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Palladium Separation by Pd-Catalyzed Gel Formation via Alkyne Coupling

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ABSTRACT: Selective entrapment of precious metals from industrial wastes containing various metals is a most challenging branch of environmental science. Developed methods like solvent or solid-phase extraction, ion exchange, co-precipitation, membrane filtration and adsorption rely on chelation, electrostatic attraction or ion exchange, and these methods present limited selectivity and require post-treatment for further application. Herein, an original concept is reported involving utilization of the superior catalytic properties of Pd selectively for efficient Pd entrapment from other metals. Specifically, side chains of polyvinyl alcohol (PVA) functionalized with alkynyl groups are catalytically dimerized using Pd(II), which forms gels. The Pd(II) ions are coordinatively encapsulated into the gel networks, while the other metal ions are excluded from the networks, thus allowing to separate and immobilize Pd. The entrapped Pd(II) is also reduced to Pd(0) nanoparticles (PdNPs) forming PdNPs@alkyne-PVA aerogels that exhibit a high catalytic activity for the Suzuki-Miyaura cross-coupling reaction. PdNPs@alkyne-PVA aerogels are further carbonized to PdNPs@C networks for efficient electrochemical hydrogen evolution reaction (HER). This method provides an effective way not only to selectively separate Pd, but also to utilize the entrapped Pd resources for multiple catalysis without further post-treatment of entrapped Pd source.

INTRODUCTION

Among the Pt-group metals, Pd is the most widely used in industry due to its specific physical and chemical properties, and in particular its high catalytic activity.[1-4] This causes Pd traces in industrial wastes to be usually higher than those in natural minerals, making waste electric and electronic equipment considerable secondary raw Pd sources.[5] Therefore, effective entrapment of Pd sources from industrial wastes is of great significance to ecological and economical full utilization of Pd.[6-10] In general, the recycle of Pd sources follows two steps: (i) dissolving Pd and other metals derived from solid wastes in strong acid, and (ii) separation of Pd from other metal ions in solution. There are several methods, e.g., solvent extraction,[11-13] ion-exchange,[14] membrane separation[15-17] and adsorption[18-20] that are available in the literature for the second step. Basically, these methods work obeying two main principles: (i) the preparation and functionalization of guest materials; (ii) the "entrapping" of metal ions using the functionalized features of host materials like chelation, electrostatic attraction, ion exchange, or physical encapsulation of ions in porous structures such as MOFs[6, 21-24] or COFs.[25] However, the recycle processes using aforementioned methods mainly depend on the chemical and physical properties of host materials. Consequently, these methods are considered as "passive" methods with a relatively low selectivity. In other words, the common disadvantage of these strategies is the difficult selective "recognition" of each metal ion from the others. Hence, designing a smart and "positive" method that allows distinguishing a metal from others in a group of metal ions using its own "unique feature" is greatly desired. Pd is one of the most popular catalytic metals with outstanding activities in numerous chemical reactions.[26-29] Therefore it is possible to devise a way to separate and entrap Pd *via* the use of its "unique feature", superior catalytic activities.

Inspired by this concept, we propose a new strategy for the separation and entrapment of Pd(II) ions from solutions containing mixtures of various non-precious metal ions based on the high catalytic activity of Pd for the Glaser coupling reaction.[30-32] In brief, terminal alkynes functionalized with side chains of polyvinyl alcohol (PVA) are synthesized, and then cross-linked to bis-alkyne-PVA by fast Pd(II)-catalyzed Glaser coupling, which forms the gel. Following dimerization catalysis, the Pd ions remain coordinated in the bis-alkynyl environment, i.e. embedded in the network, whereas the other metal cations that are not located in the catalytic site environment remain free in the solution. Finally, Pd(II) ions are selectively screened out and embedded in the gel by immersion of the gel into ion-free water and washing away other metal ions that are only physically absorbed. Meanwhile, theses entrapped Pd(II) sources that are homo-dispersed in the bis-alkynyl network were directly reduced by $NaBH_4$ to Pd^0 nanoparticles (PdNPs). Subsequently they efficiently catalyze the Suzuki-Miyaura cross-coupling reaction[33-35] and electrochemical hydrogen evolution reaction (HER) without further treatment.

EXPERIMENTAL SECTION

Preparation of Alkyne-Substituted PVA: Alkyne-Substituted PVA (Alkyne-PVA) was prepared according to previous reports.[36] In brief, 400 mg PVA was dissolved in 10 mL DMF stirred at 80 °C for 2 h. After cooling to room temperature, 1.22 g (7.5 mmol) CDI was added in one portion to the PVA solution under nitrogen atmosphere. After the reaction mixture was stirred under nitrogen at room temperature for another 3 h, 413 mg (7.5 mmol) propargylamine was added. Stirring was continued at room temperature for 16 h. Afterward 4 mL of a concentrated aqueous ammonia solution was added, and then the mixture was stirred at room temperature for another 1 h. The solvent was reduced to ~5 mL volume by rotary evaporation. Finally, the alkynes substituted polymer was precipitated from the residual DMF solution by adding to 50 mL ethanol drop by drop. The precipitation was washed by ethanol and diethyl ester and dried in vacuum at 70 °C to give a light yellow powder.

