	2	85
13	Н	Cl	6	20

<sup>a</sup>Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.5 mmol),  $K_2CO_3$  (2 mmol), 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> and EtOH-H<sub>2</sub>O (v/v = 4: 1, 25 ml) at 80 °C under air.

<sup>b</sup>GC yield.

more difficult than aryl iodide, but our synthetic catalyst, 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> can also show good catalytic performance (Table 3 entry 6–12). Meanwhile, for aryl halides bearing an electron-withdrawing group (-NO<sub>2</sub>) gave a little higher yields than the aryl halides bearing electron-donating groups (-CH<sub>3</sub>, -NH<sub>2</sub>, -OH). This is due to the change in electron density of the aromatic ring, which affects the ability of the halogen atom to be removed from the substrate.<sup>[25]</sup> As expected, the ortho-substituted aryl halides show lower reactivity than the para-substituted aryl halides, which can be explained by the steric hindrance effect (Table 3 entry 2, 6, 10, and 12).

### 3.3 | Reusability tests

To study catalytic stability, we chose iodobenzene and phenylboronic acid as model substrates for the above optimized conditions and the recycling experiment were shown in Figure 6. It described that the 3D IL-rGO/Pd<sub>2.5-</sub> Cu<sub>2.5</sub> catalyst could be reused up to ten times with almost stable activity in iodobenzene conversion and diphenyl yield. We also used ICP-AES to detect the hot-filtered reaction solution after 10 cycles of 3D IL-rGO/Pd2.5Cu2.5 catalyst, the results showed that the leaching amount of Pd and Cu is very low. (Pd is only 24 ppb, and Cu is only 49 ppb.) The Pd leaching amount is lower than the single metal palladium catalyst (36 ppb) after 10 cycles. The TEM characterization of catalyst 3D IL-rGO/Pd<sub>2</sub> <sub>5</sub>Cu<sub>2</sub> <sub>5</sub> catalyst after 10 cycles of use is shown in Figure 7. The Pd-Cu alloy was evenly distributed on the graphene sheets without any agglomeration and the particle size was hardly changed increasing only from 2.78 nm to 2.82 nm. It indicated that the bimetallic nanoparticles are very stable in the catalytic reaction. The excellent



**FIGURE 6** Reusability of 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> for the Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid



FIGURE 7 TEM image (a) and the particle size distribution (b) of 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> catalyst after 10 cycles.

catalytic activity and stability is also closely related to the good synergy between the bimetals.

### 4 | CONCLUSION

In summary, Pd-Cu alloy nanoparticle supported on ionic liquids functional three dimensional graphene with recyclable and stability were synthesized by a mild chemical reduction with ascorbic acid. The results from XRD, HAADF-STEM, EDS mapping, XPS clearly indicated that the Pd-Cu alloy NPs with small particle size were uniformly dispersed on the surface of the graphene nanosheets successfully. It is worthy to note that the catalyst 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> can efficiently catalyze the Suzuki cross-coupling reaction with the yield up to 100% in 1/4 h, almost one-fold higher than that by the pristine IL-rGO/Pd<sub>2.5</sub> catalyst (52%). Moreover, the catalyst 3D IL-rGO/Pd<sub>2</sub> <sub>5</sub>Cu<sub>2</sub> <sub>5</sub> also activity remained nearly unaltered up to ten cycles. The alloying of Cu and Pd not only lower the costs but also form a highly active catalyst thanks to the synergistic effects between Cu and Pd. Furthermore, the 3D IL-rGO/Pd<sub>2.5</sub>Cu<sub>2.5</sub> also has broad applicability in a variety of Suzuki cross-coupling reactions, which may open up new avenues for the practical application of organic coupling reactions.

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