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Formation and Stabilization of Palladium Nanoparticles on Colloidal Graphene Quantum Dots

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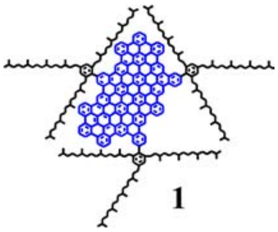
Supporting Information

ABSTRACT: Metal particles supported by carbon materials are important for various technologies yet not well understood. Here, we report on the use of well-defined colloidal graphene quantum dots as a model system for the carbon materials to study metal—carbon interaction. In the case of palladium, our studies show high affinity between the metal nanoparticles with the graphene. IR spectroscopy reveals covalent nature of the interaction between the two, which had been predicted by theoretical calculations yet never directly proven before.

Metal nanoparticles supported by carbon, including active carbon, carbon fibers, nanotubes, and graphene, are important for a variety of purposes[1a,b,c] ranging from catalysis,[1b] sensing,[1c] to fuel cells and other renewable energy-related applications. Despite the long usage history of carbon-supported metal particles, experimental studies on metal—carbon interaction have been complicated by inhomogeneity and complexity of the carbon materials. As a result, our knowledge on metal—carbon interaction comes mainly from theoretical calculations, and direct comparison between experiments and the calculations has been very challenging.[2] For example, it is widely believed that oxygen-containing functionalities, such as carboxylic, carbonyl, and phenolic groups, are necessary for anchoring of metal nanoparticles on the carbon supports,[1a,3] whereas calculations have shown considerable affinity between the metals and pristine graphene or carbon nanotubes.[4,5] Further, there is little experimental study to directly prove the theoretically predicted structural changes in the carbon supports caused by anchoring metal nanoparticles.[4] Herein, we use colloidal graphene quantum dots (QDs)[6] as a model system for carbon materials to study metal—carbon interaction. Palladium nanoparticles are synthesized in the presence of the graphene QDs and subsequently stabilized by them, indicating high affinity between the metal nanoparticles and the carbon surface even in the absence of oxygen-containing groups. Infrared (IR) spectroscopy further reveals that the nanoparticles significantly alter the graphene conjugation, indicating the covalent nature of their interaction. Our results provide important insights on mechanisms of various functions of carbon—metal-based composites. The results also have important implications on future electronics made of carbon nanotubes or graphene where metal contacts are necessary.[7]

In our studies, we use colloidal graphene QD **1** (Scheme 1) which we previously reported[6b] as the model system for the carbon supports. Containing 132 conjugated carbon atoms, **1** has a dimension of ~2.5 nm on the longest edge, large enough to support metal particles that can readily be imaged with electron microscopy techniques. **1** was made with stepwise solution chemistry,[6b] has uniform structure and well-defined optical and electronic properties.[6c] The well-defined and defect-free graphitic structures in the basal plane of the colloidal graphene QDs, in comparison with other carbon materials such as graphite or bulk graphene that abound in defects and contaminants, greatly simplify experimental studies of the metal—carbon interaction. In addition, because of the solubilizing trialkyl phenyl groups around the graphene core (marked black and blue in Scheme 1, respectively), **1** is highly soluble in common organic solvents such as toluene, allowing for ensemble studies to be conducted in solution with great sensitivity.

Scheme 1. Molecular Structure of Graphene Quantum Dot (QD) 1



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We chose palladium nanoparticles in our studies because Pd particles on carbon support are widely used in heterogeneous catalysis[3,8] and Pd was found to form reproducible Ohmic contacts with carbon nanotubes and graphene.[7] In addition, interaction between Pd and various carbon supports has been extensively studied.[3,4] In our studies, graphene QDs **1** are used as a mimic for the carbon substrates and meanwhile as a probe to study the metal—carbon interaction.

Thermal decomposition of palladium acetate[9] ($Pd(OAc)_2$) in toluene with **1** present leads to stable colloidal Pd nanoparticles. In a typical experiment (details in the Supporting Information (SI)), the reaction solution containing toluene, QD **1**, and a large excess of $Pd(OAc)_2$ (typically larger than 100 equivalence) was prepurged with argon, and then heated at 110 °C for various lengths of time. The reduction of the palladium salt was monitored *in situ* with UV—vis absorption spectra, as shown in Figure 1a. Before heating, the spectrum (labeled 0 h

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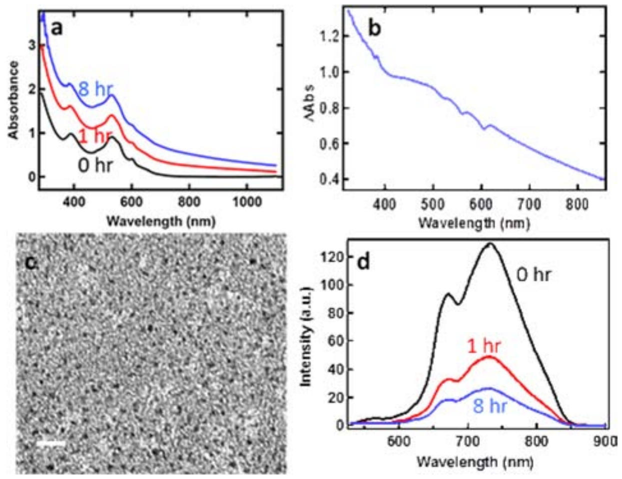