Preparation of Pd(II)@alkyne-PVA gels: 50 mg Alkyne-PVA was dissolved in 0.8 mL DMF in a vial. A certain amount of Na_2PdCl_4 was dispread in mixture of DMF and water (or a certain concentration of HCl aqueous solution) (200 μL, 1:1, v/v). The Na_2PdCl_4 solution was dropped into Alkyne-PVA solution and wobbled to a homogenized mixture. The resulting solution was sealed to form a gel under natural light and air at room temperature. The obtained wet gel was subjected to solvent exchange with 15 mL deionized water for 24 h. The gelation possibility of other metal ions was investigated by using the same method as that used for the Pd(II)@alkyne-PVA gel.

Preparation of PdNPs@alkyne-PVA aerogels: The PdNPs@alkyne-PVA aerogel was in situ reduced from Pd(II)@alkyne-PVA gel by $NaBH_4$. In briefly, Pd(II)@alkyne-PVA gel was soaked in 5 mL water with 10 equivalents of $NaBH_4$. Black Pd(0)@alkyne-PVA gel was obtained until no bubbles were generated from the solution. The black gel washed with water (10 mL × 6), and finally freeze-drying to obtained aerogel catalyst.

Preparation of PdNPs@CNWs: The PdNPs@alkyne-PVA aerogel was annealed at 700 °C for 6 h in a Ar filled tube furnace with a heating rate of 2 °C min^{-1} to foam PdNPs embedded carbon networks (designated PdNPs@CNWs).

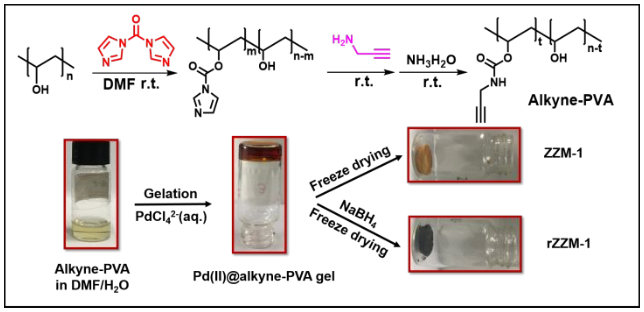
NMR analysis of Pd(II)-catalyzed N-Methyl proparylamine: N-Methyl propargylamine (0.25 mmol) and Na_2PdCl_4 (0.5 mol%) were dissolved in 400 μL *d*$_6$-DMSO and 40 μL D_2O. The mixture was transferred to a NMR tube and monitored by 1H NMR spectroscopy.

Separation of Palladium: A series of solution of Pd^{2+} mixed with another metal ions (3 times Pd^{2+} concentration) were prepared by DMF/HCl(aq) (400 μL, 1:1, v/v) in advance. Then, the above mixture was added into the prepared alkyne-PVA solution (50 mg in 0.8 mL DMF). After gelation the gels were washed by water a several times and freeze dried to Pd-entrapped aerogels.

RESULTS AND DISCUSSION

Pd(II)@alkyne-PVA gel is prepared *via* a spontaneous Pd^{2+}-induced gelation of Alkyne-PVA in a DMF/H_2O solution at room temperature (r.t.) (Scheme 1). The Pd(II)@alkyne-PVA aerogel, ZZM-1, is obtained by freeze-drying of the Pd(II)@alkyne-PVA gel. The PdNPs@alkyne-PVA aerogel, rZZM-1, is fabricated through reduction of Pd(II)@alkyne-PVA gel with $NaBH_4$ and followed by freeze-drying.

Scheme 1. Preparation of Pd(II)@alkyne-PVA aerogel (ZZM-1) and PdNPs@alkyne-PVA aerogel (rZZM-1)



The microstructure of ZZM-1 was first investigated using scanning electron microscopy (SEM), and the result showed that it was an intensive network with a porous structure (Figure 1a). The Brunauer, Emmett and Teller (BET) test confirmed the porous feature revealing a surface area of 46 m^2 g^{-1} (Figure S1). Further thermogravimetry analysis (TGA) data (Figure 1b) showed that Pd was entrapped by ZZM-1 and rZZM-1. The differences of thermogravimetry in Alkyne-PVA, ZZM-1 and rZZM-1 after 500 °C are because of the introduction of Pd.

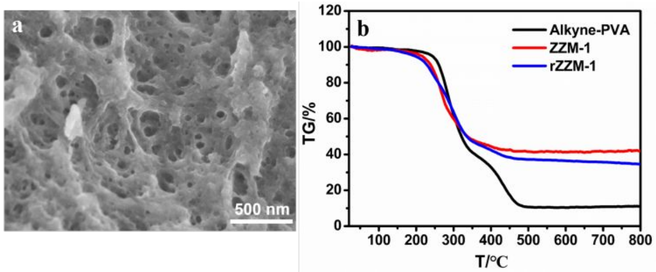


Figure 1. SEM images of ZZM-1 (a); TG curve of Alkyne-PVA, ZZM-1 and rZZM-1 (b).

