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Influence of Graphene Oxide Supports on Solution-Phase Catalysis of Thiolate-Protected Palladium Nanoparticles in Water

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Abstract

The influence of graphene oxide supports and thiolate surface ligands on the catalytic activity of colloidal Pd nanoparticles for alkyne hydrogenation in water is investigated. The studies show that unsupported, water-soluble thiolate-capped Pd nanoparticle catalysts favor the semi-hydrogenation over full-hydrogenation of dimethyl acetylene dicarboxylate (DMAD) under the atmospheric pressure and at room temperature. Pd nanoparticles supported on graphene oxide exhibit a similar activity for the hydrogenation of DMAD, but they show an improved long-term colloidal stability in aqueous solution after multiple catalytic cycles. After the heat treatment of Pd nanoparticles supported on graphene oxide at 300 °C, these heated hybrids exhibit an enhanced catalytic activity towards the full-hydrogenation. Overall, the studies suggest some influences of graphene oxide supports on the stability and thiolate surface ligands on the activity and selectivity of Pd nanoparticle catalysts.

Graphical abstract

The colloidal stability and catalytic activity of Pd nanoparticles are affected by the presence of graphene oxide and surface ligands.

Introduction

Due to high surface area-to-mass ratio and size/shape dependent activity,^{1–3} metal nanoparticles have gained more interests for practical applications as efficient catalysts that offer the combination of activity, selectivity, and recyclability.^{4–6} Especially, palladium

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nanoparticles (PdNP) have been frequently used as catalysts in organic reactions including hydrogenation and cross-coupling reactions.^{7,8} Since small PdNP are thermodynamically unstable and tend to aggregate or experience core dissolution during the catalytic reactions, the increase in stability of the PdNP is necessary for the improved recovery and recycling by using either solid supports or more effective stabilizing ligands.⁷⁻¹¹

Previous studies have shown that the performance of nanoparticle catalysts was influenced by the presence of various surface ligand stabilizers, such as polymers,⁹ dendrimers,¹¹ and small organic ligands including alkylammoniums, thioethers, isocyanides and amines.⁷ Both inorganic (sulfur, selenium, barium sulfate, calcium carbonate or lead acetate) and organic (nitrogen heterocycles like pyridine and quinoline) reagents were also known as surface-bound poisons that control the activity of Pd catalysts.^{12,13} Lindlar's catalyst is an excellent example of poisoned heterogeneous Pd catalysts useful for selective hydrogenation of alkynes to alkenes.¹² Recent studies have shown that thiols can be utilized to deactivate the surface of supported Pd catalysts providing higher selectivity for certain organic reactions.¹⁴⁻¹⁶ Previous work from our group has also proved that alkanethiolate-capped PdNP generated from sodium S-alkylthiosulfate is an excellent catalyst for regio- and chemo-selective organic reactions including the hydrogenation and/or isomerization of various alkenes, dienes, alkynols, and allylic alcohols.¹⁷⁻²⁰

Controls over the structure and functionality of thiolate ligands of this PdNP also provided the ability to create either homogeneously soluble or heterogeneous catalytic systems in different solvents.^{21,22} For example, the presence of a terminal carboxylate group in the thiolate ligand allowed for the formation of homogeneously soluble aqueous systems while that of simple alkanethiolate ligands led to heterogeneous systems in water.²² This enabled PdNP capped with water-soluble thiolate ligands useful for colloidal catalytic reactions in aqueous environments as nanoparticle-based green catalysts.

In consideration of the relatively low colloidal stability of nanoparticles in solution phase, the attachment of PdNP to water-dispersible support materials would be an ideal strategy for enhancing the utility of nanoparticle catalysts as support-stabilized aqueous catalytic systems.²³⁻²⁵ Graphene oxide (GO) would be a perfect candidate as support materials for colloidal catalysts considering its characteristics of forming a highly stable aqueous dispersion and possessing a large flat area-to-mass ratio. Therefore, the catalytic PdNP could possibly avoid the extensive aggregation in solution phase after the immobilization on GO.^{26,27} In addition, the presence of hydrophobic groups in GO surfaces may facilitate the adsorption of substrates and accelerate the catalytic reactions for hydrophobic organic compounds.

