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Polyaniline-supported nano metal-catalyzed coupling reactions: Opportunities and challenges

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ABSTRACT

Polyanilines (PANIs) can be easily prepared from the available and cheap anilines *via* the oxidative polymerization reactions. Owing to the coordination of nitrogen in the material with metals, PANIs are widely used as the support of nano metal catalysts. In comparison with inorganic supports, the nano metals on PANIs were firmly anchored *via* the coordination bond so that they are not easily to lose during the reaction process. Moreover, since PANIs are versatile materials and their chemical features can be adjusted by introducing functional groups onto the monomers, the catalytic activities of the prepared catalysts are tunable. During the past decade, PANIs-supported nano metal catalysts have been widely applied in a variety of coupling reactions. This review aims to summarize the recent advances and give a perspective.

1. Introduction

Coupling reactions are important transformations not only for the laboratory synthesis, but also for the production of medicines and their intermediates at industrial level [1–6]. They are able to introduce functional groups into the molecules precisely under mild conditions. The traditional coupling reactions can be catalyzed by transition metals, such as Pd, Ni, Cu, and phosphorus ligands are always required. Homogeneous catalysts, such as $Pd(PPh_3)_4$, are difficult to be recycled and reused, and this obviously enhances the cost for large-scale production. The reactions are so significant in pharmaceutical industry that improvement in the field never stops. Enhancing the efficiency of the catalytic metal, using phosphorus-free ligand and reducing the reaction cost are the major developing trend from both of the economy and environment-protection viewpoints. Therefore, developing novel heterogeneous catalyst systems that can meet the above requirements is an important research direction and has attracted continuous attention during the past decade [7–11].

Yet, nano-metal catalysts are found to be of great industrial application potential for the high turnover numbers (TONs) and recyclable and reusable features of the catalyst, and the green features of the reaction processes free of ligands or additives [12–14]. A variety of materials, such as the activated carbon [15–17], γ-Al_2O_3 [18,19], TiO_2 [20,21], SiO_2 [22], are employed as supports to anchor the catalytic nano-metal particles. Polyanilines (PANIs) are also applicable supports for nano-metal catalyst design, and comparing with the traditional supports, the advantages of them are obvious. First, PANIs can be easily synthesized *via* the oxidative polymerization of anilines, and the process has been improved by using clean oxidants such as H_2O_2 and molecular oxygen [23]. Since anilines are accessible and low-cost chemicals, PANIs are not expensive for large-scale application; The most important is, PANIs are more versatile than inorganic supports, *i.e.*, their properties can be adjusted by introducing functional groups onto the monomers, so that the catalytic activities of the prepared catalysts are tunable. This paper aims to review recent advances in PANI-supported nano metal (M/PANI)-catalyzed coupling reactions and give a perspective.

2. Suzuki-Miyaura coupling reactions

In 2005, Houdayer *et al.* reported the PANI-supported nano palladium-catalyzed Suzuki-Miyaura coupling reaction [24]. The catalyst was prepared *via* the oxidative polymerization of aniline with palladium. In the process, $Pd(OAc)_2$ was employed as the palladium source and it was initially mixed with NaH/*t*-BuONa to produce the nano palladium clusters being surrounded with *t*-BuO^-, in which the palladium has been reduced to Pd(0), while the coor-

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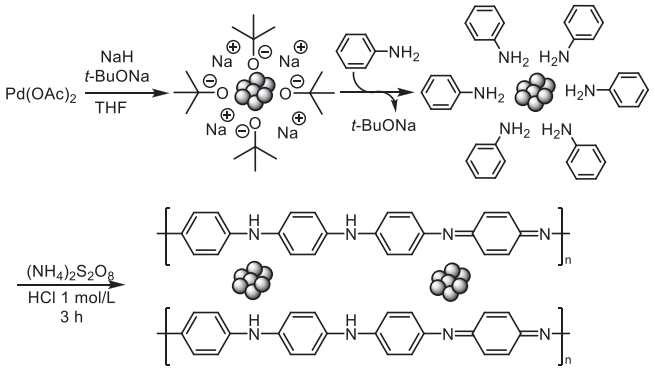
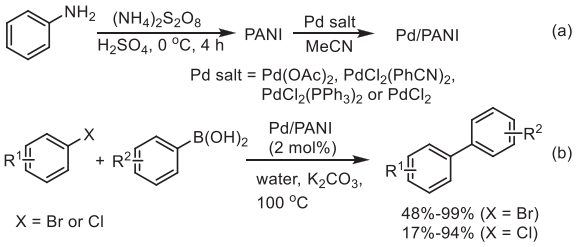


Scheme 1. Synthesis of Pd(0)/PANI nanocomposites.



Scheme 2. Two-step synthesis of Pd/PANI catalyst for aqueous Suzuki-Miyaura coupling reactions.

dination effect between oxygen and palladium could stabilize the complex. Aniline was then introduced and because of the even stronger coordination between nitrogen with palladium, it could replace the *t*-BuO^- anions to form the aniline-nano palladium complex. Oxidation of aniline with $(NH_4)_2S_2O_8$ led to PANI, which could anchor the nano palladium clusters through the nitrogen-palladium coordination to afford the Pd(0)/PANI nanocomposites (Scheme 1).

In the material, the nano palladium particles with diameters of *ca.* 4.9 nm were homogeneously dispersed in PANI, and it could catalyze the Suzuki-Miyaura coupling reactions of aryl iodide with aryl boric acid. The reactions employed 1 mol% of palladium with K_3PO_4 additive and were performed in 1,4-dioxane. Heating the reaction systems at 100 °C for 15 h could produce the related biaryl products in 74%–89% yields. In comparison with traditional palladium-catalyzed Suzuki-Miyaura coupling reactions, the method can avoid the use of phosphorus ligands, and this feature makes it friendly to the environments. However, since the dosage of palladium was high, the catalyst TONs of the reactions were low. Considering the fact that the catalyst recycling and reusing experiments were not reported, further improvements were still needed to make the strategy applicable for large-scale production from the economical viewpoint.

