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1. Introduction

The derivatives of a biaryl structure have wide applications in agrochemical, pharmaceutical and material industries.^{1,2} It is known that the Ullmann coupling reaction is one of the frequently used protocols to architecture the chemicals of these biaryl-based structures.^{3–5} Specifically, the Ullmann coupling reaction makes use of aryl halides as reaction substrates to convert them into biaryl products, as shown in Scheme 1, where normally successful C–C bond coupling needs a temperature as high as more than 373 K^{3,6,7} and essential high-alkali solution environment.^{8,9} Moreover, the copper (Cu) catalysts should be equivalent or even excessive to the amount of aryl halides to obtain a considerable yield.^{2–4,10} Obviously, the harsh reaction conditions of the traditional Ullmann coupling reaction conflict the green chemistry concept, which should be urgent to promote.

Actually, in the past decades, numerous efforts were made to simplify the conditions of Ullmann coupling reactions.^{1,4,5} To

Electrochemical coupling halobenzene into biphenyl on a reusable Pd nanoparticle-coated carbon-paper electrode at ambient conditions;

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Electrochemical organic synthesis (EOS) employing electrons to directly activate the reactants can readily complete the chemical conversion under mild conditions. Here, it presented an efficient electrochemical coupling halobenzene into biphenyl on a Pd nanoparticle-coated cathode. The biphenyl product can be obtained with a yield up to 77% at 35 mA, 6 h (3.9 F mol⁻¹). In addition, after consecutive fifth run of the coupling reaction, the yield still remained at *ca.* 40%, suggesting its considerable recyclable capacity. In addition, the preliminary kinetics study *via* the off-line gas chromatography analysis of the reaction mixture shows a two-section reaction process, including the introduction process (IP) and fast conversion process (FCP). Further, the estimated reaction kinetics constant value of 0.196 min⁻¹ for FCP suggests a more effective conversion than that obtained by the previous study. This study adopts a simple way to fabricate a low-cost and reusable Pd electrode, achieving a high-efficiency electrochemical strategy for the Ullmann-type coupling reaction at mild conditions, and holds a great promise to extend this synthesis route to other important organic synthesis.

receive better efficiency of Ullmann coupling reactions, homogeneous palladium (Pd) and nickle (Ni) catalysts were introduced into these reactions. However, the cost and toxicity of these metal catalysts limited their utilization and development.^{11,12} Furthermore, numerous groups have tried to modify the ligands of Cu homogeneous catalysts, which led to the enhancement of the catalytic performance of copper metals,^{13–15} so that they can use fewer metal catalysts to complete the transformation, dramatically decreasing the consumption of catalysts. Among these, Ma et al. demonstrated a mild method for Ullmann coupling reaction using either N-methyl glycine or L-proline as the ligand of copper catalyst.¹⁶ Moreover, in recent years, numerous advanced materials such as biodegradable microbeads/microcapsules,17,18 magnetic lignin,^{19,20} modified kaolin,²¹ modified boehmite,²² polymeric nanocomposite,23 graphene oxide24 and other



Scheme 1 The typical chemical reaction formula of the traditional Ullmann coupling reaction.



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materials^{25,26} were used to load Pd nanoparticles for synthesizing biphenyl molecules. These support materials can efficiently modulate the catalytic performance of Pd catalysts. However, they still need high temperature and strong alkaline environment, which limit their further development.

Fortunately, in recent years, electrochemical organic synthesis²⁷⁻³⁰ has obtained increasing attention because of the growing environmental protection concept. This method directly employs electrons and/or protons as the key reagent to activate the substrate molecules; thus, it can ready complete the organically chemical conversions under mild conditions (at room temperature and standard atmospheric pressure). Moreover, the reaction conventionally occurs without any other additives, so there will be little extra by-products. Actually, several important molecules such as azaindoles,³¹ imidazole and its derivatives,³²⁻³⁴ diamine,^{35,36} hindered dialkyl ether,³⁷ O-heterocycles,³⁸ and amidyl compounds³⁹ have been obtained via the electrochemical organic synthesis. Regarding the Ullmann-type reactions, Rothenberg et al.40 presented a roomtemperature electrocatalytic alternative to the traditional Ullmann coupling reaction, obtaining the biphenyl product from iodobenzene with a yield up to 80%. However, they used high-purity Pd wires as the sacrificial anode to generate the Pd nanoclusters to promote the C-C coupling of aryl halides, which likewise leads to much waste of the noble metals. Moreover, the Pd cluster catalysts that are randomly dispersive in the reaction solution, thus the Pd clusters are disposable. Besides, the ionic liquids serving as the electrolyte are conceivably expensive. Therefore, their synthesis strategy is high-cost and non-recyclable, which should be further improved to meet the high-efficiency and low-cost principles.