Previously, others have shown that metal nanoparticles anchored on graphene sheets can exhibit enhanced catalytic, magnetic, electrical and optical activities.²⁸⁻³⁴ Most other attempts to develop the hybrid GO materials were aimed at maximizing their potentials for device applications such as batteries, supercapacitors, fuel cells, photovoltaic devices, sensors and surface enhanced Raman scattering (SERS).³⁵⁻³⁷ This paper specifically focuses on understanding the effects of GO supports and surface thiolate ligands on controlling

activity and selectivity of water-soluble PdNP catalysts for a model hydrophobic alkyne hydrogenation reaction.

Experimental

Materials and methods

The following materials were purchased from the indicated suppliers and used as received: Potassium tetrachloropalladate (II) (K_2PdCl_4), tetraoctylammonium bromide (TOAB), sodium borohydride ($NaBH_4$) and 6-bromohexanoic acid were purchased from ACROS. Dimethyl acetylene dicarboxylate (DMAD) and graphene oxide (GO) [4 mg/mL in H_2O] were purchased from Sigma Aldrich. D_2O was purchased from Cambridge Isotope Laboratories. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), toluene, acetone, acetonitrile, methanol, ethanol, chloroform and tetrahydrofuran (THF) were obtained from Fisher Scientific. Spectra/Por cellulose ester (CE) dialysis membranes (M.Wt. = 8,000–10,000 Daltons) were purchased from Spectrum Laboratories, Inc. Water was purified by Barnstead NANOpure Diamond ion exchange resins purification unit.

Preparations

Sodium ω -Carboxyl-*S*-hexanethiosulfate Ligands— ω -Carboxyl-*S*-hexanethiosulfate sodium salts were prepared according to the following procedure.²⁴ In a 500 mL round-bottom flask, 6-bromohexanoic acid (25 mmol) in 50 mL of ethanol and sodium thiosulfate pentahydrate (25 mmol) in 50 mL of water were mixed. The reaction mixture was refluxed for 3 h and the solvents were removed by rotary evaporation. The crude product was dissolved in hot ethanol and recrystallized overnight resulting in pure sodium ω -carboxyl-*S*-hexanethiosulfate.²²

ω -Carboxylate-1-hexanethiolate-capped Pd nanoparticles— K_2PdCl_4 (0.4 mmol) was dissolved in 12 mL of nanopure water and TOAB (2.0 mmol) was dissolved in 25 mL of toluene. Both solutions were mixed and continuously stirred until the organic layer turned dark orange and the aqueous layer became clear, indicating the completion of the phase transfer of $PdCl_4^{2-}$. The aqueous layer was discarded and the organic layer was placed in a 250 mL round-bottom flask. ω -Carboxyl-*S*-hexanethiosulfate sodium salt (0.8 mmol) dissolved in 10 mL of 25% methanol was added to the organic layer; additional TOAB (2.0 mmol) was then added to the reaction flask. The reaction mixture was continuously stirred for 15 min. Afterwards, $NaBH_4$ (8.0 mmol) in 7 mL of nanopure water vortexed for *ca.* 10 sec was rapidly delivered to the vigorously stirred mixture using a ceramic Hirsh funnel for a continuous delivery. Consequently, the solution darkened immediately indicating the formation of nanoparticles. Upon the completion of 3 h stirring, the organic layer was discarded by using a separatory funnel and the remaining solvent was removed by rotary evaporation. The resulting crude nanoparticles were suspended in 25 mL of methanol and poured down on to a coarse funnel frit (F). The PdNP were then further washed with several aliquots of methanol, ethanol, THF, chloroform, acetonitrile and acetone. The resulting nanoparticles were dissolved in water and placed in dialysis tubes overnight. Afterwards, the water was removed by rotary evaporation and the nanoparticles were dried in vacuum overnight at a pressure of 25 psi.