Kantam *et al.* synthesized Pd/PANI *via* a quite different two-step method [25]. In their protocol, PANI was initially prepared *via* the oxidative polymerization of aniline with $(NH_4)_2S_2O_8$ as oxidant. The material was then immersed in palladium salt solution to upload palladium (Scheme 2a). A series of palladium salts such as $Pd(OAc)_2$, $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$ and $PdCl_2$ were tested, and $PdCl_2$, the most common and cheap one, was found to be preferable palladium source, affording the highest catalytic activity of Pd/PANI. The prepared Pd/PANI could catalyze the Suzuki-Miyaura coupling reactions of a series aryl bromides or chlorides with aryl boric acids (Scheme 2b). The reactions were performed in water using K_2CO_3 additive. Generally, the coupling reactions of aryl bromides afforded higher product yields. The reactions of aryl bromides could finish within 25–480 min, while it took 12–24 h for the coupling reactions of aryl chlorides. Substituents on substrates also exerted significant influences on the reaction. Electron-withdrawing groups on aryl halides could activate the related C-X bond, resulting in the accelerated reaction process and the elevated product yield. In comparison with traditional homogeneous catalytic reactions, the green features such as the phosphorus-ligand-free and aqueous conditions and using cheap aryl bromide and chloride substrates both make the reaction more preferable for practical applications.

Pd(II) salts, such as $Pd(OAc)_2$, are indeed oxidants. Thus, dropping $Pd(OAc)_2$ solution into aniline could initiate its oxidative polymerization, which was reflected by the color change (from colorless to green) indicating the formation of conjugated structures of PANI chain. The prepared Pd/PANI was found to contain *ca.* 1.7 wt% of palladium. It could catalyze the Suzuki-Miyaura coupling reactions of aryl bromides or iodides with phenylboronic acid in toluene at 70–80 °C for 6–8 h to produce the related biphenyl derivatives in 63%–97% yields. Notably, the turnover frequencies (TOFs) of the catalyst were as high as 758–2309 h^{-1} [26].

Dutt *et al.* reported a novel method to prepare Pd/PANI without alkali [27]. In the process, high valent palladium salt, *i.e.,* K_2PdCl_4 was chosen as the palladium source, and it was initially dissolved in water to prepare the aqueous solution. Aqueous solution of aniline hydrochloride was then dropped into aqueous K_2PdCl_4 at 3–5 °C, and the redox reaction between high valent palladium and aniline led to Pd/PANI composites, which were isolated by centrifugation. The material was found to be catalytically active for Suzuki-Miyaura coupling reactions. Interestingly, besides bromobenzene, bromo octane, a $C(sp^3)$-Br containing bromide, could also react with phenylboronic acid to produce octyl benzene, indicating that the novel catalyst might lead to a comprehensive application scope of substrates in comparison with traditional palladium catalysts.

As an active transition metal with changeable valences, palladium can catalyze the aerobic oxidation reactions. Thus, it may catalyze the oxidative polymerization of aniline using molecular oxygen as the oxidant. According to this principle, we developed the method to synthesize Pd/PANI composites by exposing the mixed solution of $PdCl_2$ and aniline in open air [28]. The material could catalyze Suzuki-Miyaura coupling reactions in refluxing ethanol. The substrate scope of the reaction was very wide. Both electron-enriched and deficient aryl iodides and aryl boric acids were fit for the reaction, affording biphenyl derivatives in moderate to excellent yields (Table 1, entries 1–15). Impressively, the catalyst was tolerable to sulfur-containing substrate, which might poison the catalytic metal for the too strong sulfur-metal coordination (Table 1, entry 15). Thus, this method may be applicable for the formation of sulfur-containing molecular skeletons, which widely exist in pharmaceutical intermediates. Besides iodides, the reactions of aryl bromides could also occur, but they required prolonged reaction time for the higher bond energy of C-Br (Table 1, entries 16 and 17). Introducing electron-withdrawing group such as CF_3 could activate the C-Br bond lead to the high product yield of coupling reaction (Table 1, entry 18).

We then found that, in the presence of H_2O_2, the oxidative polymerization reaction of aniline could occur with reduced $PdCl_2$ dosage [29]. This method could prepare the Pd/PANI composites with decreased palladium content but enhanced catalytic activity. In Suzuki-Miyaura coupling reactions, the palladium loading could be reduced to 0.021 mol% (*vs.* 0.12 mol% in Table 1), affording the significantly enhanced TON to 4.7×10^3.

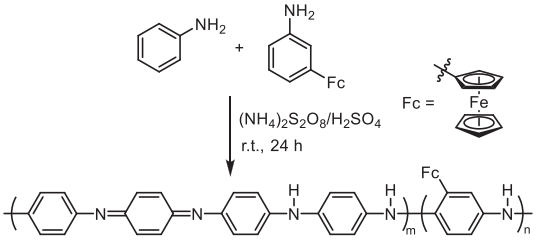
Chaicharoenwimolkul *et al.* reported a novel method adjusting the catalytic activities of PANI by introducing ferrocene substituents [30]. The copolymerization of aniline with ferrocene-substituted aniline led to poly(aniline-*co*-*m*-ferrocenylaniline) (Scheme 3). It was found that introducing electron-withdrawing ferrocene moieties could reduce the electron delocalization on

Table 1
Pd/PANI-catalyzed Suzuki-Miyaura coupling reactions [28].[a]

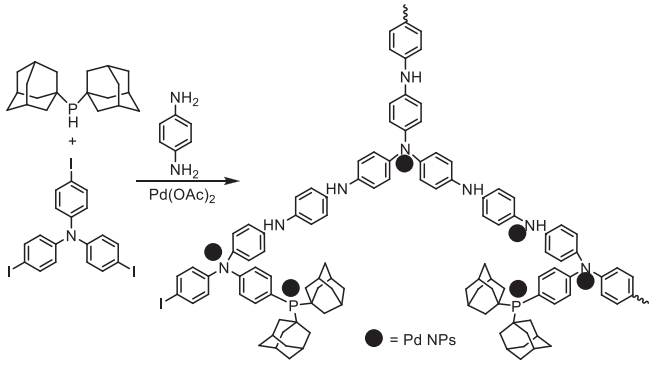
$Ar^1X + Ar^2B(OH)_2 \xrightarrow[K_2CO_3,\ EtOH,\ reflux,\ N_2]{Pd/PANI\ (0.12\ mol\%)} Ar^1\text{-}Ar^2$