Considering the above-mentioned facts, in this study, we fabricated a reusable carbon paper cathode through simply coating the premade carbon-supported Pd nanoparticles. In addition, an electrochemical cell was assembled using a carbon paper as the anode and the conventionally used organic solvent such as acetonitrile associated with certain amount of quaternary ammonium as the electrolyte. The electrochemical Ullmann-type C-C coupling of iodobenzene (PhI) into biphenyl molecule was successfully carried out at ambient conditions, with a production yield up to 77%. In addition, a 40% yield was still obtained after a consecutive five-time recyclable use of the Pd nanoparticlescoated cathode. The similar coupling reactions that employed other monosubstituted aryl halides as reactants were also performed with a considerable yield. This study may illuminate a promising route towards the low-cost and high-efficiency green synthesis of valuable molecules.

2. Experimental methods

2.1 Preparation and characterization of Pd catalysts

As shown in Scheme 2, 43 mg of Vulcan XC-72 and 2.23 mL of 45 mM $PdCl_2$ (Sinopharm Chemical Reagent) were added into 40 mL of Milli-Q water and the mixture was kept under vigorous stirring for *ca.* 4 h. Then, the solution alkalinity was adjusted to



Scheme 2 The schematic of the synthesis process of Pd/C and the fabrication process of the working electrode.

the designated pH value (ca. 9.5) using a 0.1 M Na₂CO₃ solution. Successively, a 10 mL 3 mg mL⁻¹ NaBH₄ + 0.05 M Na₂CO₃ mixture was added dropwise to the suspension under vigorous stirring by a peristaltic pump at 0.5 mL min⁻¹. After 12 h stirring, the suspension was filtered and washed with copious amounts of Milli-Q water and then dried in vacuum at 323 K overnight.⁴¹ The obtained catalysts are named as Pd/C. The as-prepared Pd/C catalysts were detected by a SPECTRO ARCOS inductively coupled plasma-atomic emission spectrometer (ICP-AES) to analyse the metal loading. The morphology and size distributions of Pd nanoparticles were characterized by a Tecnai G2F20 transmission electron microscope (TEM). The electronic and lattice structure was analysed by a Thermo Fisher K-Alpha X-ray photoelectron spectrometer (XPS) and a D8 QUEST X-ray diffractometer with Cu Ka radiation (0.15418 nm), respectively. The Cyclic voltammograms (CVs) of Pd/C were obtained on a CHI 660E electrochemistry work station using an untreated carbon paper (1 cm \times 6 cm) as the counter electrode and Ag/AgCl as the reference electrode.

2.2 Electrochemical organic synthesis

The electrochemical synthesis was performed in a twoelectrode cell, taking a Pd/C-coated carbon Paper (Toray) electrode (designated as PdCPE hereafter) and carbon paper electrode as the cathode and anode, respectively. As shown in Scheme 2, PdCPE was fabricated through brushing the catalyst ink on the carbon paper (8 cm \times 1.5 cm) surface on a heating plate at *ca.* 50 °C to dry the solvent. The catalyst ink including 22 mg of the as-prepared Pd/C dispersed in the solution of 0.5 mL water + 0.5 mL ethanol + 50 mg 5% Nafion ethanol solution. The coating area was controlled to be 2 cm imes 1.5 cm, and the coating amount of Pd/C was 22.0 \pm 1.0 mg determined by weighing. Then, the PdCPE and same-size carbon paper were symmetrically assembled into the electrochemical cell. 20 mL of acetonitrile (MeCN, KESHI, AR) or dimethylformamide (DMF, KESHI, AR) or CH2Cl2 (KESHI, AR) containing 0.05 M tetrabutylammonium tetrafluoroborate (TBATFB, Adamas 98% +) were added into the cell to serve as the electrolyte, while the amount of reactant aryl halides was kept as 2 mmol. A LP220DE direct-current power supply purchased from Shenzhen Lodestar

CO., Ltd was used to provide the cell voltage and current to ensure that the reaction occurs.

