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# Fabrication of palladium nanoparticles as effective catalysts by using supramolecular gels

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#### ABSTRACT

Two-component supramolecular gels were made through self-assembly of tetrazolyl derivatives and Pd(OAc)<sub>2</sub>. The robust gels indicated high storage modulus (>10,000 Pa) and loss modulus, which were studied by rheological measurements. The formed Pd nanoparticles (~9 nm) obtained during the formation of the gel showed effective catalytic hydrogenation of nitrobenzene and could be recovered and reused without loss of activity.

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### 1. Introduction

Supramolecular chemistry and molecular self-assembly have been widely used to fabricate various functional new materials [1– 8]. For example, supramolecular gels (SGs) obtained from lowmolecular-weight gelators *via* non-covalent interactions have received considerable attention because of their potential applications in drug delivery and chemical sensor [9–21]. The application of gels is dependent on their mechanical properties in a great extent. For example, the gel for the culture of isolated stem cells needs to have the elastic modulus of about 10<sup>4</sup> Pa to provide the enough mechanical resistance, which promotes cell adhesion and spreading [22]. Compared with the covalently bonded gels, SGs generally lack enough mechanical strength and viscoelasticity due to the relatively weak and reversible non-covalent interactions. So it still remains a challenge to control the mechanical strength for developing functional gels.

The synthesis of metal nanoparticles for heterogeneous catalysis has received great attention because of their unique catalytic properties and wide-ranging applicability. However, metal nanoparticles with ultra-small size are prone to aggregate because of their high surface energy. Much effort has been devoted to immobilization of metal nanoparticles inside the porous

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frameworks to avoid the aggregation [23,24]. Synthesis of metal 31 nanoparticles supported by robust frameworks usually was 32 finished by the direct nanoparticle encapsulation or post-33 modification of frameworks [25-27]. However, these methods 34 possess multiple steps and harsh reaction conditions, like high 35 temperature and pressure, or even a large amount of catalysts. It is 36 necessary to develop a straightforward method to prepare the 37 framework-supported metal nanoparticles [28]. The unique 38 stable gels are suitable matrices for the synthesis of metal 39 nanoparticles. We envisioned the ultrafine metal nanoparticles 40 could be obtained during the preparation of gels. In this work, we 41 reported the in situ formation of Pd nanoparticles during the 42 process of gel formation. 43

Tetrazoles and their derivatives are interesting materials and 44 have been used in various areas, such as materials science, 45 pharmaceutics and biological fields due to their easy functiona-46 lization. Recently, two-component SGs were prepared based on the 47 tetrazolyl derivatives by hydrogen bonds and coordination 48 chemistry and used for self-healing materials and oil spill recovery 49 [29,30]. In our recent work, we have reported synthesis of cross-50 linked polymers by the chemistry of 2,5-disubstuted tetrazoles 51 [31,32]. 52

Herein, SGs were synthesized by simple two-component53supramolecular chemistry, and showed quite high mechanical54strength by changing the non-covalent interaction. More impor-55tantly, the ultrafine palladium nanoparticles were obtained during56the self-assembly of gel, and could be used as effective heteroge-57neous catalysts for hydrogenation of nitrobenzene.58