Entry	Ar^1X	Ar^2	*t* (h)	Ar^1-Ar^2 yield (%)[a]
1	PhI	Ph	16	>99
2	PhI	*p*-$CH_3C_6H_4$	24	72
3	*p*-$NO_2C_6H_4I$	*p*-$CH_3C_6H_4$	36	57
4	PhI	*p*-FC_6H_4	23	81
5	PhI	*m*-ClC_6H_4	19	95
6	PhI	*m*-$NO_2C_6H_4$	19	80
7	*p*-$CH_3C_6H_4I$	Ph	19	83
8	*m*-$CH_3C_6H_4I$	Ph	12	>99
9	*p*-$CH_3OC_6H_4I$	Ph	21	>99
10	*p*-$EtOC_6H_4I$	Ph	20	80
11	*p*-$NH_2C_6H_4I$	Ph	12	36
12	*p*-FC_6H_4I	Ph	12	94
13	*p*-$NO_2C_6H_4I$	Ph	12	>99
14	1-$C_{10}H_7I$	Ph	12	97
15	2-Iodothiophene	Ph	24	65
16	PhBr	Ph	24	76
17	PhBr	*p*-$CH_3C_6H_4$	24	49
18	3,5-$(CF_3)_2C_6H_3Br$	*m*-$NO_2C_6H_4$	12	84

[a] Isolated yields.



Scheme 3. Synthesis of poly(aniline-*co*-*m*-ferrocenylaniline).

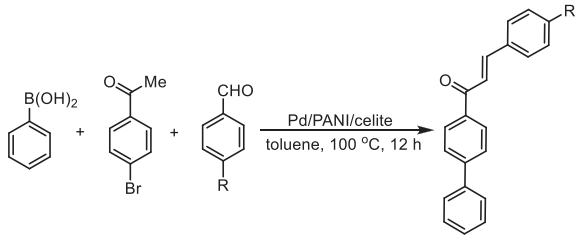


Scheme 4. Preparation of the palladium nanoparticle/cross-linked PANI catalyst.

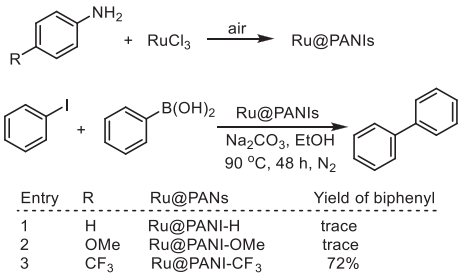
the polymer main chain. The catalytic activity of the material for Suzuki-Miyaura coupling reactions of arylbromide with arylboronic acids in toluene was obviously enhanced.

As a kind of coating material, PANI could be placed onto the surface of magnetic Fe_3O_4 nanoparticles and immersing the composites into the MeCN solution of $Pd(OAc)_2$ could afford the magnetically separable and reusable catalyst for Suzuki-Miyaura coupling reactions [31]. The catalytic activity of the material was high, and besides good product yields, it could lead to excellent catalyst TOFs to as high as 51,368 h^{-1}.

Fan *et al.* prepared the Pd/PANI catalyst *via* a completely different route (Scheme 4) [32]. Instead of the oxidative polymerization of aniline, they synthesized the PANI chain *via* the coupling reaction of tris(4-iodophenyl)amine with benzene-1,4-diamine and di-adamantane-substituted phosphane. The reaction led to cross-linked polyaniline bearing phosphane moieties, in which both nitrogen and phosphorus could coordinate with the catalytic metals. $Pd(OAc)_2$ in the reaction could catalyze the coupling reaction to build the PANI skeleton, and its palladium was also absorbed by the produced PANI to give palladium nanoparticle/cross-linked PANI catalyst for Suzuki-Miyaura coupling reactions. Notably, the catalyst was so active that it could catalyze the reaction of aryl chlorides, which were considered to be less active substrates for the high C–Cl bond energy. The substrate scope of the Suzuki-Miyaura coupling reactions was wide, while the catalyst could be recycled and reused for at least five times.



Scheme 5. Pd/PANI/celite-catalyzed one-pot Suzuki–aldol reactions.



Entry	R	Ru@PANs	Yield of biphenyl
1	H	Ru@PANI-H	trace
2	OMe	Ru@PANI-OMe	trace
3	CF_3	Ru@PANI-CF_3	72%

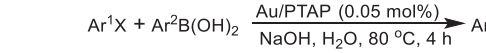
Scheme 6. Ru/PANIs-catalyzed Suzuki-Miyaura coupling reaction of iodobenzene with phenylboric acid.

The oxidative polymerization reaction of aniline with $(NH_4)_2S_2O_8$ in the presence of celite could produce the PANI-coated celite particles (*i.e.*, PANI/celite). Stirring PANI/celite in MeCN solution of $PdCl_2$ led to the Pd/PANI/celite composites. It was found that Pd/PANI/celite was stable to alkali, so that the catalyzed Suzuki-Miyaura coupling reaction and aldol reaction could occur on 1-(4-bromophenyl)ethan-1-one simultaneously to synthesize a series of substituted chalcone derivatives, which were key intermediates in pharmaceutical industry (Scheme 5) [33].

Beside palladium, other transition metals were also employed to prepare the PANI-supported nanocatalysts. Stirring aniline derivatives with $RuCl_3$ in open air afforded the Ru/PANIs, which were then employed as catalysts in the Suzuki-Miyaura coupling reaction of iodobenzene with phenylboric acid to produce biphenyl. The materials prepared from simple aniline and anisidine were found to be inactive and only traces of the desired biphenyl were generated (Scheme 6, entries 1 and 2). Interestingly, by introducing electron-withdrawing CF_3 in to the aniline monomer, the as-prepared electron-deficient PANI-CF_3 supported Ru could well catalyze the reaction and led to biphenyl in 72% yield (Scheme 6, entry 3). It was supposed that larger electron affinity of Ru than Pd resulted in its poor catalytic activity in coupling reactions, and introducing the electron-withdrawing groups into PANI support could weaken the electron affinity of Ru to enhance its catalytic activity [34].