2.3 Product separation and analysis

After the determined reaction time, the reaction solution was pumped out to separate effectively through a chromatographic separation in a home-made silica gel column (200–300 mesh column chromatography silica gel). Typically, the petroleum ether (KESHI, AR) was chosen as the mobile phase to extract the products. When DMF is used as solvent, it should be removed before column chromatographic separation by washing with water because of its high boiling point. The molecule structures of as-obtained products were confirmed by an Agilent 400-MR DD2 400 MHz nuclear magnetic resonance (HNMR) spectrometer and an Agilent Cary 660 FTIR spectrometer. The deuterated chloroform (CCl₃D) with tetramethylsilane (TMS) was chosen to dissolve *ca.* 20–25 mg products to carry out the HNMR measurements.

All the chemicals were obtained commercially and used without further purification. All experiments were carried out at room temperature (25 ± 2 °C) and atmosphere pressure.

3. Results and discussion

3.1 Catalyst's Characterization

It is generally known that particle sizes and distribution of nanoparticles play a key role in their catalysis process.^{42,43} It can be seen in Fig. 1a that Pd nanoparticles are evenly distributed on the carbon surface, without distinct aggregation. The histograms of the particle size and distribution are obtained based on the measurements of *ca.* 400 nanoparticles in a randomly selected area, showing the average particle size of 2.88 \pm 0.5 nm. Fig. 1b shows the XRD patterns of the asprepared Pd/C catalysts, featuring the face-center-cubic (fcc) crystalline structure of Pd (PDF#46-1043). Thus, the average particle size of Pd nanoparticles can also be estimated as *ca.* 2.83 nm according to the Scherrer equation $D = 0.89 \lambda/(\beta \cos \theta)$, where *D* is the average particle diameter, λ is the wavelength of X-ray (0.15418 nm), β is the half-height width of the Pd (111) diffraction peak in radians and θ is the diffraction angle of the



Fig. 1 (a) TEM image of Pd NPs loaded on the activate carbon surface, (b) X-ray diffraction patterns of as-prepared Pd/C catalysts. (c) Core-level XPS spectrum in the Pd 3d region for Pd/C catalysts.

(111) peak. This result is in reasonable agreement with the value estimated by TEM. The ICP-AES detection of the as-prepared catalysts obtained a *ca.* 19.1 wt% of Pd loading for the as-prepared Pd/C catalysts, which is approximately corresponding to our expectation. The *ex situ* XPS spectra of Pd 3d in Fig. 1c show the Pd 3d core levels split into $3d_{5/2}$ (*ca.* 335 eV) and $3d_{3/2}$ (*ca.* 340 eV) states, and both the Pd $3d_{5/2}$ and the Pd $3d_{3/2}$ peaks can be deconvoluted into two peaks of Pd⁰ and Pd^{II} species. It is worthwhile to note that the catalysts were exposed under ambient condition before XPS measurements. Hence, the presence of Pd^{II} species may be attributed to the oxidation of Pd active sites.^{44,45}

The electrochemical response of the as-prepared Pd/C towards the C-C coupling of iodobenzene was roughly investigated via cyclic voltammetry. Typically, the cyclic scanning was performed in a three-electrode cell containing 10 mL MeCN + 0.05 M TBA TFB + 0.01 M iodobenzene, employing the Pd/ C-coated glassy carbon, carbon paper (1 cm \times 6 cm) and Ag/ AgCl electrode as the working electrode, counter electrode and reference electrode, respectively. As shown in Fig. 2, during the negative scanning, the peak at -0.75 V could be related to the reduction of iodobenzene into the radical intermediates (vide infra), and the peak at -1.75 V could be attributed to the C-C coupling of the intermediates. The peak at -1.75 V was only observed on the Pd/C surface, which suggested that the C-C coupling of radical intermediates could occur on the Pd/C surface rather than that on the glassy carbon surface. To confirm this, we also performed the chromatographic separation of reaction residual and undetectable biphenyl product was obtained when the cyclic scanning was carried out on the bare glassy carbon electrode.