To take insight into the mechanism and specificity of the gelation processes, a series of experiments and theoretic calculations have been carried out. First, various metal ions including Pd^{2+}, Ru^{3+}, Rh^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+} and Mn^{2+} have been introduced into the Alkyne-PVA solution to estimate if these ions can trigger the Alkyne-PVA polymerization. Only Pd^{2+} induces the gelation within 2 min to form the Pd(II)@alkyne-PVA gel (Figure 2), whereas no obvious changes were observed from the solutions containing the other metal ions even for 6 months, suggesting that the gelation processes were preferably conducted in the presence of Pd(II). Additionally, $PdCl_2$ that is regarded as another Pd(II) source also shows a process of gelation comparable to that of Na_2PdCl_4 (Figure S2). Based on the outstanding catalytic performance of Pd(II), one might assume that other noble metal ions, such as Au(III) and Pt(IV), could also display some catalytic activities towards the Glaser coupling-induced gelation. However, we found that Au(III) and Pt(IV) are not able to induce gelation even after 72 h (Figure S3). Accordingly, in our case, it appears that Pd(II) is an extremely selective catalyst among all metals.

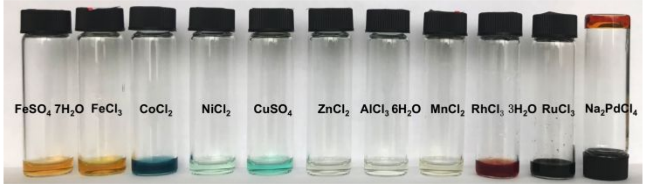


Figure 2. Comparison of the gelation process induced by different metal ions through this strategy.

To explain this gelation processes, Density Functional Theory (DFT) calculations (Figure 3) have been conducted taking the Co^{2+}, Ni^{2+} and Pd^{2+} ions as examples for research models. The interaction between metal ions and alkyne (C≡C) forming π-type complexes has been previously reported.[37-38] The results show that the binding energies of the metals bonded with the neighboring ethynyl group of one Alkyne-PVA chain are about 50 kcal/mol more positive than those of metals bonded with two ethynyl groups in two different Alkyne-PVA chains (Figure 3a and 3b) . This means that the above metals link with the ethynyl groups in two different Alkyne-PVA chains to achieve more stable structures. Meanwhile, the π-type binding strength between two ethynyl groups in different Alkyne-PVA chains and metal ions follows the order Ni^{2+} $>Pd^{2+}$ $>$ Co^{2+} (Figure 3a). Alkynes are slightly more strongly coordinated with Ni^{2+} than with Pd^{2+} and Co^{2+}, which means that Ni^{2+} would induce the gelation more easily than Pd^{2+} and Co^{2+} if coordination was responsible for the reaction. The experiments show the opposite, however, i.e. only Pd^{2+} induced the gelation, (Figure 2). Hence, the gelation process was kinetically controlled rather than simply related to the coordination of ligands to metal ions. Nevertheless, it has been reported that Pd(II), in the presence of Cu(I), is a good catalyst for the Glaser reaction that involves the coupling of two terminal alkynes, forming diynes.[32] Thus, the gelation process is taken into account by the Glaser crosslinking of alkynes in PVA with the expectation that Pd(II) is also playing the role of Cu(I) in the catalytic process. The Glaser-coupling reaction between alkynyl-terminated side chains of ZZM-1 was confirmed by FT-IR spectroscopy (Figure S4a). Compared to Alkyne-PVA, the peak belonging to the stretch of C≡C terminal alkyne at 2130 cm^{-1} disappears in ZZM-1. In addition, the ^{13}C solid-state NMR spectrum of ZZM-1 (Figure S4b) exhibits a strong shift of the signal corresponding to the carbon-carbon triple bond of alkyne at 73 ppm in ZZM-1. This clearly shows the formation of a new carbon-carbon bond upon Glaser-coupling reaction. To further confirm the Glaser-coupling catalyzed by Pd(II) under ambient conditions, *N*-methyl propargylamine, that is similar to the side chain of Alkyne-PVA, was utilized as a test example. The dimerization reaction of *N*-methyl propargylamine catalyzed by $PdCl_2$ was monitored by ^1H NMR (Figure 4a, 4b and 4c). The intensity of the signal of proton 1 in the terminal alkyne at 3.0 ppm decreases as the reaction progresses. Meanwhile, the signals of proton 2 of the methyl group at 2.24 ppm and proton 3 of the methylene group at 3.22 ppm are slightly shifted upfield. These results are in good agreement with previous literature[39] confirming alkyne dimerization to *N, N'*-dimethylhexa-2,4-diyne-1,6-diamine *via* Glaser coupling. Subsequently, the

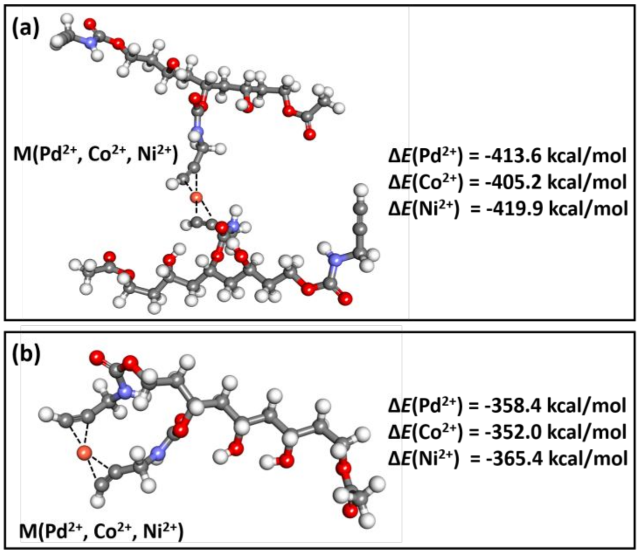


Figure 3. Two Alkyne-PVA chains (a); one single Alkyne-PVA chain (b). The binding energies of the ligands/components to the metal ions are also listed. Colors in the figure: orange-metal ion, red-O, blue-N, grey-C, white-H.