Pd nanoparticle-graphene oxide hybrids—Palladium nanoparticle-graphene oxide hybrids (PdNP/GO) were prepared by using the published procedure used for gold nanoparticle-graphene oxide hybrids.³⁸ Briefly, 10 mg PdNP were added to a solution of 2.5 mL of 4 mg/mL graphene oxide and mixed before being dried in a vacuum.

Heat-treated Pd nanoparticle-graphene oxide hybrids—The heating of the PdNP/GO was performed in a Barnstead Thermolyne 1300 Furnace. A 5 mg sample of PdNP/GO was weighed out and placed in a clean flask. The furnace was heated to 300 °C and the PdNP/GO was placed in it and heated for one hour. The flask was then removed and cooled to room temperature before storing. The same procedure was followed for the PdNP/GO prepared under different heat treatment (50–400 °C).

Catalysis

Catalysis experiments were performed by dissolving 4.8 mol% (based on Pd/substrate) of PdNP, unheated PdNP/GO or heated PdNP/GO hybrid catalysts in 2 mL D₂O in a 35 mL reaction flask. The amount of Pd was remained constant for all catalysts. The flask was sealed and purged with H₂ gas for 15 min with the pressure being monitored with a manometer to have a flow rate around 3.4 psi. Once purging was complete, 90 µL (0.73 mmol) of dimethyl acetylene dicarboxylate (DMAD) was then injected into the reaction mixture. The reaction was stirred under atmospheric pressure and at room temperature. ¹H NMR spectra of the solutions were obtained after 3, 12 or 24 hours.

Recycling of Catalysts

Recycling experiments were performed following the catalysis procedure. After the ¹H NMR data was analysed, the PdNP, PdNP/GO or heated PdNP/GO catalysts in the NMR tubes were returned to the reaction flask. The flask was then washed with methanol followed with centrifugation of the nanoparticles. The centrifugation was repeated twice more with washings of methanol. The catalysts were then dried in a vacuum before the next cycle.

Characterizations

¹H NMR spectra were recorded on Bruker Fourier or Advances II FT-NMR spectrometers operating at either 300 or 400 MHz, respectively. PdNP were dissolved in D₂O, which was internally referenced at δ 4.81 ppm. UV-vis measurements of NP solutions were taken with a UV-2450 Shimadzu UV-vis spectrophotometer using quartz cells. Spectra were recorded from 4500 to 450 cm⁻¹. Infrared spectra were taken with a Perkin Elmer Spectrum 100 FT-IR spectrometer. Spectra were recorded from 800 to 200 cm⁻¹. Transmission electron microscopy (TEM) images were taken with a JEOL 1200 EX II electron microscope operating at 90 or 80 KeV. Samples dissolved in nanopure water were cast onto carbon-coated copper mesh grids, and let dry for at least 24 h before analysis. PdNP core sizes were analysed with Scion Image Beta Release 2.0. Powder X-ray diffraction (XRD) data were collected by a PANalytical X'Pert Pro MPD diffractometer, equipped with a linear X'Celerator detector, with monochromatic Cu-Kα₁ radiation. The data were collected at room temperature in the range 17° < 2Theta < 100° with ≈ 0.008° intervals. The pattern match process was performed using the HighScore Plus software.

Results and discussion

Spectroscopic and Microscopic Characterization of Pd Nanoparticles and Pd Nanoparticle-Graphene Oxide Hybrids

Water-soluble ω -carboxylate-1-hexanethiolate-capped PdNP were synthesized by employing sodium ω -carboxyl-S-hexanethiosulfate as a ligand precursor in a biphasic synthetic system described in our previous report.²² Briefly, the synthesis began with the phase transfer of PdCl_4^{2-} to an organic layer by TOAB (Scheme 1). After the completion of phase transfer, ω -carboxyl-S-hexanethiosulfate salt was added along with additional TOAB. The addition of NaBH_4 resulted in the formation of PdNP in organic phase, which quickly transferred into the aqueous layer. FT-IR and UV-vis spectra and TGA results of isolated PdNP were identical with the previous results and confirmed the formation of thiolate-capped PdNP (Figure S1 and S2). TEM image and histogram of PdNP showed that the nanoparticles were approximately 1.9 ± 0.9 nm in diameter without any evidence of aggregation and their cores were spherical and relatively monodisperse (Fig 1(a)).