Han *et al.* prepared the gold nanoparticles that were stabilized by poly(2-aminothiophenol) (PATP) [35]. Although sulfur might poison the catalytic metal in many reactions, in this case, it did not reduce the catalytic activity of the material. The prepared Au/PATP was so active that it could catalyze the Suzuki-Miyaura coupling reactions of aryl chlorides with aryl boric acids to give the related

Table 2
Au/PATP-catalyzed Suzuki-Miyaura coupling reactions [35].[a]



Entry	Ar^1X	Ar^2	Ar^1-Ar^2 yield (%)[b]
1	*p*-$HOOCC_6H_4Cl$	Ph	95
2	*p*-$MeOC_6H_4Cl$	Ph	92
3	*o*-$MeOC_6H_4Cl$	Ph	91
4	*p*-$CHOC_6H_4Cl$	Ph	95
5	PhCl	*m*-$MeOC_6H_4$	74
6	PhBr	*m*-$MeOC_6H_4$	82
7	PhI	*m*-$MeOC_6H_4$	90
8	PhCl	*p*-$MeOC_6H_4$	81
9	PhCl	*m*-$NO_2C_6H_4$	79
10	PhCl	2,6-$Cl_2C_6H_3$	56

[a] 2 mmol of aryl halide, 2.4 mmol of arylboric acid and 8 mmol of NaOH were employed.
[b] Isolated yields.

biphenyls in excellent yields up to 95% (Table 2, entries 1–10). The results showed that coordination of sulfur with gold might significantly enhance its catalytic activity, and the work was enlightening for the development of novel catalysts that could work without the use of additional phosphorus ligands [36].

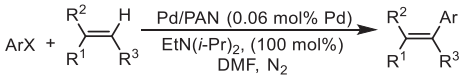
3. Heck reactions

In 2005, PANI-supported nickel [Ni(0)/PANI] was reported to be effective catalyst for Heck reaction [37]. The material could be synthesized *via* three steps: (1) Synthesis of Ni(0) particles being stabilized by *t*-BuONa; (2) Functionalization of the nickel surface by aniline; (3) Oxidative polymerization of the nickel absorbed aniline to generate Ni(0)/PANI. In the first step, NaH was employed to reduce $Ni(OAc)_2$ so that Ni(0) could be generated. Owing to the large steric hindrance of *tert*–butyl, the low valent nickel in generated Ni(0)/2*t*-BuONa complex could be well stabilized. The addition of aniline could replace the nickel surface absorbed *tert*–butoxy due to the strong coordination of aniline nitrogen with nickel. Surprisingly, the coordination of nitrogen was so strong that the addition of $(NH_4)_2S_2O_8$ for the oxidative polymerization of aniline could not oxidize the coordinated Ni(0), and Ni(0)/aniline could be smoothly converted into Ni(0)/PANI without the nickel valence state increasing. Ni(0)/PANI could catalyze the Heck reactions of aryl iodides with terminal alkene such as styrene and acrylates. The material is of profound industrial application value for its low cost as well as the phosphorus-free reaction conditions. Moreover, Pd/PANI that was prepared *via* similar method could also catalyze the Heck reactions to produce the modified terminal alkenes in good yields, in regardless of the relatively higher cost of the catalyst metal [24]. Unfortunately, the focuses of the above works were on the materials design, while substrate scopes of the catalyzed reactions were not comprehensively extended.

In our cases, we synthesized Pd/PANIs catalyst *via* the aerobic oxidative polymerization of aniline in the presence of palladium ions [28]. The material was employed as catalyst for Heck cross-coupling reactions in *N*,*N*-dimethylformamide (DMF) [38]. In the reactions, only 0.06 mol% of Pd was employed, leading to the high TONs (upto 1.7×10^3). The reactions covered for very wide substrate scope, both electron-enriched (Table 3, entries 1–5) and -deficient (Table 3, entries 6–10) aryl halides were favorable substrates. Notably, the protonic groups, such as phenol hydroxyl, did not affect the reaction (Table 3, entry 5). 1-Iodonaphthalene, the halide bearing bulky group could also react with styrene to afford the product in 75% yield (Table 3, entry 11). The reaction was fit for heterocycle-containing substrates (Table 3, entries 12 and 13), and sulfur in the molecules could not poison the catalyst, affording the desired product in moderate yield (Table 3, entry 13). For alkenes, the substrates scope was also wide (Table 3, entries 14–20). It was found that the electron-deficient alkenes were preferable, and the product yield could reach to as high as 87%–96% (Table 3, entries 18 and 19). The reactivities of aryl bromides were weaker, and the catalyst dosage should be enhanced to 0.6 mol% of Pd in most cases (Table 3, entries 21–29). Introducing electron withdrawing -NO_2 into the aryl bromide could significantly activate the C(sp^2)-Br to give the related product in excellent yield (Table 3, entry 25). Reactions of aryl chlorides were also tested, but were unfortunately failed due to the too strong C–Cl bond that could be hardly activated (Table 3, entries 30–34). It seems that special design of catalyst may be required to achieve the C–Cl activation for the PANI-supported metal-catalyzed reactions [35,36]. As a heterogeneous catalyst, Pd/PANIs could be recycled and reused for at least 8 times without obvious deactivation (Fig. 1), and this feature might significantly reduce the catalyst cost for large scale application.

Moreover, PANI could be employed as the coating materials to cover the carbon nanotubes (CNTs) endowing the materials coordination ability to immobilize the palladium nanoparticles firmly

Table 3
Pd/PANI catalyzed Heck cross-couplings of aryl halides with alkenes [38].[a]