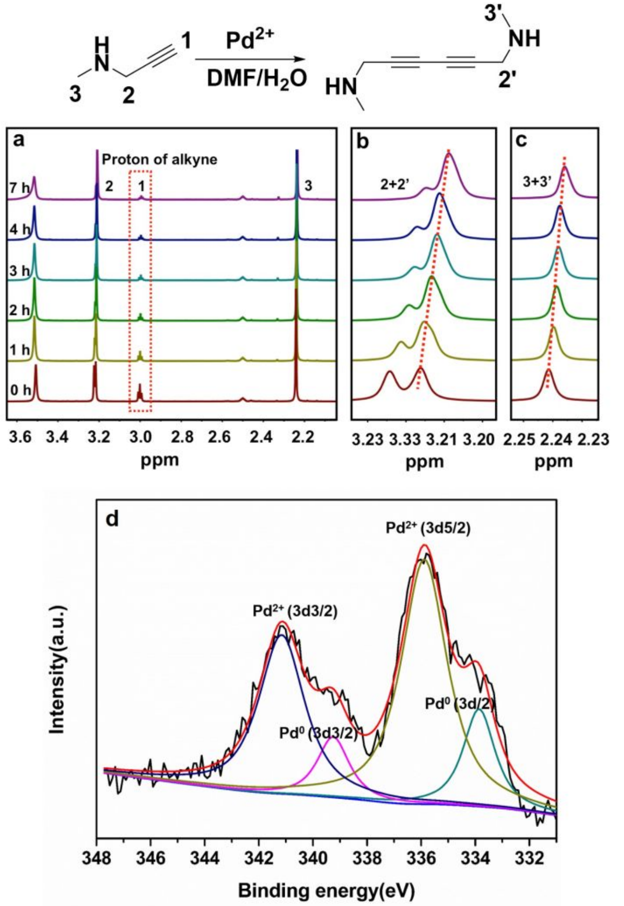
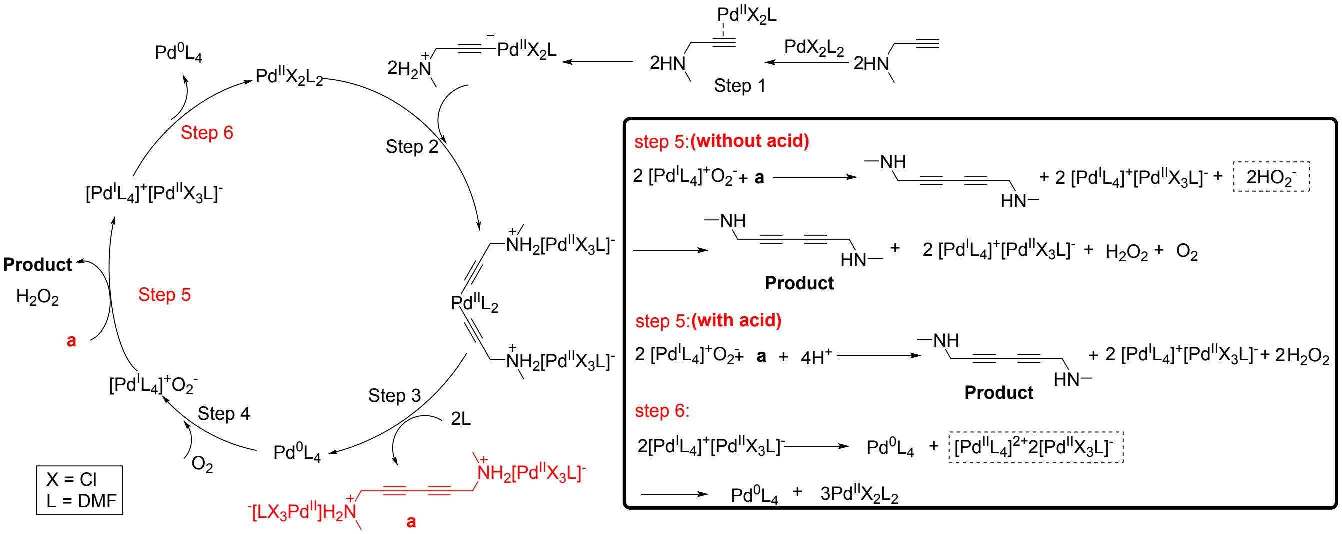


Figure 4. ^1H NMR of *N*-methyl propargylamine at different reaction times (a); signal of proton 2 in methane (b); signal of proton 3 in methyl (c); and XPS spectra of ZZM-1 (d).