3.2 Electrochemical C-C coupling on Pd/C

The homo-coupling of PhI was chosen as the model reaction for optimizing and screening the reaction conditions, which



Fig. 2 Cyclic voltammograms (CVs) collected on a bare (dash line) and Pd/C-coated glassy carbon electrode (solid line) in an electrolyte of 10 mL MeCN + 0.05 M TBA TFB (0.05 M) + 0.01 M iodobenzene at room temperature. Scan rate, 50 mV s⁻¹.

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Fig. 3 Recycling experiments for the electrochemical Ullmann reaction on the as-prepared Pd/C catalysts. Reaction conditions: 20 mL MeCN, 0.1 M PhI, 0.05 M supporting electrolyte, room temperature, 35 mA, 6 h.

included solvent and applied cell current. Initially, we found that the solvent has a significant influence to this reaction. It is clear that the yield of product gradually decreased with the sequence of the usage of the solvents: MeCN (77% yield), DMF (63% yield), MeOH (42% yield) and CH_2Cl_2 (35% yield) under the same reaction conditions (entries 1–3,7 Table 1). In the traditional Ullmann reaction, an aprotic solvent such as DMF, MeCN or tetrahydrofuran (THF) has been frequently used, and similarly, the product yield was usually different with the variation of solvent.^{4,5} Moreover, in the organic electrochemistry, MeCN and DMF have the widest electrochemical working windows; therefore, these solvents are the best organic solvents used for electrochemical studies.⁴⁶ In our study, the experimental results apparently show that MeCN could be more suitable and

 Table 1
 Optimization of the electrochemical homo-coupling reaction of iodobenzene^a

2 Carbon Paper PdCPE R.T., TBA TFB					
Entry	Solvent	Current (mA)	Weight of Pd/C (20 wt%)	Time (h)	Yield ^b (%)
1	DMF	35	22 mg	6	63
2	CH_2Cl_2	35	22 mg	6	35
3	MeOH	35	22 mg	6	42
4	MeCN	0	22 mg	8	NR
5	MeCN	10	22 mg	8	34
6	MeCN	25	22 mg	6	58%
7	MeCN	35	22 mg	6	77 ^c
8	MeCN	45	22 mg	6	64
9	MeCN	35	0 mg	6	0
10	MeCN	35	15 mg	6	66
11	MeCN	35	22 mg (10 wt%)	6	54

^{*a*} Reaction conditions: 20 mL solvent, 0.1 M iodobenzene, 0.05 M TBATFB, room temperature. ^{*b*} Isolated yields of products after column chromatography. NR means no reaction. ^{*c*} 6 h (3.9 F mol⁻¹)

effective for this electrochemical coupling reaction, which is in line with previous investigation on electrochemical organic reactions.^{32,33,38,47}

Furthermore, the applied cell current was taken as an important factor to probe since this C-C coupling reaction was electrochemically triggered here. A higher current makes this reaction a higher yield. When the current was 10 mA, PhI is successfully turned into biphenyl with the yield of 34%. With the current rising to 35 mA, it can be obviously seen that the product yield rapidly increases to 77%. However, it should be noticed that excessive current may conversely inhibit the reaction. When the applied current increased to 45 mA, the yield of biphenyl decreased to 64% (entries 5-8, Table 1). Thus, 35 mA current was finally determined as the best condition in this study. In addition, the coating quantity of Pd/C catalysts on the carbon paper surface also exhibited influence to this reaction (entries 10 and 11 Table 1). Among these, we successfully transform the substrate to the biphenyl product with the highest yield of 77%. As a result, we get optimized reaction conditions in this electrochemical organic synthesis system, being the solvent of MeCN, 22 mg Pd/C (20 wt%) catalysts, 35 mA cell-current and a 6 h reaction time (3.9 F mol^{-1}). This result is pretty effective compared with those obtained in the traditional catalysis process in Table S2 in the ESI.†