PdNP was self-assembled onto the surface of GO via interactions between the $\text{COO}^-/\text{COOH}/\text{OH}$ groups of GO and the COO^-/COOH groups of PdNP.³⁹⁻⁴¹ The UV-vis spectrum of PdNP/GO hybrids shown in Fig S3 (a) was consistent with the spectra of other palladium nanoparticles with similar core sizes, which showed no absorption or plasmon bands with only an exponential decay with increasing wavelength from 300 nm to 800 nm.¹⁹ IR spectrum of PdNP/GO shown in Fig S3 (b) showed a C=O stretch at 1725 cm^{-1} , $\text{sp}^3\text{ C-H}$ stretch at $2938 - 2878\text{ cm}^{-1}$ and a broad O-H stretch at $3300 - 2800\text{ cm}^{-1}$, corresponding to the IR characteristics of ω -carboxylate-1-hexanethiolate ligands and GO. Fig 1(b) showed TEM image and histogram of PdNP after the immobilization on GO, indicating the retention of core size and dispersity of assembled nanoparticles (2.0 ± 0.8 nm) compared to the PdNP before the adsorption (1.9 ± 0.9 nm).

Heat Treatments of Palladium Nanoparticle-Graphene Oxide Hybrids

Heat treatments of PdNP/GO at the temperature ranging from 50 to 400 °C in air were performed to understand the chemical and morphological transformations of PdNP on GO. IR and UV-vis spectra of PdNP/GO heated at 50–400 °C are shown in Figure S4. IR spectra confirmed the near-absence of hexanethiolate ligands after heat treatment at the temperature of 300 °C. UV-vis spectra showed a steady decrease in the intensity of the exponential curves indicating a gradual loss in the solubility of PdNP/GO with heat treatments at the higher temperatures. TEM images showed that the extensive coarsening process started to take place for the PdNP/GO when heated at temperature of 300 °C and above (Fig 2). Based on IR results, however, this treatment was necessary for the removal of most thiolate ligands from nanoparticles. Table S1 summarizes the transitions of the average core size of the heated PdNP/GO. The average core size of the heated PdNP/GO at 300 °C was 7.1 ± 2.9 nm. However, TEM image in Fig 2(a) shows the presence of many small particles on GO after heat treatments at this temperature. The results, therefore, confirmed an efficiency of GO in preventing PdNP from extensive aggregation and coarsening even after the removal of the surface thiolate ligands at 300 °C. The heated PdNP/GO at 300 °C were no longer dispersed in water due to the loss of solubilizing ligands of nanoparticles and carboxyl

groups of GO.³⁹ The powder XRD pattern of the heated Pd/GO at 300 °C clearly indicated the presence of Pd oxide in the hybrid after the treatment (Fig S5). The lack of stabilizing surface ligands on Pd surface should be the main reason for this facile oxidation of exposed Pd surface under atmospheric environment with high temperature. In comparison, well-defined XRD pattern could not be obtained from PdNP and PdNP/GO samples due to the lack of crystalline structure related to the presence of surface ligands and GO supports.

Catalysis Studies Comparing PdNP, PdNP/GO and Heated PdNP/GO

The activity and selectivity of PdNP, PdNP/GO, and heated PdNP/GO (300 °C) were analysed using dimethyl acetylene dicarboxylate (DMAD) as the model alkyne substrate in a reaction involving 4.8 mol% (based on Pd:DMAD mole ratio) of the catalysts. Reactions were run with a balloon as a constant source of H₂ gas, in an attempt to push the reactions to completion and to keep the system at equilibrium for catalysts. The reactions were monitored using ¹H NMR spectroscopy (see Figure S6 for examples). DMAD has one distinct chemical shift at δ 3.86 ppm ($-\text{OCH}_3$). The semi-hydrogenation product has two distinct hydrogens at δ 3.80 ppm ($-\text{OCH}_3$) and δ 6.50 ppm ($\text{C}=\text{C}-\text{H}$). The full-hydrogenation product also has two distinct hydrogens at δ 3.70 ppm ($-\text{CO}_2\text{CH}_3$) and δ 2.69 ppm (CH_2-CH_2). By comparing the integrations of methoxy group ($-\text{OCH}_3$: δ 3.70 – 3.86 ppm) of DMAD, the reaction progress could be easily monitored. ¹H NMR results were taken after 3 h, 12 h, and 24 h in order to monitor the progress of the reactions.