Entry	ArX	R^1	R^2	R^3	T (°C)	t (h)	Yield (%) (*E*/*Z*)[b]
1	4-MeC_6H_4I	Ph	H	H	80	24	71
2	3-MeC_6H_4I	Ph	H	H	80	24	73
3	2-MeC_6H_4I	Ph	H	H	120	12	96
4	4-$MeOC_6H_4I$	Ph	H	H	120	12	99
5	4-HOC_6H_4I	Ph	H	H	80	24	82 (87:13)
6	4-FC_6H_4I	Ph	H	H	80	24	79
7	3-FC_6H_4I	Ph	H	H	80	24	60
8	2-FC_6H_4I	Ph	H	H	80	48	67
9	4-ClC_6H_4I	Ph	H	H	80	24	66
10	4-AcC_6H_4I	Ph	H	H	80	48	76
11	1-$C_{10}H_9I$	Ph	H	H	80	24	75
12	2-Iodopyridine	Ph	H	H	120	24	61
13	2-Iodothiophene	Ph	H	H	80	48	55
14	PhI	4-ClC_6H_4	H	H	80	48	82
15	PhI	4-BrC_6H_4	H	H	80	48	70
16	PhI	Ph	Ph	H	120	24	36 [c]
17	PhI	$PhCH_2$	H	H	80	48	69
18	PhI	CO_2Me	H	H	80	24	96
19	PhI	CN	H	H	80	24	87 (90:10)
20	PhI	H	Ph	Ph	120	24	93
21[d]	PhBr	Ph	H	H	150	48	53 [c]
22[d]	4-$MeOC_6H_4Br$	Ph	H	H	150	48	23 (80:20) [c]
23[d]	4-FC_6H_4Br	Ph	H	H	150	48	45 [c]
24[d]	3,5-$(CF_3)_2C_6H_3Br$	Ph	H	H	150	48	55 (95:5) [c]
25	4-$NO_2C_6H_4Br$	Ph	H	H	80	24	91 (92:8)
26[d]	1-$C_{10}H_9Br$	Ph	H	H	150	48	60 [c]
27[d]	PhBr	CO_2Me	H	H	150	48	30 [c]
28[d]	PhBr	CN	H	H	150	48	58 [c]
29[d]	PhBr	H	Ph	Ph	150	48	24 [c]
30[d]	PhCl	Ph	H	H	120	48	Trace [c,e]
31[d]	4-$NO_2C_6H_4Cl$	Ph	H	H	120	48	Trace [c,e]
32[d,f]	PhCl	Ph	H	H	120	48	Trace [c,e]
33[d,g]	PhCl	Ph	H	H	120	48	Trace [c,e]
34[d,h]	PhCl	Ph	H	H	120	48	Trace [c,e]

[a] 1 mmol of aryl halide, 1 mmol of alkene and 1.5 mL of DMF were employed and the reactions were monitored by TLC.
[b] Isolated yields (*E*/*Z* ratios were calculated by ^{1}H NMR and were given in brackets; *E*-isomers only if no *E*/*Z* was provided).
[c] Reaction not completed.
[d] 0.6 mol% of Pd catalyst employed.
[e] Product yield <3%.
[f] 0.1 mmol of dppe was employed as ligand.
[g] 0.1 mmol of PCy_3 was employed as ligand.
[h] 0.1 mmol of P(*n*-Bu)$_3$ was employed as ligand.

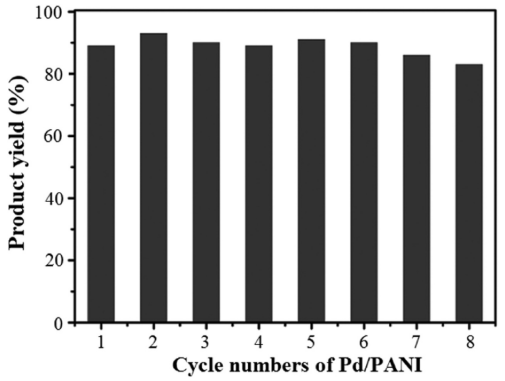
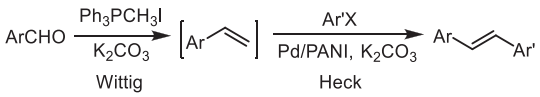


Fig. 1. Catalyst recycling and reusing for Pd/PANI-catalyzed coupling reaction of aryl iodide with styrene [38].



Scheme 7. Pd/PANI-catalyzed one-pot Wittig-Heck reactions.

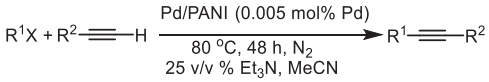
[39]. The as-prepared nano composites could catalyze the Heck coupling reactions. It was found that the PANI layer thickness was the key determining the stability of the catalyst. Protonation of PANI with CNTs led to the electron transfer between the layers strengthening the interaction. Therefore, the relatively higher CNTs content, *i.e.*, PANI/CNTs = 0.5/1, could well stabilize the composites, resulting in the better recycling performances of the materials.

PANIs can be protonized under acidic conditions so that their coordination ability may be reduced. In contrast, they are very stable under alkaline conditions. Therefore, the Pd/PANI-catalyzed reactions may be combined with the reactions occurring under alkaline conditions to enhance the synthetic efficiency. For example, the Pd/PANI-catalyzed one-pot Wittig–Heck reactions could afford substituted alkenes from aldehyde and aryl halide directly (Scheme 7). Similar Pd/PANI-catalyzed one-pot Wittig–Suzuki reactions were also successfully achieved by the same group [40].

4. Sonogashira reactions

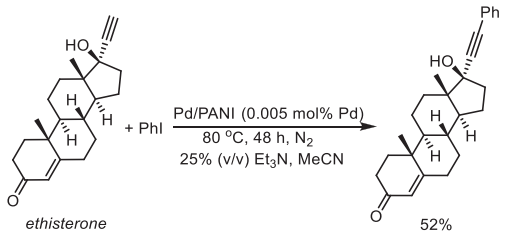
The PANI-supported palladium catalyst has been successfully employed in the Sonogashira coupling reactions, which afforded efficient tools for the functionalization of terminal alkynes (Table 4) [41]. The terminal C–H of alkynes is even more active than sp^2-C-H in alkenes. Thus, the catalyst dosage of the reaction could be reduced and only 0.005 mol% of Pd was employed (Table 4 *vs.* Table 3 in which 0.06 mol% of Pd was used). The reaction did not require special amine base such as EtN(*i*-Pr)$_2$, and just Et_3N, the simple and cheap amine, could work well as the base to neutralize the released hydrogen halides of the reaction process. Moreover, MeCN was employed as solvent instead of DMF. By heating halides with terminal alkynes in the presence of Pd/PANI and Et_3N in MeCN at 80 °C for 48 h under N_2 protection, the desired coupling products could be smoothly produced (Table 4, entries 1–20). Both electron-enriched (Table 4, entries 1–4) and –deficient (Table 4, entries 5–11) aryl iodides were favorable substrates, and the reaction was not affected by steric hindrance of the substrates (Table 4, entry 12). Heterocycle iodides, including the one containing sulfur, could be employed to modify the terminal alkyne (Table 4, entries 13 and 14). The reactivity of aryl bromides was weaker, but could still afford the product in moderate yields (Table 4, entries 15 and 16). Interestingly, the reaction of acyl chloride with terminal alkyne could directly produce alkynyl ketone, a useful molecular skeleton

Table 4
Pd/PANI-catalyzed Sonogashira reactions [41].[a]