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#### 59 2. Experimental

60 All starting materials were purchased from Aldrich and Fisher and used without further purification, unless otherwise noted. 61 62 Anhydrous solvents were dried by standard procedures. The 63 thermogravimetric analysis (TGA) was performed by a Netzch Sta 64 449c thermal analyzer system at the heating rate of 10  $^{\circ}$ C/min in N<sub>2</sub> 65 atmosphere. The FT-IR spectra were measured by a Nicolet Impact 66 410 Fourier transform infrared spectrometer. TEM micrographs 67 were recorded using JEM 1011 with an acceleration voltage of 68 100 kV. The specimens were prepared by gently placing the sample 69 on a surface of a carbon-coated copper grid, dried for 2 h at room 70 temperature, and then subjected to observation. High-resolution 71 transmission electron microscopy (HR-TEM) images were measured 72 on a Tecnai G2 F20 S-TWIN electron microscope operated at 200 kV. 73 Particle size data were obtained by analyzing TEM images using 74 software Nano Measurer 1. 2. 5. SEM micrographs were performed 75 on JEOL JXA-840 under an accelerating voltage of 15 kVX and the 76 elemental mapping was also characterized on it under an 77 accelerating voltage of 20 kVX. For SEM imaging, a drop of freshly 78 prepared sample solution was cast onto a silicon slice, and then Au 79 (1-2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity. <sup>1</sup>H NMR spectra were recorded at 80 81 400 MHz in DMSO- $d_6$  and CDCl<sub>3</sub> as internal standard with TMS, and the solid-state <sup>13</sup>C NMR spectra were recorded at 5 kHz. The Pd 82 83 content of the sample was determined by inductively coupled 84 plasma atomic emission spectroscopy (ICP-AES) analysis with an 85 ICPX series II, Thermoscien-tific. Rheology test was also performed 86 to investigate the sol-gel transition of the gelation process by a 87 dynamic stress-controlled US 302 Rheometer (Anton Paar) equipped 88 with a parallel plate (diameter = 25 mm, gap = 0.5 mm) in oscillato-89 ry mode. After the samples were loaded, the edge of the plate was 90 overlaid with a layer of low viscosity silicone oil to minimize the 91 evaporation of solvent. The storage moduli G' and loss moduli G" 92 were then measured as a function of time at a frequency of 1 Hz and a 93 strain of 1%, and the samples were incubated at 37 °C for 30 min with 94 60 data points were collected over the entire process.

#### 95 2.1. Synthesis of 5,5-(1,4-phenylene)bis(1H-tetrazole) (PBTZ)

A mixture of terephthalonitrile (10 mmol), sodium azide 96 97 (60 mmol) and triethylamine hydrochloride (60 mmol) in dry 98 toluene (70 mL) was heated under reflux for three days. The 99 reaction mixture was mixed with NaOH solution (1 mol/L, 100 100 mL), stirred for 30 min and filtered, then the aqueous part 101 was acidified (pH 1) with concentrated HCl and filtered to give the 102 crude powder of 1. The crude powder was suspended in NaOH 103 solution (50 mL, 1 mol/L), stirred at ambient temperature for

30 min and filtered. The filtrate was adjusted to pH 5 with addition104of HCl (1 mol/L) solution and filtered to give pale grayish powder,105which was washed with distilled water until no Cl<sup>-</sup> remained. <sup>1</sup>H106NMR spectrum was deposited in Fig. S1 in supporting information.107

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#### 2.2. Synthesis of SG-1

 $\begin{array}{lll} \mbox{PBTZ} (13.9 \mbox{ mg}, 0.065 \mbox{ mmol}) \mbox{ and } \mbox{Pd}(OAc)_2 (14.7 \mbox{ mg}, 0.065 \mbox{ mmol}) & 109 \\ \mbox{were dissolved in DMF} (100 \mbox{ } \mbox{$\mu$L}) \mbox{ in a Scintillation vial by heating} & 110 \\ \mbox{up to } 100 \ ^{\circ}\mbox{C}. \mbox{ Then the two solutions were mixed together quickly.} & 111 \\ \mbox{The brown opaque gel could be achieved within about 30 s when} & 112 \\ \mbox{the mixture was cooled down to the room temperature.} & 113 \\ \mbox{sample was simply confirmed by the "stable to inversion of a test} & 114 \\ \mbox{tube" method.} & 115 \\ \end{array}$ 