The kinetic plots of the catalytic hydrogenation of DMAD by three catalysts revealed that PdNP and PdNP/GO catalysts are more selective towards the semi-hydrogenation product (Fig 3). The presence of GO seemed to have no significant impact over the catalytic activity and selectivity of PdNP. The increase in the kinetics of substrate delivery by the spill-over, that has been observed by others for catalysts on graphene substrates, was absent for the colloidal PdNP/GO catalysis.^{40,41} For PdNP catalysts, most DMAD was hydrogenated to maleic ester, the semi-hydrogenated product in a cis-form (>99% selectivity), in less than 3 h reaction time. However, the initial rate of reaction using PdNP/GO catalysts was slightly slower despite that the reaction resulted in the products with similar selectivity (shown in Table S2, which summarizes the turn-over-frequency (TOF) for semi- and full-hydrogenation products in the hydrogenation of DMAD). Overall, the catalytic activity and selectivity of PdNP and PdNP/GO were quite comparable to those of other supported Pd catalysts with surface modifiers, which exhibited the typical conversion yield of 93–99 % with selectivity ranging from 88 to 96 % for semi-hydrogenation products at room temperature and under atmospheric pressure.^{11,22}

The catalytic activity of heated PdNP/GO at 300 °C, which contained the extensive amount of Pd oxide on the surface was compared to that of the unheated PdNP/GO catalyst. The heated PdNP/GO catalysts mainly produced the full-hydrogenation product (~87%) indicating their high catalytic activity and the availability of active metal surface capable of further hydrogenation. Powder XRD pattern of heated PdNP/GO after 1 catalytic cycle showed no signals corresponding to palladium oxide, which can be understood based on the reduction of PdO during the catalytic reaction in the presence of excess H₂ gas (Fig S7). This also explains why the heated PdNP/GO could exhibit enhanced catalytic activity,

despite the initial formation of PdO on the surface. The results confirmed that the strategy of using GO as a colloidal support for ligand-capped nanoparticle catalysts can be applied for the calcination of thiolate ligands from PdNP catalysts. The initial rate of the reaction was, however, not improved compared to the rate of those in presence of PdNP and PdNP/GO. This is likely due to the delay time required for the initial reduction of Pd(II) to Pd(0) and the heated PdNP/GO being a heterogeneous system with low dispersity.

Since GO has shown some activity as carbocatalysts for reactions such as nitrobenzene hydrogenation, GO itself was tested for DMAD hydrogenation.⁴² The conclusion after these tests was that the effect of direct GO participation in hydrogenation of DMAD was less than 5 % over a 24 h period. The PdNP/GO catalysts heated at 150 °C were also tested for the DMAD hydrogenation, which resulted in poor conversion yields for both semi- and full-hydrogenation products. The results suggested that the annealing at 150 °C caused the rearrangement of thiolate ligands on the surface rather than the removal from the surface, decreasing the overall activity of PdNP.