Entry	R^1X	R^2	Product yield (%)[b]
1	PhI	Ph	86
2	2-MeC_6H_4I	Ph	52
3	3-MeC_6H_4I	Ph	61
4	4-MeC_6H_4I	Ph	50
5	3-$NO_2C_6H_4I$	Ph	96
6	2-FC_6H_4I	Ph	96
7	3-FC_6H_4I	Ph	77
8	4-FC_6H_4I	Ph	70
9	4-ClC_6H_4I	Ph	72
10	4-BrC_6H_4I	Ph	57
11	4-AcC_6H_4I	Ph	50
12	1-$C_{10}H_7I$	Ph	81
13	2-Iodopyridine	Ph	40
14	2-Iodothiophene	Ph	70
15	3-$NO_2C_6H_4Br$	Ph	50
16	3,5-$(CF_3)_2C_6H_3Br$	Ph	64
17	PhCOCl	Ph	53
18	PhI	4-MeC_6H_4	68
19	PhI	4-ClC_6H_4	10
20	PhI	*c*-C_3H_5	58

[a] 1 mmol of halide, 1 mmol of terminal alkyne, 0.5 mL of Et_3N and 1.5 mL of MeCN were employed.
[b] Isolated yields.



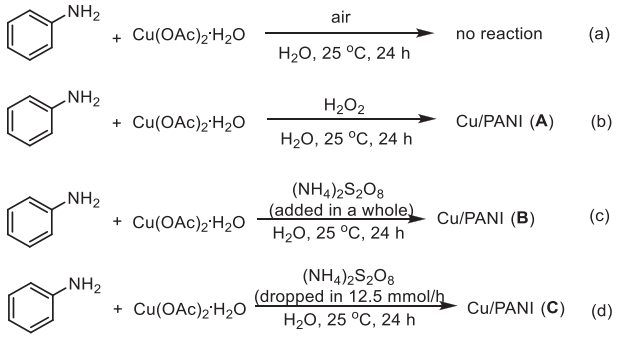
Scheme 8. Modification of *Ethisterone via* the Pd/PANI-catalyzed Sonogashira coupling reaction.

in organic synthesis (Table 4, entry 17). It was found that electron-deficient alkyne was less active (Table 4, entries 19 *vs.* 18), while aliphatic alkyne was also fit for the reaction (Table 4, entry 20).

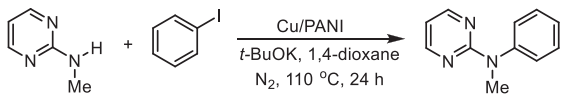
The reaction could be successfully applied on the substrate with complex molecular structure. For example, the terminal alkyne in *Ethisterone*, a pharmaceutical intermediate, could be modified by phenyl *via* the Pd/PANI-catalyzed reactions with iodobenzene (Scheme 8). As a heterogeneous catalyst, Pd/PANI could be recycled and reused for the next turn of reaction. For the reaction of 3-$NO_2C_6H_4I$ with phenylacetylene, the catalyst was so stable that could be reused for at least 6 times with the product yield over 80%. Moreover, since the employed palladium was very few and PANI itself could firmly coordinate with the metal to avoid its releasing, the metal residue in product was very low, and this feature well met the requirements of pharmaceutical industry.

5. Buchwald-Hartwig coupling reactions

We have developed the PANI-supported copper catalyst (Cu/PANI) for Buchwald-Hartwig couplings of pyrimidine 2-amine, which are useful for pharmaceutical industry because pyrimidine 2-amine moieties widely exist in a variety of medicines [42,43]. The oxidative polymerization reaction of aniline with Cu(OAc)$_2$ in open air was initially performed to synthesize Cu/PANI, but failed (Scheme 9a). O_2 as a stronger oxidant was also found to be ineffective for the reaction. Failure of the attempts was probably due to the low electric potential difference of Cu(II) *vs.* Cu(I), which



Scheme 9. Methods for the preparation of Cu/PANIs.



Entry	Cu/PANI catalyst	Yield of product
1	Cu/PANI (**A**)	74%
2	Cu/PANI (**B**)	21%
3	Cu/PANI (**C**)	12%

Scheme 10. Buchwald-Hartwig coupling reactions of *N*-methylpyrimidin-2-amine with iodobenzene.

could not meet the requirements for the oxidative polymerization of aniline. Therefore, we then tried to promote the reaction by using chemical oxidant and H_2O_2 was chosen for its green features (Scheme 9b). In this case, Cu/PANI (**A**) as a black powder could be prepared. By using $(NH_4)_2S_2O_8$ as oxidant, Cu/PANIs (**B** and **C**) were also synthesized similarly for comparison (Schemes 9c and d).

Cu/PANI (**A**) could well catalyze the Buchwald-Hartwig coupling reaction of *N*-methylpyrimidin-2-amine with iodobenzene, affording 74% of the product yield (Scheme 10, entry 1). In contrast, Cu/PANIs (**B** and **C**) showed very poor catalytic activities (Scheme 10, entries 2–3). Materials characterizations indicated that this was due to the disordered morphologies of Cu/PANIs (**B** and **C**) being caused by the too quick oxidative polymerization reaction of aniline in the presence of $(NH_4)_2S_2O_8$. Moreover, sulfur pollution from $(NH_4)_2S_2O_8$ might lead to the catalytic metal poisoning and deactivate the copper catalytic sites.

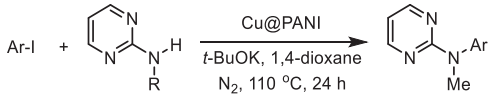
Substrate scope of the reaction was then extended. Both electron-enriched and deficient iodides were favorable substrates for the reaction (Table 5, entries 1–8). The reaction of 2-iodinaphthalene could also occur smoothly, in regardless of the large steric hindrance of the substrate (Table 5, entry 9). Notably, the catalyst was tolerable to sulfur-containing substrate, and this feature might be beneficial for the application of the material in sulfur-containing medicine synthesis (Table 5, entry 10). Primary amine, such as pyrimidin-2-amine, was too active, and its coupling reaction with iodobenzene led to a series of inseparable mixtures (Table 5, entry 11). By contrast, *N*-isopropylpyrimidine-2-amine was too stable for the reaction (Table 5, entry 12).

The reaction did not need additional ligand and its catalyst TONs ranged from 254 to 366. As a heterogeneous catalyst, Cu/PANI (**A**) can be separated from the reaction system by centrifugation and reused for at least 5 times without deactivation.