2.3. Catalytic test

In a typical run of catalytic activity test of SG-1, nitrobenzene 117 (0.5 mmol) and catalysts were added to ethanol (2 mL) under the 118 atmosphere of  $H_2$  (1 atm), then the solution was stirred at 25 °C for 119 1 h. **SG-1** (4 mg), Pd/C (10%, 10 mg), Pd(OAc)<sub>2</sub> or PBTZ was used as 120 catalysts, respectively. After the reaction was completed (moni-121 tored by TLC), the mixture was centrifuged at 5000 rpm and the 122 solid was washed with dichloromethane  $(3 \times 5 \text{ mL})$ . Then the 123 product was collected and the conversions were determined by <sup>1</sup>H 124 NMR spectroscopy. For comparatively and recycle test, the catalyst 125 was isolated by centrifugation after the same cycle and washed 126 with dichloromethane  $(3 \times 5 \text{ mL})$ . Then the isolated catalyst was 127 used for the next cycle reaction with further treatment and the 128 process was repeated for 3 times. For the Suzuki-Miyaura coupling 129 reactions, SG-1, 1,3,5-tribromobenzene or 2-bromopyridine 130 (1.0 mmol), phenylboronic acid (1.5 mmol), potassium carbonate 131 (276 mg, 2.0 mmol), and SG-1 (5 mg, 1.2 mol%) were added to a 132 pressure flask with dry toluene (4 mL). Then the reaction mixture 133 was stirred at 120 °C at ambient atmosphere. After 2 h, the mixture 134 was centrifuged, and the solid was washed with dichloromethane 135  $(3 \times 5 \text{ mL})$ . The combined organic phase was washed with water 136  $(3 \times 15 \text{ mL})$  to remove potassium carbonate. The organic phase 137 was then evaporated under reduce pressure to leave the crude 138 products which were further purified by column chromatography 139 over silica gel to obtain the desired products. 140

#### 3. Results and discussion

The ligand 5,5'-(1,4-phenylene)bis(1H-tetrazole) (PBTZ) was prepared according to literature method [33]. **SG-1** was formed 143 immediately after mixing PBTZ and Pd(OAc)<sub>2</sub> in DMF at 100 °C. As shown in Fig. 1, inversion tests were used to confirm formation of 145



**Fig. 1.** Picture of **SC-1** and a schematic representation of the DMF-mediated possible coordination mode between the PBTZ and the Pd<sup>2+</sup>. Color code: C(gray), N(blue), O(red), H(white) of the ligand PBTZ, Pd(yellow), and the OAc<sup>-1</sup> anion was omitted for clarity (drawn in ChemBio3D Ultra 12.0 with MM2 stimulation with the lowest energy).

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Fig. 2. HR-TEM (scale bar: 10 nm) (a) and SEM (scale bar: 40  $\mu$ m) (b) of SG-1. The inside in (b) shows the corresponding EDS mapping images of the selected region of the SG-1.

Table 1

Hydrogenation of introbenzene.				
NO	$\frac{H_2 \text{ (1 atm), EtOH}}{25 \text{ °C, 1 h}}$	NH <sub>2</sub>		
Entry	Catalyst/dosage (mg)		Conversion (%) <sup>b</sup>	
1	SG-1,	4	98	
2	Pd/C(10% Pd)	10	>99	
3	SG-1, reuse 1,	4	98	
4	SG-1, reuse 2	4	98	
5	SG-1, reuse 3	4	98	
6	$Pd(OAc)_2$	2	0	
7	PBTZ	4	0	

 $^a$  Reaction condition: nitrobenzene (0.5 mmol) and 1 mol% of catalyst, ethanol (2 mL), 1 atm of H\_2, 25 °C, 1 h.

<sup>b</sup> Conversions were determined by <sup>1</sup>H NMR spectroscopy.

146 SG-1 with color of brown. The gel formation was ascribed to the 147 cooperative hydrogen bonding interaction between tetrazoles and 148 Pd. In order to obtain an aerogel of the SG, the wet gel was 149 immersed sequentially in methanol and water to exchange the 150 DMF, and then was freeze-dried. The lyophilized powder of SG-1 151 was insoluble in all of organic solvents tested and water, even in concentrated hydrochloric acid. SG-1 was characterized by 152 153 transmission and scanning electron microscopy (TEM, HR-TEM 154 and SEM), infrared spectroscopy (IR), thermogravimetric analysis (TGA), solid-state <sup>13</sup>C NMR spectrum, (ICP-AES) analysis and 155 156 rheological measurements.

