

Graphdiyne Oxides as Excellent Substrate for Electroless Deposition of Pd Clusters with High Catalytic Activity

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S Supporting Information

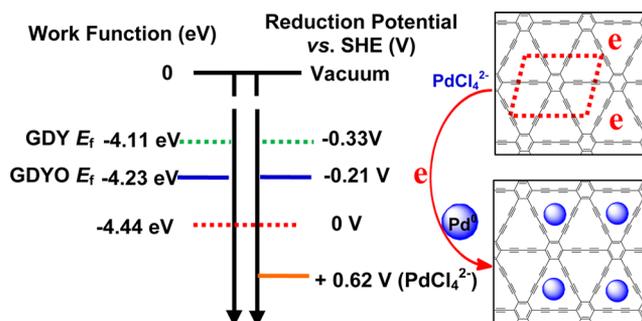
ABSTRACT: Graphdiyne (GDY), a novel kind of two-dimensional carbon allotrope consisting of sp - and sp^2 -hybridized carbon atoms, is found to be able to serve as the reducing agent and stabilizer for electroless deposition of highly dispersed Pd nanoparticles owing to its low reduction potential and highly conjugated electronic structure. Furthermore, we observe that graphdiyne oxide (GDYO), the oxidation form of GDY, can be used as an even excellent substrate for electroless deposition of ultrafine Pd clusters to form Pd/GDYO nanocomposite that exhibits a high catalytic performance toward the reduction of 4-nitrophenol. The high catalytic performance is considered to benefit from the rational design and electroless deposition of active metal catalysts with GDYO as the support.

Developing highly efficient and stable metal catalysts has become one of the increasingly important goals in chemistry and materials science owing to both economic and environmental reasons.¹ To accomplish this goal, metal catalysts with small sizes are preferred since they can provide a high accessible surface area for efficient catalysis. However, the surface energy increases with the decreasing particle size, which usually leads to serious aggregation of the metal particles, resulting in the gradual decrease of the catalytic activity.² For this problem, using supporting substrate is a possible solution, especially for nanometer sized metal catalysts.³ The catalytic activity per surface metal atom of the metal catalysts strongly depends on the nature of supporting materials when particle size is smaller than 6 nm.⁴ For this reason, extensive interests have been drawn to the uses of sp^2 -hybridized carbon materials as the supporting materials because they have lower reduction potentials than some kinds of metal ions and could enable electroless deposition of metals⁵ in a technically simple way without the use of surfactants or extra reducing agents or catalysts but with capability for large-scale production.⁶ Moreover, the sp^2 -hybridized carbons could interact with and thereby bind with metal atoms strongly since more interaction states and transmission channels are generated between both, as predicted theoretically.⁷ These properties enable the formation of carbon-supported metal catalysts with remarkably enhanced activity and stability.^{5c} So far, carbon nanotubes and graphene have been used for electroless deposition of metals.^{5,6b} For instance, Dai et al. first reported electroless

deposition of metals onto carbon nanotubes through spontaneous reduction of metal ions on nanotubes.^{5a} Dai et al. reported an elegant general approach to electroless deposition of various metals onto carbon nanotubes based on substrate-enhanced electroless deposition of metals.^{5b} Recently, Xie et al. observed electroless deposition of Pd onto graphene oxides.^{5c}

As a new carbon allotrope, graphyne family has been theoretically proposed to possibly feature as assembled layers of sp - and sp^2 -hybridized carbon atoms with striking applications in device and energy materials such as lithium ion batteries.⁸ More remarkably, graphdiyne (GDY) is first synthesized through cross-coupling on the surface of copper foil using hexaethynylbenzen.⁹ GDY, comprising benzene rings and carbon-carbon triple bonds in the structure and each benzene ring is connected to six adjacent benzene rings through two carbon-carbon triple bonds, resulting in a flat porous structure (Scheme 1).^{9,10} The structure of GDY is related to that of

Scheme 1. Schematic Illustration of Formation of Pd/GDYO through Electroless Deposition of Pd onto GDYO



graphene, but with the introduction of butadiyne linkages ($-C\equiv C-C\equiv C-$) to form 18-C hexagons. It comprises sp^2 - and sp -hybridized carbon atoms and exhibits unique electronic structure, and high chemical stability and electrical conductivity.¹¹ Very recently, self-catalyzed growth of large-area nanofilms of GDY and the applications of GDY in various research fields have been reported.¹² The unique atomic arrangement and electronic structure of GDY practically inspire

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the present investigation on the uses of GDY to develop high efficient catalysts in this study.