6. Ullmann reactions

Pd/PANIs were also employed as catalysts for Ullmann reactions [44]. In the study, four types of aniline monomers such as aniline, 4-(trifluoromethyl)aniline, 4-methoxyaniline and 3,5-dimethoxyaniline were employed to prepare the corresponding Pd/PANIs such as Pd/PANI-H, Pd/PANI-CF_3, Pd/PANI-OMe and Pd/PANI-$(OMe)_2$ successfully. Palladium contents of the materials were similar, varying from 8.8 wt% to 9.9 wt%. The materials could catalyze the Ullmann reactions of aryl iodides using hydrazine hydrate as the reductant. By heating aryl iodides with hydrazine hydrate in the presence of $(i\text{-Pr})_2$NEt in *N*-methylpyrrolidone (NMP) at 140 °C for 24 h, the desired biphenyls could be produced (Table 6, entries 1–32). It was found that, the substituents in PANI supports exerted obvious influences on the catalytic activities of the materials. Bearing electron-donating MeO-, Pd/PANI-$(OMe)_2$ was screened out to be the best catalyst among the candidates, affording bi-phenyls in upto 77% yield, while the catalyst TON could reach 1469 at the highest. Both electron-enriched (Table 6, entries 1–12) and -deficient (Table 6, entries 13–24) aryl iodides were fit for the reaction, while the substrate bearing bulky naphthyl resulted in poor product yield (Table 6, entries 25–28). 2-Iodidepyridine as the example of heterocycle-containing substrate was employed, and the reaction could produce bi-pyridine derivatives in moderate yield (Table 6, entries 29–32).

Table 5
Cu/PANI-catalyzed Buchwald-Hartwig coupling reactions.[a]



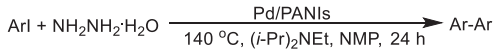
Entry	ArI	R	Yield (%)[b]
1	PhI	Me	72
2	4-ClC_6H_4I	Me	72
3	4-BrC_6H_4I	Me	68
4	4-FC_6H_4I	Me	73
5	4-MeC_6H_4I	Me	71
6	4-$MeOC_6H_4I$	Me	63
7	3,5-$(Me)_2C_6H_3I$	Me	64
8	2-$MeOC_6H_4I$	Me	70
9	2-$C_{10}H_7I$	Me	65
10	3-Iodothiophene	Me	54
11	4-$MeOC_6H_4I$	H	Mixture
12	PhI	*i*-Pr	No reaction

[a] 1 mmol of aryl iodide, 1.5 mmol of *N*-pyrimidine-2-amine, 2 mmol of *t*-BuOK and 20 mg Cu/PANI were stirred in 2 mL 1,4-dioxane at 110 °C for 24 h under N_2 protection.
[b] Isolated yields.

Materials characterizations indicated that the materials possessed similar micro-morphologies. The different catalytic activities were probably caused by the substituents in PANIs. It was supposed that, electron-donating groups in PANI support could enhance the electronegativity of nitrogen in PANIs to strengthen the coordination with the palladium. The even more negatively charged palladium centres could lead to Pd(0) more easily to accelerate the oxidative addition reaction with C-I during the reaction process. Moreover, it was also found that the Pd/PANIs bearing electron-donating groups could absorb the reactants better. All of the above reasons led to the high catalytic activity of the material.

In 2020, Wang *et al.* synthesized Pd^{2+}/PANI composites by combining self-stabilized dispersion polymerization method with *in-situ* composite materials [45]. The polyaniline carrier synthesized by this method possessed a high reduced structure (75%), which showed good synergistic effect in catalytic Ullmann reaction and greatly reduced the use of reducing agents such as hydrazine hydrate. The results of material characterization showed that the divalent palladium in the catalyst and the zero-valent palladium in the *in-situ* reaction promoted the reaction, while the polyaniline support, as a stabilizer and dispersant, prevented the agglomeration of metal particles and extended the service life of the catalyst. $PdCl_2$/PANI catalyst (pre-$PdCl_2$/PANI) was prepared by self-stabilizing dispersion polymerization (SSDP) *in-situ* reac-

Table 6
Pd/PANIs-catalyzed Ullmann reactions [44].[a]



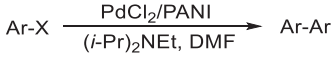
Entry	Ar	Catalyst (mol%)[b]	Yield (%)[c]	TON[d]
1	Ph	Pd/PANI-H (0.054)	65	1214
2		Pd/PANI-CF_3 (0.050)	16	322
3		Pd/PANI-OMe (0.056)	67	1200
4		Pd/PANI-$(OMe)_2$ (0.052)	74	1411
5	4-MeC_6H_4	Pd/PANI-H (0.054)	43	803
6		Pd/PANI-CF_3 (0.050)	14	282
7		Pd/PANI-OMe (0.056)	44	788
8		Pd/PANI-$(OMe)_2$ (0.052)	68	1297
9	4-$MeOC_6H_4$	Pd/PANI-H (0.054)	50	934
10		Pd/PANI-CF_3 (0.050)	22	443
11		Pd/PANI-OMe (0.056)	58	1039
12		Pd/PANI-$(OMe)_2$ (0.052)	77	1469
13	4-FC_6H_4	Pd/PANI-H (0.054)	62	1158
14		Pd/PANI-CF_3 (0.050)	9	181
15		Pd/PANI-OMe (0.056)	63	1129
16		Pd/PANI-$(OMe)_2$ (0.052)	72	1373
17	3-FC_6H_4	Pd/PANI-H (0.054)	56	1046
18		Pd/PANI-CF_3 (0.050)	10	202
19		Pd/PANI-OMe (0.056)	57	1021
20		Pd/PANI-$(OMe)_2$ (0.052)	70	1335
21	4-ClC_6H_4	Pd/PANI-H (0.054)	64	1195
22		Pd/PANI-CF_3 (0.050)	24	484
23		Pd/PANI-OMe (0.056)	64	1147
24		Pd/PANI-$(OMe)_2$ (0.052)	77	1469
25[e]	1-$C_{10}H_7$	Pd/PANI-H (0.054)	15	280
26[e]		Pd/PANI-CF_3 (0.050)	3	60
27[e]		Pd/PANI-OMe (0.056)	17	305
28[e]		Pd/PANI-$(OMe)_2$ (0.052)	26	496
29	2-pyridine	Pd/PANI-H (0.054)	53	990
30		Pd/PANI-CF_3 (0.050)	17	343
31		Pd/PANI-OMe (0.056)	54	967
32		Pd/PANI-$(OMe)_2$ (0.052)	60	1144