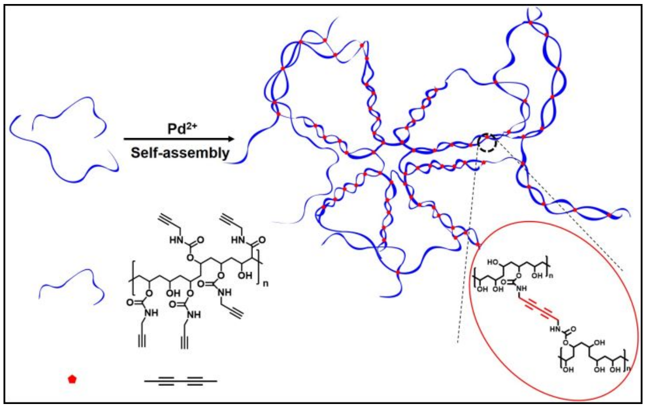
Pd(II)-catalyzed alkyne coupling for gelation is followed by reductive elimination (Scheme 2), since both Pd(II) (located at 337 and 342.1 eV) and Pd(0) (located at 339 and 344.2 eV) were found in the XPS of ZZM-1 (Figure 4d). Finally, the gelation rate of Pd(II)@alkyne PVA gel was shown to be closely related to the concentration of Pd(II), as the gelation process was much accelerated by increasing the concentration of Pd(II), confirming that Pd(II) catalyzed the gelation (Table S1).

Scheme 2. General mechanism for the Pd(II)-catalyzed homocoupling of *N*-methyl-propargylamine



The long-known Glaser coupling is usually carried out under aerobic conditions, as it is here, because O_2 is consumed stoichiometrically in the reaction. The reaction is generally catalyzed by a mixture of Pd and Cu salts, because the Cu salt is necessary to mediate Pd(0) re-oxidation by O_2 to Pd(II) in the catalytic cycle, as in the Wacker process.[40] Here, only Pd(II) is present, thus Pd(II) must also play the role of responsible for alkyne deprotonation and transmetallation agent as in the Sonogashira reaction[41-42] and as oxidation mediator. It is also found that the presence of acid (Table S2) accelerates the process of gelation, which corresponds well to step 5 (Scheme 2) in our mechanism. Therefore, as shown in Scheme 3, Pd(II) catalyzes cross-linking of Alkyne-PVA. Then it becomes encapsulated inside the alkyne network of PVA, because the alkyne group contains π electrons and herewith strongly coordinates to Pd(II).

Scheme 3. Proposed mechanism of the gelation process for Pd(II)@alkyne-PVA



Given the mechanism of this gelation process and the location of Pd(II) inside the cross-linked Alkyne-PVA, a new strategy based on Alkyne-PVA gel was performed for separation and entrapment of Pd(II) from a mixture of various metal ions. In brief, the appropriate amount (50 mg) of Alkyne-PVA was added into a series of solutions of Pd(II) (0.017 mmol) mixed with another metal ion. Residual metal ions inside the gel were determined by ICP-OES. As shown in Figure 5, after gelation, most of Pd(II) was obviously separated from the mixture and strongly immobilized inside the gel, while only a trace amount of another corresponding completive ion was found in each sample. Besides, the experiment was also extended to more complex solutions that included Pd^{2+} together with Fe^{3+}, Co^{2+}, Ni^{2+}, $Zn^{2+}$and Al^{3+}. In this case, a large amount of Pd(II) (79%) was successfully entrapped by the gel, achieving a significant efficiency for separation and entrapment of Pd(II) from a mixture solution. The entrapment performance of this gelation based strategy was also investigated. (Table S3) The result indicates that with the increase of the concentration of Pd(II), the maximal ratio of gelation entrapped Pd(II) ions is 152.37 mg/g, which is comparable to the conventional adsorption based strategy. (Table S4).

Strong acids are always utilized as lixiviants to dissolve Pd(II) from waste or mineral, which results in high acidic conditions for the dissolved Pd(II) solution. Thus, an ideal material which would be able to directly separate and immobilize Pd(II) from the acidic solution should be searched.[43] In this work, Pd(II)@alkyne-PVA is shown to be able to effect rapid gelation in a wide range of pH values. In addition, the state-of-art methods are all "passive", relying on the chelation, electrostatic attraction, ion exchange, or unique hollow

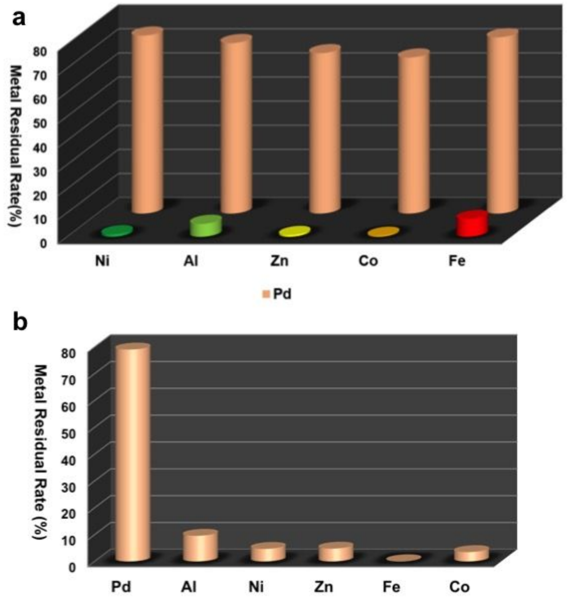
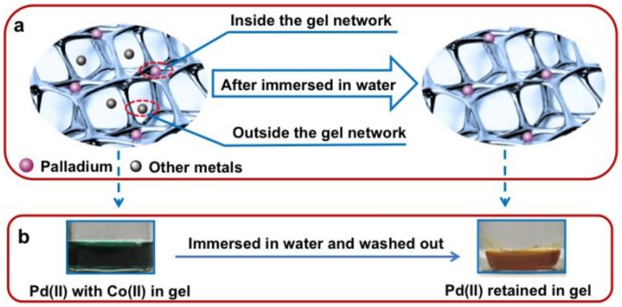