In this communication, we demonstrate that GDY can be used for electroless deposition of Pd nanoparticles (NPs) through the direct redox reaction between GDY and PdCl_4^{2-} , in which GDY acts as the reducing agent and stabilizer. Moreover, we observe that GDY oxides (GDYO) can be used as an even excellent substrate for electroless deposition of ultrafine Pd clusters. The as-formed Pd/GDYO nanocomposite is found to show a high catalytic performance toward the reduction of 4-nitrophenol (4-NP) with sodium borohydride (NaBH_4) as a reductant.

The GDY used here was synthesized on the surface of copper via a cross-coupling reaction using hexaethynylbenzene precursors, as reported in our early study (for more details, Supporting Information).⁹ As schematically shown in Scheme 1, GDY is 2D network with the connecting units consisting of a six-membered carbon ring in the center and six carbon triple bonds attached to each of the ring carbon atoms. The flat carbon networks contain only sp^2 - and sp^3 -hybridized carbon atoms with a high π -conjugation.^{9,10} To explore the direct redox reaction property of GDY and GDYO with PdCl_4^{2-} ion, E_{cutoff} values of GDY and GDYO were measured with ultraviolet photoelectron spectra (UPS) (Figure 1). The work

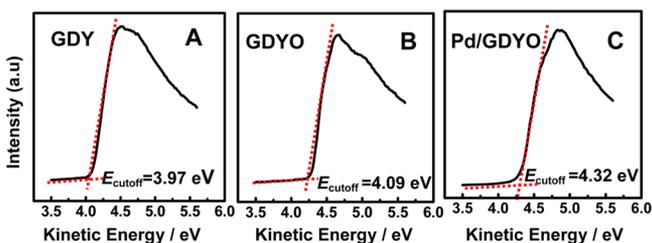


Figure 1. UPS spectra of GDY (A), GDYO (B), and Pd/GDYO (C).

functions (Φ) were thus calculated with the equation,¹³ $\Phi = h\nu - E_{\text{Fermi}} + E_{\text{cutoff}}$ where $h\nu$, E_{Fermi} and E_{cutoff} are the photo energy of the excitation light (21.22 eV), the Fermi level edge (21.08 eV in this case), and the inelastic secondary electron cutoff measured in Figure 1, respectively. The reduction potential was obtained from the equation,^{5a,14} $\Phi/e = E_{(\text{vs SHE})} + 4.44$ V, where Φ is the work functions, E is the reduction potential versus standard hydrogen electrode (SHE). On the basis of these equations, the parameters for GDY, GDYO and Pd/GDYO were calculated and the results were summarized in Table 1. The reduction potential of GDY was estimated to be

Table 1. Material Parameters: Sample, Work Function, and Reduction Potential

samples	E_{cutoff} (eV)	work function (eV)	$E_{\text{vs SHE}}$ (V)
GDY	3.97	4.11	-0.33
GDYO	4.09	4.23	-0.21
$\text{PdCl}_4^{2-}/\text{Pd}$			+0.62
Pd/GDYO	4.32	4.46	+0.02

about -0.33 V vs SHE, which was lower than that of PdCl_4^{2-} ion (+0.62 V vs SHE), suggesting its ability as the substrate for electroless deposition of Pd. The reduction potential of GDY is even lower than those of other kinds of carbon allotropes such as carbon nanotubes (+0.50 V vs SHE)^{5a} and graphene oxides (+0.48 V vs SCE),^{5c} suggesting GDY is the excellent reducing

agent among all the carbon materials for electroless deposition of metals.

To demonstrate the electroless deposition of Pd onto GDY, in a typical synthesis, homogeneous suspension of GDY was mixed with an aqueous solution of PdCl_4^{2-} and the mixture was put into an ice bath for 30 min under vigorous stirring. The resulting sample was then collected by centrifugation and washing for several times with water. X-ray photoelectron spectroscopy (XPS) spectra of the sample indicates the presence of Pd (Figure S2A); the peaks at 337.4 and 342.7 eV correspond to $3d_{5/2}$ and $3d_{3/2}$ components of the metallic Pd,¹⁵ revealing the formation of metallic Pd(0) and thereby indicating the successful electroless deposition of Pd onto GDY. Transmission electron microscopy (TEM) image of the sample (Figure 2A,B) suggests that the as-formed Pd NPs have