Recyclability and Colloidal Stability of PdNP, PdNP/GO and Heated PdNP/GO

The recyclability of the catalysts was tested in order to determine the reusability and stability of PdNP with and without GO.^{43,44} Results obtained from the reactions after the third cycle of the catalyst recycling were compared to the averages of the 24 h reaction results using fresh catalysts to determine the catalysts' effectiveness after multiple cycles (Fig 4). The recycling of the PdNP and the PdNP/GO hybrid catalysts was successful with both catalysts retaining their catalytic property after three uses. It was found that the overall rate of hydrogenation dropped slightly (Table S2), which was likely due to a small loss of the catalysts during the catalyst purification and product isolation. The reactions were still all completed in less than 24 h reaction time. This showed that both the PdNP and the PdNP/GO hybrid catalysts retained their properties as selective hydrogenation catalysts for alkyne. The heated PdNP/GO experienced, however, a dramatic decrease in catalytic activity after multiple uses, producing more semi-hydrogenation products than full-hydrogenation products after the third cycle. The permanent adsorption of substrate or intermediates to the bare surface of the heated PdNP/GO was likely the reason for decrease in the number of more active sites and its overall activity as a consequence. Similar deactivation of metal catalysts has been observed many times by others.^{45,46} This adsorption problem was confirmed by successful regeneration of the heated PdNP/GO, which required a reheating of the hybrid at 300 °C for 1 hour. This regenerated, heated PdNP/GO catalysts yielded the fully hydrogenated product almost quantitatively, indicating that catalytic activity was regained after the second heat treatment. Powder XRD pattern of the 3rd cycled PdNP/GO did not show any evidence for presence of palladium oxide.

It was found that PdNP catalysts occasionally lost their colloidal stability in water after the catalytic reaction and formed precipitates, indicating possible particle agglomeration through ligand interactions (Fig 5(a)). In comparison, the recycling studies of PdNP/GO catalysts showed that the presence of GO as a support for PdNP could enhance the colloidal stability of PdNP and allow the catalysts to maintain their dispersity in water after multiple

recycling of the catalysts (Fig 5(b)). The heated PdNP/GO catalysts meanwhile were already in heterogeneous condition with low dispersity even before the catalytic reaction (Fig 5(c)).

A change in pH of the reaction solution before and after the reaction was monitored and its role on the colloidal stability of the catalyst was investigated. For PdNP, the pH of the solutions before reaction was around neutral (pH = ~7.8), but during the course of the reaction with DMAD, the pH decreased by more than a couple of units. The decrease in pH for PdNP solution would cause some protonation of the carboxylate ligands, potentially affecting the solubility of the PdNP. In comparison, the initial pH of both the heated and unheated PdNP/GO was already below neutral (pH = 5–6). This was caused by the addition of graphene oxide solution, which itself has a pH of 2–3. For both the unheated and heated PdNP/GO, the pH of the solution increased slightly with the progression of the reaction. With no additional decrease in the pH of solution after the catalytic reaction, PdNP/GO could maintain their dispersity in aqueous environment indicating the positive influence of GO on the colloidal stability of PdNP.

UV-vis spectra of crude reaction mixtures were taken in order to observe the integrity of catalysts and the formation of any side product.⁴⁷ The UV-vis spectra showed a very small peak around 400 nm for both PdNP and PdNP/GO catalysis samples indicating the formation of small amount of Pd (II) species. This suggested that the small leaching of Pd atoms could not be completely eliminated in water using either thiolate ligand protection or GO supporting strategy. However, the presence of small amount of leached Pd atoms clearly did not have any noticeable influence on the catalytic activity and selectivity of both catalytic systems. TEM images were also obtained for the recycled catalysts to determine if recycling caused any morphological change to the PdNP or PdNP/GO catalysts. TEM images of both PdNP and PdNP/GO catalysts after the reaction showed the formation of some small aggregates among many small nanoparticles, but no significant shape changes (Fig S8). In addition, TEM image of PdNP/GO clearly showed the presence of many small nanoparticles still deposited on the surface of GO indicating the relatively strong interactions between GO and PdNP.

Conclusions

This article described the synthesis of water-soluble palladium nanoparticles capable of catalysing selective hydrogenation of alkyne under the mild condition (atmospheric pressure and room temperature). The palladium nanoparticles supported on graphene oxide nanosheets were prepared using the strategy of pre-formed nanoparticle self-assembly. The annealing studies at different temperatures revealed that most thiolate ligands could be removed from the palladium nanoparticle-graphene oxide hybrids at 300 °C without an extensive coalescence of particles. By comparing the activity and selectivity of three different catalysts, it was concluded that the catalytic properties of palladium nanoparticles and palladium nanoparticle-graphene oxide hybrids were similar. However, with the addition of the graphene oxide support, palladium nanoparticle-graphene oxide hybrids could exhibit a better colloidal stability during catalytic reaction. When the surface ligands were removed from the palladium nanoparticle-graphene oxide hybrids by heat treatment, the activity of the hybrid catalysts was increased producing the fully hydrogenated products in high yields.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Notes and references