[a] 1 mmol of aryl iodide, 1 mmol of $NH_2NH_2·H_2O$, 1 mmol of $(i\text{-Pr})_2NEt$, 0.6 mg of Pd/PANI catalyst and 1.5 mL of NMP were employed in the reaction.
[b] Molar percent (mol%) of the palladium in catalyst (0.6 mg) on the basis of the aryl iodide amount were given in the parenthesis.
[c] Isolated yields based on the aryl iodide substrate.
[d] TONs of the catalyst *vs.* product (mol/mol).
[e] Reaction performed in 72 h.

tion using small molecular acids such as hydrochloric acid and trace amounts of $PdCl_2$ as guiding agent and dopant. The prepared pre-$PdCl_2$/PANI catalyst had obvious D-π conjugation effect. In addition, in the subsequent coupling reactions, the as-prepared catalyst was partially reduced to zero-valent palladium by *in situ* reaction, resulting in the original bivalent palladium and the new zero-valent palladium species uniformly supported on the PANI network. On this basis, a novel catalyst (Pd^{2+}-Pd^0/PANI) was synthesized.

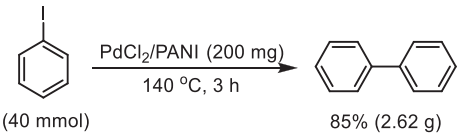
The results of substrate expansion showed that $PdCl_2$/PANI catalyst could well catalyze Ullmann reactions. Although the substituents on benzene ring exerted certain influences on the reactions, for substrates with electron-enriched or -deficient substituents, the reactions could lead to good product yields (Table 7, entries 1–5, 7–12). Substituent at ortho-position or with large steric hindrance might led to reduced substrate activity (Table 7, entries 6, 13, 15). Protonic substituent in substrate, such as the phenol hydroxyl, was found to be tolerable in the reaction (Table 7, entry 14). The catalyst could not be poisoned by sulfur-containing substrates (Table 7, entry 16). Besides, $PdCl_2$/PANI could catalyze the Ullmann coupling reactions of aryl bromides, but the yields were lower than the reactions of iodides for the higher C-Br bond energy (Table 7, entries 17–19). The catalyst could be recycled and reused for at least 8 times, while the reaction of iodobenzene could be successfully magnified to 40 mmol, affording 2.62 g of biphenyl (Scheme 11).

Table 7
Ullmann coupling reactions of aryl iodide and aryl bromide over $PdCl_2$/PANI catalysts [45].[a]



Entry	ArX	Time (h)	Yield (%)[b]	TON[e]	TOF (h^{-1})[f]
1	PhI	2	85	1124	562 (50)
2	4-FC_6H_4I	2.5	80	1058	423
3	4-ClC_6H_4I	2.5	85	1124	450
4	4-BrC_6H_4I	2.5	85	727	290
5	3-ClC_6H_4I	6	85	1124	187
6	2-ClC_6H_4I	6	30	396	66
7	4-MeC_6H_4I	2.5	67	886	354
8	4-$MeOC_6H_4I$	2.5	76	873	349
9[c]	4-$NO_2C_6H_4I$	6	70	793	132
10	4-CNC_6H_4I	2.5	82	1084	433
11[c]	4-$MeCOC_6H_4I$	6	55	727	121
12[c]	4-$MeOOCC_6H_4I$	6	63	833	138
13	1-$C_{10}H_7I$	2.5	40	529	211
14[c]	4-OHC_6H_4I	6	61	674	112
15	2-Cl-4-FC_6H_4I	6	35	463	77
16	2-Iodothiophene	6	95	1256	209
17[d]	PhBr	12	50	661	55
18[d]	4-ClC_6H_4Br	12	70	926	77
19[d]	4-$MeOC_6H_4Br$	12	45	595	49

[a] 1 mmol of aryl iodide, 2 mmol of $(i\text{-Pr})_2NEt$, $PdCl_2$/PANI (0.075 mol% Pd), 0.5 mL of DMF, 140 °C.
[b] Isolated yields.
[c] Recrystallization yield.
[d] 1 mmol of aryl bromide and 1 mL dioxane.
[e] TONs were calculated based on the ICP results and molar percentages of the catalysts.
[f] TOF is the turnover frequency, represents the amount of reactant that is converted per unit time by the unit active site.



Scheme 11. The gram-scale preparation of biphenyl *via* the $PdCl_2$/PANI-catalyzed coupling.

7. Conclusions and perspective

Investigations on PANI-supported nano metal catalysts are booming. Indeed, the PANI supports are a type of non-phosphorus ligands that can stabilize the nano metal particles and enhance their catalytic activities [46,47]. As organic polymer carriers, PANIs are versatile materials and can be modified by introducing a variety of functional groups, affording additional optional parameters for catalyst activity tuning [44]. The catalysts have been widely applied in coupling reactions, which can modify the organic molecules precisely and provide useful tools for drug development. The strong coordination of nitrogen in PANIs can obviously reduce the loss of metals during the reaction process, affording the products with very low metal residue [41,48]. These techniques are of great application potential for pharmaceutical industry.

However, there are still challenges in the field. The conflict of polymerization degree of PANIs with the catalyst activities is a typical issue that needs to be resolved. Catalysts with low polymerization degree PANIs were soluble in many solvents and cannot be recycled and reused, resulting in the high cost for industrial-grade application [49]. Over polymerization of aniline, however, may reduce the catalyst activity for the elevated steric hindrance of the support [50,51]. Giving full play to the interdisciplinary research advantages of polymer chemistry, material chemistry and organic

chemistry to develop the functionalized PANIs with good stability, may resolve the issue. In addition, controlling the microstructure of the materials and probing the relationships of the substituents with their catalytic activities are also significant protocols for further improvement of the catalysts. Very recently, the PANIs-supported bimetallic sub-nanoparticles were found to be efficient for Sonogashira and Suzuki coupling reactions, opening a new door in the research of PANI materials [52]. The interactions of multi metals on PANI support may be beneficial for the catalyzed reactions, and the details of mechanism need to be further clarified [53]. This research field is full of opportunities and challenges and may deserve further investigations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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