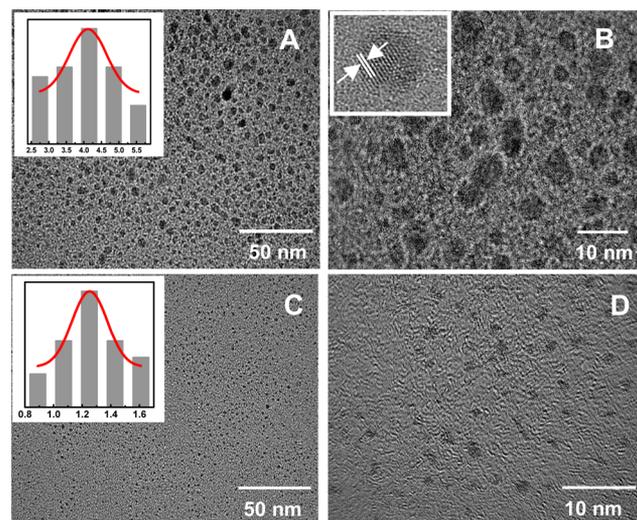


Figure 2. TEM (A, C) and HRTEM (B, D) images of Pd/GDY (A, B) and Pd/GDYO (C, D).

a uniform size of 4 ± 0.5 nm and are well dispersed on the surface of GDY. High-resolution Transmission electron microscopy (HRTEM) image (Figure 2B, inset) shows that the interplanar spacing of the particle lattice is 0.220 nm, which agrees well with the (111) lattice spacing of face-centered cubic Pd (0.224 nm).^{5c} These results revealed that the GDY could serve as excellent substrate for electroless deposition of Pd NPs. Moreover, the results demonstrated here also suggest that GDY could act as stabilizer for Pd NPs, which may be attributed to a strong anchoring effect between Pd nuclei and GDY, presumably owing to the high π -conjugated structure of GDY that can interact with the as-formed Pd NPs, which was similar to the case of graphene.^{5c,7}

To deposit Pd nanostructures with even smaller size, GDY was oxidized into GDY oxides (GDYO) in a concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture (volume ratio, 3:1) containing KMnO_4 . We observed that GDYO possesses a slightly higher work function (4.23 eV) than that of GDY (4.11 eV) (Table 1) since the acidic oxidation introduces surface oxygen-containing groups and thereby disrupts the π -conjugation of GDY and introduces surface dipole moments.¹⁶ The reduction potential of GDYO was calculated to be -0.21 V vs SHE (Table 1), suggesting that GDYO could also be used as substrate for the electroless deposition of Pd. Moreover, compared with GDY, GDYO was more readily stabilized in water, facilitating the

formation of Pd/GDYO in an aqueous solution by the electroless deposition method. Similar to that with GDY, the binding energy 337.6 and 342.9 eV in the XPS of the sample prepared with GDYO and PdCl_4^{2-} were observed, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ components of the metallic Pd(0) (Figure S2B),¹⁵ again demonstrating the formation of Pd/GDYO nanocomposite. The reference binding energies of the metallic bulk Pd at 335.1 and 340.0 eV are lower than the observed Pd values, suggesting that the values of the binding energy of Pd clusters on a GDYO surface are influenced by the nature of the support, as reported previously.¹⁷ TEM image reveals that Pd particles have a uniform size of 1.3 ± 0.1 nm and are fairly well dispersed on the surfaces of GDYO (Figure 2 C,D). These results demonstrated that the GDYO could be used as an excellent substrate for electroless deposition of Pd clusters to form Pd/GDYO as well. Theoretical estimation suggests that Pd atom tends to approach the C–C triple bonds of GDY and GDYO (Figure S3). As could be observed in Table 1, the work function of the as-formed Pd/GDYO was measured to be 4.46 eV, suggesting that the deposition of Pd clusters onto the GDYO essentially lowers the reduction activity toward PdCl_4^{2-} precursor. The small size of Pd clusters deposited on the GDYO surface further indicates that oxygen-containing groups generated on the GDYO surface may play an important role in controlling the formation of Pd clusters through increasing the anchoring ability of Pd nuclei on the GDYO surface and avoiding Ostwald ripening following nuclei.^{5c} This interaction may also be responsible for the good stability of the as-formed Pd clusters/GDYO, which was reflected by almost no change in morphology or size after the as-prepared Pd/GDYO was dispersed in water for 3 months (Figure S4).