Figure 5. Metal residual rate of Pd(II) gel formed from binary metallic mixture (a); multi-metallic mixture (b).

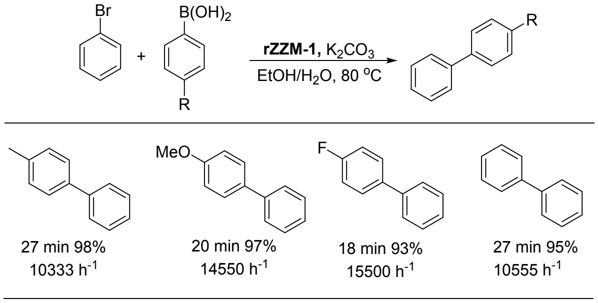
structure of guest materials. On the contrary, the strategy shown here represents an "active" way that mainly relies on process of Glaser coupling catalyzed by Pd(II). The Pd(II) ions that are entrapped inside the alkyne network of PVA during the gelation are difficult to remove, while other completive metal ions are located outside the network and easily washed out (Scheme 4).

Scheme 4. Possible mechanism for Pd^{2+} entrapped in the gel.



PdNPs have long been shown to be excellent catalysts.[44-45] Thus, entrapped Pd(II) inside Alkyne-PVA was reduced by $NaBH_4$ followed by dry freezing, yielding the rZZM-1. The TEM image of the rZZM-1 (Figure 6a) shows that the PdNPs inside the gels are nearly monodispersed with a diameter of ~1.9 nm. The small size and relative monodispersity of the PdNPs is attributed to the confinement effect of alkyne ligands that encapsulate Pd(0) inside the network. This aerogel composite exhibited a remarkable catalytic activity towards Suzuki-Miyaura cross coupling without further treatment. The recycled rZZM-1 that contains 0.005 mmol Pd source has been investigated for coupling between iodobenzene and 4-methoxyphenyl boronic acid in various solvents, and EtOH/H_2O (2:1) has been the most favorable solvent for this system (Table S5). In order to screen the optimal reaction conditions, bromobenzene and 4-methoxy phenyl boronic acid have been probed under various conditions.

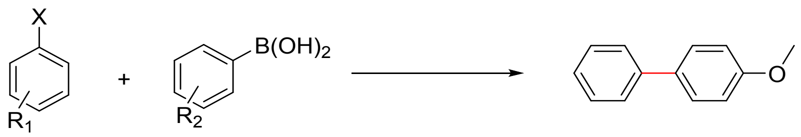
Scheme 5. Suzuki-Miyaura coupling catalyzed by rZZM-1



Reaction conditions: aryl halide (0.65 mmol), arylboronic acid (0.5 mmol), K_2CO_3 (2.0 mmol), rZZM-1 (0.35 mg, 0.02 mol% Pd), EtOH (96%) (2 ml), deionized water (1 mL). Yields are isolated yields.

When the catalytic amount was reduced to 200 ppm, rZZM-1 still achieved an excellent catalytic performance with a TOF value at 14550 h^{-1} at 80 °C (Table S6), and no obvious decrease of the catalyst activity was observed during the first 6 cycles (Figure S5). In addition, rZZM-1 also catalyzed C-C coupling between various substrates with high yields and high TOF values including upon recycling (Scheme 5 and Table S7). Meanwhile, the separated rZZM-1, after entrapped Pd(II) from mixed metallic solution, also performed well catalytically, as initial rZZM-1 (Table 1).

Table 1. Comparison of turnover frequencies reported for other Pd(0) catalyst in the Suzuki cross-coupling reaction.



Entry	Catalyst	X/R_1/R_2	Reaction conditions	TOF(h^{-1})	Ref.
1	rZZM-1	Br/H/OMe	EtOH:H_2O/K_2CO_3/0.02 mol%/353 K/20 min	14550	This work
2	Pd/PDA	Br/H/OMe	EtOH/ K_2CO_3/0.031 mol%/298	580	[46]