1. Astruc D, Lu F, Aranzaes JR. *Angew Chem Int Ed*. 2005; 44:7852–7872.
2. Astruc D. *Inorg Chem*. 2007; 46:1884–1894. [PubMed: 17348719]
3. Bhattacharjee S, Dotzauer DM, Bruening ML. *J Am Chem Soc*. 2009; 131:3601–3610. [PubMed: 19231847]
4. Crespo-Quesada M, Cardenas-Lizana F, Dessimoz AL, Kiwi-Minsker L. *ACS Catal*. 2012; 2:1773–1786.
5. Chng LL, Erathodiyil N, Ying JY. *Acc Chem Res*. 2013; 46:1825–1837. [PubMed: 23350747]
6. Cong H, Porco JA. *ACS Catal*. 2012; 2:65–70. [PubMed: 22347681]
7. Gavia DJ, Shon YS. *ChemCatChem*. 2015; 7:892–900. [PubMed: 25937846]
8. Deraedt C, Astruc D. *Acc Chem Res*. 2014; 47:494–503. [PubMed: 24215156]
9. Wagener P, Schwenke A, Barcikowski S. *Langmuir*. 2012; 28:6132–6140. [PubMed: 22417054]
10. Mai Y, Eisenberg A. *Acc Chem Res*. 2012; 45:1657–1666. [PubMed: 22839780]
11. Myers VS, Weir MG, Carino EV, Yancey DF, Pande S, Crooks RM. *Chem Sci*. 2011; 2:1632–1646.
12. Lindlar H. *Helv Chim Acta*. 1952; 35:446.
13. Gan LY, Zhang YX, Zhao YJ. *J Phys Chem C*. 2009; 114:996–1003.
14. Marshall ST, O'Brien M, Oetter B, Corpuz A, Richards RM, Schwartz DK, Medlin JW. *Nat Mater*. 2010; 9:853–858. [PubMed: 20835234]
15. Pang SH, Lien CH, Medlin JW. *Catal Sci Technol*. 2016; 6:2413–2418.
16. Chauhan BPS, Rathore JS, Bando T. *J Am Chem Soc*. 2004; 126:8493. [PubMed: 15238006]
17. Zhu JS, Shon YS. *Nanoscale*. 2015; 7:17786–17790. [PubMed: 26455381]
18. Gavia DJ, Koeppen J, Sadeghmoghaddam E, Shon YS. *RSC Adv*. 2013; 3:13642–13645. [PubMed: 27642511]
19. Gavia DJ, Shon YS. *Langmuir*. 2012; 28:14502–14508. [PubMed: 22924990]
20. Sadeghmoghaddam E, Gaïeb K, Shon YS. *App Catal A, General*. 2011; 405:137–141.
21. Sadeghmoghaddam E, Gu H, Shon YS. *ACS Catal*. 2012; 2:1838–1845. [PubMed: 27642537]
22. Gavia DJ, Maung MS, Shon YS. *ACS Appl Mater Interfaces*. 2013; 5:12432–12440. [PubMed: 24246150]
23. Long W, Brunelli NA, Didas SA, Ping EW, Jones CW. *ACS Catal*. 2013; 3:1700–1708.
24. Yabe Y, Sawama Y, Monguchi Y, Sajiki H. *Catal Sci Technol*. 2014; 4:260.
25. Tan C, Huang X, Zhang H. *Materials Today*. 2013; 16:29–36.
26. Zhang Z, Sun T, Chen C, Xiao F, Gong Z, Wang S. *ACS Appl Mater Interfaces*. 2014; 6:21035–21040. [PubMed: 25375195]
27. Sabater S, Mata J, Peris E. *ACS Catal*. 2014; 4:2038–2047.
28. Sun S, Wu P. *ACS Appl Mater Interfaces*. 2013; 5:3481–3486. [PubMed: 23521719]
29. Scheuermann GM, Rumi L, Steurer P, Bannwarth W, Mülhaupt R. *J Am Chem Soc*. 2009; 131:8262–8270. [PubMed: 19469566]
30. Ismaili H, Geng D, Sun AX, Kantzas TT, Workentin MS. *Langmuir*. 2011; 27:13261–13268. [PubMed: 21928860]