The TEM images of SG-1 (Fig. S2 in Supporting information) 157 158 indicated the SG-1 constituted with nanoparticles with average diameter of several nanometers. Small Pd nanoparticles with low 159 dispersity could be seen in whole horizon. In addition, HR-TEM was 160 used to see the details of Pd nanoparticles as shown in Fig. 2a. 161 Uniform spherical Pd particles can be seen obviously with average 162 163 diameter of 9 nm. SEM shows rough surface of SG-1 (Fig. S3 in 164 Supporting information), and the EDS mapping gives clear 165 homogeneous distribution of Pd element in SG-1 (Fig. 2b). The Pd 166 content in SG-1 determined by ICP-AES is 26 wt%, which is similar to the calculated value of 24 wt%. The IR spectra of SG-1 exhibited 167 168 obvious different patterns with PBTZ, indicating the interaction between PBTZ and Pd as shown in Fig. 3a. Solid-state <sup>13</sup>C cross 169 polarization/magic angel spinning nuclear magnetic resonance (CP/ 170 MAS/NMR) spectroscopy was used to confirm the composition of 171 SGs. As shown in Fig. 3b, two characteristic signals for benzene and 172 173 tetrazole carbon in **SG-1** appeared at 128 and 163 ppm, respectively. 174 TGA analysis showed that SG-1 were stable up to 250 °C at the 175 heating rate of 10 °C/min in N<sub>2</sub> atmosphere, as shown in Fig. 4a.

176 The mechanical intensity of the gel is an important parameter177 for their potential application. Rheological measurements are used

to study the behavior of the gels when they are exposed to 178 mechanical stress. The "storage" modulus G' represents the ability 179 of the deformed materials to "snap back" to its original geometry, 180 while the "loss" modulus G" means the tendency of a materials to 181 flow under stress [34]. The storage modulus G' and loss modulus G'' 182 was measured as a function of time. As shown in Fig. 4b, the G'183 values exceeded the G" value by about 1 order of magnitude for SG-184 1, which was indicative of an elastic gel rather than viscous 185 material [35–37]. It is worthy to mention that G' for SG-1 is more 186 than 10,000 Pa, which is seldom seen for supramolecular gels 187 [38,39]. This high mechanical intensity of **SG-1** benefits to the 188 potential application in cell adhesion, but the biocompatibility 189 needs to be investigated in details. 190

As revealed by HR-TEM, the ultrafine Pd nanoparticles were 191 obtained after freeze-drying the wet gel of SG-1. The catalytic 192 performances of SG-1 were investigated by hydrogenation of 193 nitrobenzene at room temperature under 1 atm of H<sub>2</sub> with 194 0.1 mol% of catalysts. The conversion of the nitrobenzene was 195 determined by integrating the signals of the reactant ( $\delta$  8.19) and 196 the product ( $\delta$  7.12) in the crude reaction mixtures (Fig. S4 in 197 supporting information). As shown in Table 1, SG-1 afforded 198 almost complete conversion of nitrobenzene to aniline within 1 h, 199 which is comparable to the commercial Pd/C catalysts with same 200 content of Pd. We studied the recyclability and reusability of the 201 SG-1 catalyst. SG-1 could be readily recovered from the reaction via 202 filtration or centrifugation. The same amount of recovered SG-1 203 showed no decrease of conversion for hydrogenation of nitroben-204 zene after recycling three times. Morphologies of SG-1 revealed by 205 TEM do not show obvious changes in Fig. S5 in supporting 206 information. The control experiments using only Pd(OAc)<sub>2</sub> or PBTZ 207 as catalyst did not form any product. These results revealed the SG-208 1 possessed high catalytic activity and could be reused easily. The 209



Fig. 3. FT-IR (a) and solid-state (b) <sup>13</sup>C NMR spectra of SG-1.

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Fig. 4. TGA (a) and storage modulus and loss modulus as a function of time (b) of SG-1.

210 applicability of the **SG-1** catalysts in Suzuki coupling reaction was

211 demonstrated in Fig. S6 in supporting information. 2-Phenylpyr-

212 idine and 1,3,5-triphenylbenzene was obtained after running silica

213 column with isolated yield of 9% and 8% in 2 h, respectively. These

214 results illustrate the generality of Pd nanoparticles in catalyzing

215 organic transformations.

#### 216 **4. Conclusion**

217 In summary, two-component supramolecular gels were pre-218 pared by using tetrazolyl derivatives and Pd(OAc)<sub>2</sub> by the metal coordination and hydrogen bonding interactions. The Pd nano-219 220 particles obtained during the formation of SG-1 were shown to be 221 highly active and recyclable heterogeneous catalysts toward 222 hydrogenation of nitrobenzene. This work highlights the potential 223 of using gelation as an in situ method for developing metal 224 nanoparticles with catalytic activity.

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#### 228 Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2015.09.009.

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