			K/3 h		
3	Pd@Hal-pDA-NPC	I/H/OMe	EtOH:H_2O/K_2CO_3/1 mol%/373K/110 min	49	[47]
4	$Fe_3Pd_2(OH)_2[PA]_8(H_2O)_4$	I/OMe/H	DMF:H_2O/ K_2CO_3/TBAB/0.11 mol%/353K/20 min	2612	[48]
5	PdAS	Br/OMe/H	H_2O/ Na_2CO_3//0.05 mol%/373K/24 h	82	[49]
6	Pd@CNPCs	Br/OMe/H	DMF:H_2O/ K_2CO_3/ 0.1 mol%/323K/1 h	946	[50]
7	Pd/PIC	Br/H/OMe	H_2O/Na_2CO_3/TBAB/0.01 mol%/373K/2 h	4950	[51]
8	SMNPs-Salen Pd	Br/OMe/H	DMF:H_2O/ K_2CO_3/ 0.5 mol%/323K/373K/3 h	63	[52]
9	Fe_3O_4/SiO_2-Met-Pd$(OAc)_2$	Br/OMe/H	EtOH:H_2O/K_2CO_3/0.14 mol%/353 K/1 h	671	[53]
10	Pd^0-Mont	Br/OMe/H	H_2O/K_2CO_3/0.07 mol%/333 K/-	64	[54]
11	Pd@SAB-15	Br/OMe/H	H_2O/K_2CO_3/0.08 mol%/353 K/1 h	1200	[55]
12	SA-15/CCPy/Pd(II)	Br/OMe/H	EtOH:H_2O/K_2CO_3/0.3 mol%/353 K/1 h	320	[56]
13	KCC-1-NH_2/Pd	Br/H/OMe	EtOH:H_2O/K_3PO_4/0.5 mol%/373 K/4 h	41	[57]
14	XG-Pd	I/OMe/H	H_2O/K_2CO_3/0.15 mol%/363 K/12 h	32	[58]
15	Pd-Gel	I/OMe/H	EtOH:H_2O/K_2CO_3/1 mol%/323 K/18 h	8	[59]

The electrocatalytic HER activity of PdNPs@CNWs was investigated in 0.5 M H_2SO_4 using a three-electrode cell by linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1}. For comparison, the activity of commercial Pd on activated carbon (Pd/C)-modified GCE was also evaluated. Figure 7 presents the polarization curves of PdNPs@CNWs (left) and the commercial Pd/C (right) promotors modified on the GCE in 0.5 M H_2SO_4. PdNPs@CNWs exhibits a very good HER activity with a low onset potential of 18 mV and an overpotential at 10 mA cm^{-2} current density of 146 mV as well as a small Tafel slope of 97 mV dec^{-1}, which is comparable to those of commercial Pd/C. Remarkably, the stability of fabricated PdNPs@CNWs is much higher than that of Pd/C.

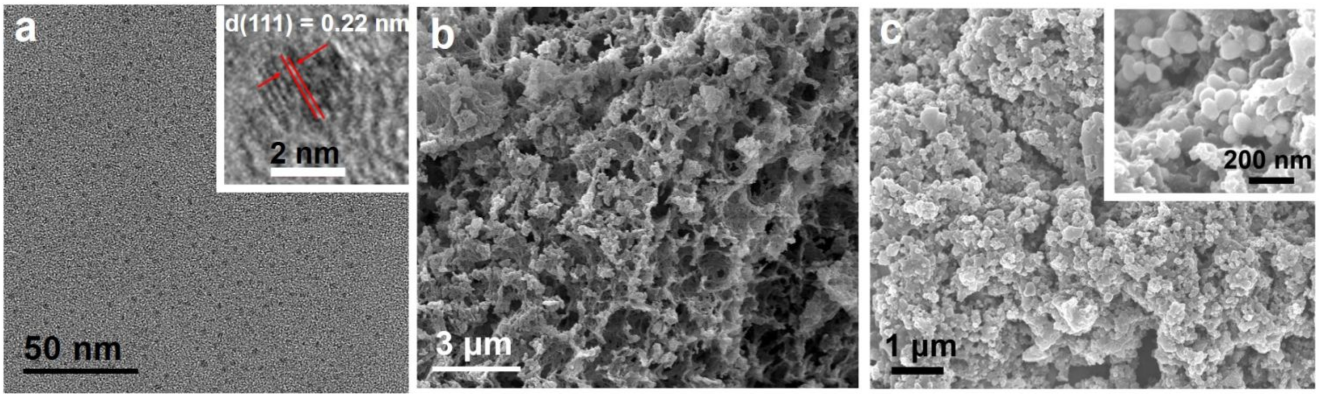


Figure 6. TEM image of rZZM-1 (a); SEM images of rZZM-1 (b) and PdNPs@CNWs (c).

The LSV curves of the first cycle and after scanning cyclic voltammetry (CV) at a scanning rate of 100 mV s^{-1} for 1,000 and 3,000 cycles are presented in Figure 7. It reveals just 7 and 14 mV shift in the overpotential after 1,000 and 3,000 CV cycles for PdNPs@CNWs, which compares with shifting values as large as 41 and 107 mV obtained with Pd/C. The negligible overpotential shifts observed from PdNPs@CNWs after continuous scanning indicate an excellent stability in long-term performance. This is ascribed to the protection generated by the carbon network preventing the PdNPs from detachment away from the carbon matrices and precluding the PdNPs from corrosion in the electrolyte.