31. Gao Y, Chen X, Zhang J, Asakura H, Tanaka T, Teramura K, Ma D, Yan N. *Adv Mater.* 2015; 27:4688–4694. [PubMed: 26179983]
32. Wang Y, De S, Yan N. *Chem Commun.* 2016; 52:6210–6224.
33. Zhang Z, Dong Y, Wang L, Wang S. *Chem Commun.* 2015; 51:8357–8360.
34. Sun T, Zhang Z, Xiao J, Chen C, Xiao F, Wang S, Liu Y. *Sci Rep.* 2013; 3:2527. [PubMed: 23982312]
35. Pyun J. *Angew Chem Int Ed.* 2011; 50:46–48.
36. Dhakshinamoorthy A, Alvaro M, Concepcion P, Fornes V, Garcia H. *Chem Commun.* 2012; 48:5443–5445.
37. Gao Y, Ma D, Wang C, Guan J, Bao X. *Chem Commun.* 2011; 47:2432–2434.
38. Pan H, Low S, Weerasuriya N, Shon YS. *ACS Appl Mater Interfaces.* 2015; 7:3406–3413. [PubMed: 25611371]
39. Zedan AF, Moussa S, Turner J, Atkinson G, El-Shall MS. *ACS Nano.* 2013; 7:627–636. [PubMed: 23194145]
40. Xu C, Yang D, Mei L, Lu B, Chen L, Li Q, Zhu H, Wang T. *ACS Appl Mater Interfaces.* 2013; 5:2715–2724. [PubMed: 23477862]
41. Pevzner S, Pri-Bar I, Lutzky I, Ben-Yehuda E, Ruse E, Regev OJ. *Phys Chem C.* 2014; 118:27164–27169.
42. Huang J, Zhang L, Chen B, Ji N, Chen F, Zhang Y, Zhang Z. *Nanoscale.* 2010; 2:2733–2738. [PubMed: 20936236]
43. Navalon S, Dhakshinamoorthy A, Alvaro M, Garcia H. *Chem Rev.* 2014; 114:6179–6212. [PubMed: 24867457]
44. Niu Z, Li Y. *Chem Mater.* 2014; 26:72–83.
45. Ananikov VP, Beletskaya IP. *Organometallics.* 2012; 31:1595–1604.
46. Buchbinder AM, Ray NA, Lu J, Van Duyne RP, Stair PC, Weitz E, Geiger FM. *J Am Chem Soc.* 2011; 133:17816. [PubMed: 21919461]
47. Huang L, Ang TP, Wang Z, Tan J, Chen J, Wong PK. *Inorg Chem.* 2011; 50:2094. [PubMed: 21338108]

Fig 1. TEM images and histograms of (a) PdNP and (b) PdNP/GO hybrids. Scale bars are 20 nm.

Fig 2.
TEM image of PdNP/GO heated at 300 °C. Scale bar is 20 nm.

Fig 3. Kinetic plot of hydrogenation of DMAD using PdNP, PdNP/GO, and the heated PdNP/GO (300 °C) catalysts. The complete hydrogenation of alkyne to alkene requires the degree of hydrogenation to be 2.

Fig 4.

Results from the 3rd recycling reactions for all three catalysts compared to the average of catalytic reactions using fresh catalysts (1st use). The catalysis result from the reaction using the regenerated PdNP/GO at 300 °C is also included in the figure. The complete hydrogenation of alkyne to alkene requires the degree of hydrogenation to be 2.

Fig 5. Reaction systems before and after 24 hour DMAD hydrogenation reactions with (a) PdNP, (b) PdNP/GO, and (c) PdNP/GO heated at 300°C.

Scheme 1.

Synthetic scheme for ω-carboxylate-1-hexanethiolate-capped palladium nanoparticles (PdNP).