Inspired by the highly dispersed and surfactant-free nature of Pd clusters and the unique structure of GDYO, we chose the reduction of 4-nitrophenol (4-NP) by NaBH_4 as a model reaction to investigate into the catalytic activity of the Pd/GDYO nanocomposite. The aqueous solution of 4-NP itself exhibits a strong absorption peak at 317 nm (Figure S5A). Upon the addition of NaBH_4 into the solution, the absorption peak at 317 nm disappears along with the appearance of a new peak at 400 nm (Figure S5A) due to the formation of 4-nitrophenolate ion, at the same time the color of the solution changed from light yellow to bright yellow (Figure S5A), which was consistent with the previous report.¹⁸ Upon the addition of Pd/GDYO into the mixture of 4-NP and NaBH_4 , the absorption peak at 400 nm significantly decreases as the reaction proceeds. Meanwhile, a new peak appears at 300 nm (Figure 3 and Figure S5), revealing the reduction of 4-NP and formation of 4-AP, according to the previous report.¹⁹ Since the concentration of NaBH_4 largely exceeds that of 4-NP, the reduction was considered as a pseudo-first-order reaction with regard to 4-NP only. The absorbance was proportional to the concentration of 4-NP in this system and the value of $\ln(A_t/A_0)$ reflects that of $\ln(C_t/C_0)$, where C_t and C_0 are the concentrations of 4-NP at time t and 0, respectively. Therefore, the reaction rate constant k was calculated from the rate equation, $\ln[C_t/C_0] = kt$. To follow the kinetics of the reaction, UV–vis spectra of the reaction mixture were monitored at 1 min intervals regularly. Figure 3B shows the time-dependent UV–vis spectra of 4-NP catalyzed by the Pd/GDYO and the rate constant k was calculated to be 0.322 min^{-1} , according to the slope of the fitted line (Figure 3B, red line). To further investigate into the influence of the supporting materials on the catalytic activity for the reduction of 4-NP, we deposited Pd

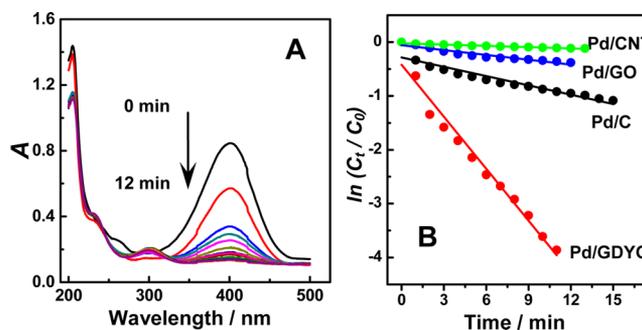


Figure 3. (A) Time-dependent UV–vis absorption spectra recorded during the catalytic reduction of 4-NP with the presence of the Pd/GDYO nanocomposite. (B) Plots of $\ln(C_t/C_0)$ as a function of the reaction time for the reduction of 4-NP catalyzed by four different catalysts of Pd/GDYO (red), commercial Pd/C (black), Pd/GO (blue), and Pd/CNT (green).

NPs spontaneously on the surface of another kinds of carbon materials including graphene oxide (GO) (Figure S6) and multiwalled carbon nanotubes (MWNTs) through the redox reaction between PdCl_4^{2-} ion and carbon materials. The rate constant k values were calculated to be 0.029, 0.008, and 0.058 min^{-1} for the Pd/GO, Pd/MWNT, and the commercial Pd/C catalysts, respectively. The rate constant on Pd/GDYO was about 40-fold higher than that of Pd/MWNT, 11-fold higher than that of Pd/GO, and 5-fold higher than the commercial Pd/C. Such excellent catalytic performance of the Pd/GDYO could be mainly attributed to synergistic effects from the highly dispersed and surfactant-free nature of Pd clusters benefited from the electroless deposition method and the unique structure of the GDYO. These results suggest that the smaller size of Pd clusters and larger π -conjugated structure of GDYO are mainly responsible for the more efficient catalysis of 4-NP as compared with those of Pd/GO, Pd/MWNT, and commercial Pd/C.

In summary, we have first demonstrated that GDY can be used as the reducing agent and stabilizer for electroless deposition of highly dispersed and surfactant-free Pd clusters owing to its low reduction potential and highly conjugated electronic structure. Further, GDYO, the oxidation form of GDY is observed to be an even excellent substrate for depositing ultrafine Pd clusters to form Pd/GDYO nanocomposite that shows a high catalytic performance toward the reduction of 4-nitrophenol. The high performance could be considered to arise from synergetic effects that occur at the Pd/GDYO nanocomposite. This work is believed to be significantly beneficial to the design and development of active metal catalysts as advanced catalytic systems for practical applications.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and additional figures as noted in the text. T This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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