To evaluate the recyclable capacity of PdCPE, we conducted the same electrochemical reaction on PdCPE for five consecutive times (Fig. 3). In the second run, under same optimized reaction conditions, the biphenyl product yield was dipped to *ca.* 58%. In the next few cycles, the product yield changed a little according to the experimental data. However, the yield dropped down to *ca.* 38% in the 5th run. According to these results, we speculate that the Pd nanoparticles may perform migration and accumulation due to the so-called Ostwald ripening effect.^{48,49}

Then, we extend this Ullmann-type electrochemical coupling to other substrates on the Pd surface, particularly other monosubstituted halobenzenes such as bromobenzene (PhBr) and chlorobenzene (PhCl) were first selected as the reaction substrates. As shown in Table 2, the yield of biphenyl transformed from PhBr can reach to 66% (entry 2, Table 2). There was no biphenyl product obtained in the case of PhCl (entry 3, Table 2). It is still a knotty problem to finish the chemical conversion of PhCl in organic reactions under simple conditions.^{50,51} Then, we employ other para-position substituted compounds to further extend our synthesis method. According to the experimental results, the electron-donating groups (here -CH₃, -NH₂ groups were used as the model) can inhibit this reaction. The stronger the electron-donating effect, the more obvious the inhibition appearance (entries 4, 5 and 10, 11, Table 2). In contrast, the electron-withdrawing groups (here -COOH, -COCH₃ groups were used as the model) can slightly promote the conversion efficiency, leading to an increase in the yield to 88% (entries 8, 9 and 12, 13, Table 2). The enhancement effect of electron-withdrawing groups could be related to the stability of intermediates of the Ph radical anion. In addition, 4-tertbutyl-iodobenzene with a large steric hindrance surprisingly obtained a 42% yield (entry 7, Table 2). It means the

 Table 2
 Pd/C NP-catalysed electrochemical homocoupling of some alkyl

 halides^a
 Pd/C NP-catalysed electrochemical homocoupling of some alkyl

Entry	Aryl halide	Yield ^{b} (%)	Time (h)
1	Г	77	6
2	Br	66	8
3	Cl	0	8
4	– Č–I	72	8
5	————Br	61	8
6	Br	14	8
7		42	8
8	ноос—	75 ^c	6
9	HOOC-Br	58 ^c	6
10	H ₂ N-	38	8
11	H ₂ N-Br	17	8
12	o -I	88	6
13)-Br	69	6

^{*a*} Reaction conditions: 20 mL MeCN, 0.1 M aryl halide, 0.05 M supporting electrolyte, constant current, room temperature. ^{*b*} Isolated yields of products after column chromatography. ^{*c*} The solvent is DMF because of the poor solubility in MeCN.

electrochemical tactics may be a promising route to overcome the steric effect, which commonly exists in organic synthesis.²⁷

3.3 Preliminary clarification of the reaction mechanism

In order to better understand the reaction process, we used the off-line FULI 9790II gas chromatography (GC) with a 30 m capillary column (KB-5) to monitor the PhI coupling reaction process. The initial column temperature of 80 °C was used, and it was then increased to 250 °C at a rate of 10 °C min⁻¹. The 2 mL reaction mixture was withdrawn per hour *via* a disposable



Fig. 4 (a) Reaction time-dependent off-line GC of the reaction mixture withdrawing from the reaction solution. (b) Reaction time-dependent variation of the integrated GC peak intensity of the PhI substance and biphenyl product, which is normalized to that obtained at 0 min.

syringe, and then injected into the GC to analyse the product distribution with reaction proceeding.