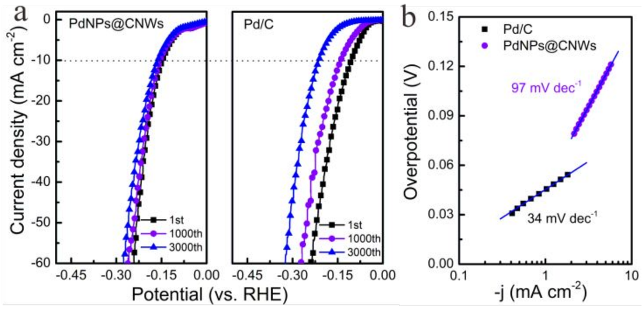


Figure 7. Polarization curves of PdNPs@CNWs and commercial Pd/C before and after CV scanning (a). Corresponding Tafel plots of PdNPs@CNWs and commercial Pd/C (b).

CONCLUSION

In conclusion, a new, facile and efficient strategy for precious palladium metal separation and entrapment was designed based on the high and specific catalytic activity of Pd(II) in the Glaser coupling reaction that is not observed with other ions. Pd(II) selectively catalyzed the crosslinking of alkyne-PVA and Pd(II)@alkyne-PVA gels rapidly formed during the process.

The Pd(II) ions are coordinately entrapped inside the "alkyne network" of the gels, which screens them from other non-precious metal ions including Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Al^{3+}. The obtained Pd(II)@alkyne-PVA gels were also reduced, and after freeze-drying Pd^0NPs@alkyne-PVA (rZZM-1) aerogels formed. These aerogels were directly utilized as a remarkably efficient and recyclable heterogeneous catalyst without any post-treatment. Fundamentally, this strategy provides a general means for metal ion separation and entrapment. Indeed, the PVA (or other polymer) with special functionality may be regarded as template for a unique entrapment of specific metal ion catalysts crosslinking the functionality in the PVA or potentially other polymers. Further investigations should concentrate on the separation of other metal ions using this strategy.

ASSOCIATED CONTENT

Supporting Information

Physical, calculation and catalysis data. The Supporting Information is available free of charge on the ACS Publications website.

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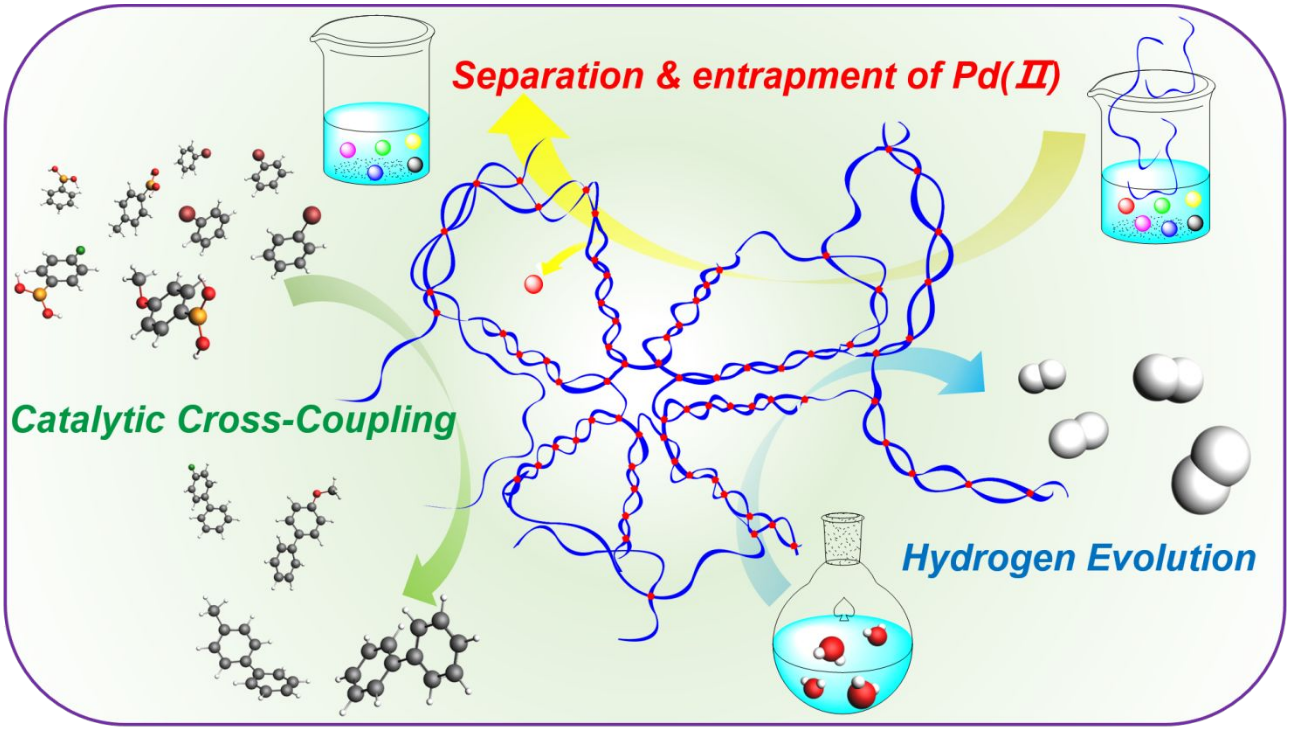
TOC graphic


Separation & entrapment of Pd(II)
Catalytic Cross-Coupling
Hydrogen Evolution