As shown in Fig. 4a, the gradual consumption of the PhI substrate (retention time centered at ca. 6 min) and formation of the biphenyl product (retention time centered at *ca.* 10 min) can be clearly observed. More directly, as shown in Fig. 4a, the integrated GC peak intensity variation apparently shows that more than 90% PhI was electrochemically transferred into the biphenyl product after a 6 h reaction. More importantly, this off-line reaction process monitoring could provide a possibility to preliminarily study the reaction kinetics shown in Table 1. As shown in Fig. 4b, the reaction process could be readily divided into two sections, where the apparent reaction kinetics constant (k) was estimated by the slope to be $k_1 = 0.075 \text{ min}^{-1}$ (1-3 h, $R^2 = 0.982$) and $k_2 = 0.196 \text{ min}^{-1}$ (3-5 h, $R^2 = 0.984$), respectively. Note that, here this PhI coupling reaction was treated with a zero-order reaction kinetics similar to that adopted in the literature⁴⁰ although the reaction mechanism was not manifested clearly. Moreover, the two-section actions of reaction kinetics could suggest that this coupling reaction of PhI should include an introducing process (IP) and a fast conversion process (FCP) similar to that observed by Rothenberg et al. in an electrochemical organic synthesis system assembled by a Pd wire anode and a Pt wire cathode. Nevertheless, they claimed that the first process should be related to the formation of the Pd cluster, which could not take place in our system with a Pd-nanoparticle cathode. Thus, we speculated that IP could mainly be due to the activation of PhI molecules and formation of Ph[•] radical anion (see below), and FCP could be mainly connected with the generation of the biphenyl product. Therefore, it can be claimed that a comparatively smaller k_2 value than that in the previously reported work $(0.38 \text{ min}^{-1})^{40}$ and it demonstrated a more effective strategy for electrochemical coupling. Note that, this hypothesis of the reaction mechanism should be further investigated and verified.

Moreover, to obtain further evidence of the mechanism about this homo-coupling reaction, we chose 2,6-di-*tert*-butyl-4-methylphenol (BHT, 1.0 equiv.) as the radical scavenger (Table S1, ESI[†]). Interestingly, the desired product yield of biphenyl was only 12%. This result implied that this reaction might involve a radical intermediate. Therefore, a preliminary



mechanism has been proposed for this Ullmann homocoupling reaction (Scheme 3). A radical anion *via* the electron transfer process on the Pd nanoparticle surface gives a $[PhX]^{-}$ • radical anion and then forms a Ph• radical, ultimately transforming to the biphenyl product.⁵²

4. Conclusions

In summary, we have presented an efficient electrochemical Ullmann-type coupling reaction from halobenzenes into a biphenyl product on the Pd nanoparticle surface at room temperature. The carbon-supported Pd nanoparticles with a ca. 2.8 nm diameter was simply prepared by a NaBH₄ reduction method. Additionally, the carbon-supported Pd nanoparticles were coated on the carbon paper surface to fabricate a PdCPE electrode. It was used as the cathode to assemble an electrochemical organic-synthesis cell, employing a carbon paper as the counterpart anode. Under this configuration, we can readily obtain a biphenyl product from PhI with the yield up to 77% with a 35 mA cell-current and 6 h conversion (3.9 F mol^{-1}) at ambient conditions. Moreover, the consecutive five runs of this coupling reaction suggested a considerable recyclable capacity of the PdCPE electrode. In addition, the preliminary kinetics study via the off-line gas chromatography analysis of the reaction mixture shows a two-section reaction process, including an introducing process of formation of Phº radical anion intermediates and a fast conversion process with respect to the generation biaryl compound. In addition, the estimated reaction kinetics constant of the fast conversion process (k_2) suggested a more effective conversion than previous study. Lastly, it was extended to other halobenzene substrates to perform a similar C-C bond coupling. It was found that the electron-donating groups could inhibit the coupling reaction, and the electronwithdrawing groups could promote the coupling process. This work showed an effective and mild synthesis route for the Ullmann-type coupling with a high-efficiency, low-cost and recyclable electrochemical strategy, which could be highly promising in the large-scale utilization. Also, this electrochemical configuration may also be extended to other important organic synthesis.

Conflicts of interest

The authors declare no conflict of interest.

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