Figure 1. (a) UV−vis absorption spectra of $Pd(OAc)_2$ solution in argon-purged toluene with graphene QD **1** present after heating for various lengths of time. The peaks in the spectra are primarily due to the absorption of the graphene QDs.[6b,c] (b) The difference spectrum between the 0 and 8 h. It shows that on top of the plasmon spectrum of Pd nanoparticles there is a dip near 400 nm due to the depletion of $Pd(OAc)_2$ during the reduction, as well as some features between 500 and 600 nm. (c) TEM image of Pd nanoparticles in solution in (a) after heating for 8 h, showing particles with diameter ∼1 nm. The scale bar is 10 nm. (d) Luminescence emission of graphene QD 1 after heating the reaction mixture for various times.

in Figure 1a) consists of absorption of pristine graphene QDs in toluene[6b,c] and $Pd(OAc)_2$. The peaks in the spectrum are predominantly due to electronic transitions in the graphene QDs.[6b,c] Upon heating, nonzero signals appear in the low energy end of the spectra, consistent with the plasmon resonance spectra of dispersed small Pd particles.[10] Difference absorption spectra allow us not only to see the plasmon spectra of Pd particles more clearly, but also to estimate the amount of $Pd(OAc)_2$ depleted within the time interval. In Figure 1b, we show the difference spectrum between 0 and 8 h after heating. It contains, on top of a background of the plasmon spectrum, a dip near 400 nm from which we estimate that ∼32 equivalence of $Pd(OAc)_2$ has decomposed during the 8-h interval (see the SI). The large equivalence of $Pd(OAc)_2$ depleted in such a homogeneous reaction environment suggests that all the graphene QDs have Pd particles attached. As a control experiment, heating $Pd(OAc)_2$ under the same condition without the graphene QDs present results in precipitation of Pd powder. This indicates that the graphene QDs can serve as a stabilizing agent for the metal nanoparticles to prevent their aggregation, revealing significant affinity between the Pd nanoparticles and the graphene QDs.

TEM images confirm the presence of well-dispersed Pd nanoparticles in the Pd-graphene mixture after heating. The TEM image shown in Figure 1c was obtained by drop-casting the reaction solution after 8 h of heating on a copper grid coated with a 15 nm-thick amorphous carbon film. The Pd particles have sizes near 1 nm, smaller than most of the Pd particles or clusters reported so far.[11] The Pd particles appear to be noncrystalline with the high-resolution TEM imaging and electron diffraction. Assuming a spherical shape we can estimate that each Pd particle contains ∼34 atoms, in excellent agreement with the number of equivalence of $Pd(OAc)_2$ depleted. This confirms that approximately all the graphene QDs have Pd particles attached. The graphene QDs could not be seen because of their low contrast on the substrate used; and whether the size of the Pd particles is determined by that of the graphene QDs will be further investigated.

The Pd nanoparticle/graphene interaction was further studied by monitoring spectral changes of QD **1** upon metal reduction. Formation of the Pd nanoparticles is accompanied by reduction in luminescence intensity of QD **1**, as shown in Figure 1d, consistent with attachment of metal particles to the QDs. Further, a careful examination of the absorption spectra in Figure 1a also reveals spectral changes from the absorption of pristine graphene QDs. These changes are highlighted in the difference spectrum shown in Figure 1b as the features between 500 and 600 nm, which in energy coincide with the electronic transitions in QD **1** (Figure S2). These spectral changes amount to a few percent of the QD absorbance, suggesting that the attachment of the Pd nanoparticles does not significantly change the electron conjugation in the graphene QDs.

To establish that the Pd particles are indeed stabilized by the conjugated π-electron system of the graphene, we used infrared (IR) spectroscopy to study the Pd/graphene mixtures obtained after metal reduction. It has been reported that in the thermal decomposition of $Pd(OAc)_2$ in an inert atmosphere, the acetate ligands are oxidized and, through mechanisms not yet understood, are turned into CO_2, acetic acid, and volatile alkanes.[11b,12] It may be anticipated that the oxygen-containing groups could be, e.g., through radical substitution, incidentally grafted to the graphene during metal reduction and contribute to the metal/graphene interaction. To examine this possibility, the Pd/graphene mixtures from the reactions were concentrated and then precipitated with methanol. After repetitive washing with methanol to remove small-molecular substances, the black powders obtained were cast on KBr plates for IR measurements. The result is shown in Figure 2 (red curve), with the IR spectrum of **1** (black curve). The comparison indicates the appearance of a new peak at 1730 cm^{-1} (marked by an arrow) which may be due to either the C=O stretching in conjugated esters or overtone (or combination) of aromatic C−H out-of-plane bending modes.[13] Treatment of the Pd/graphene mixtures with strongly basic condition (for de-esterification) followed by changing pH values leads to identical IR spectra, excluding the possibility of esters (see the SI). These results, together with the absence of ketone C=O

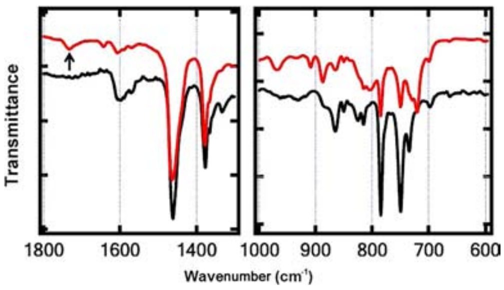

Figure 2. IR absorption spectra of the Pd/graphene mixtures (red curve) and **1** (black curve) in selected energy ranges. The spectra were normalized in intensity relative to the aliphatic C−H deformation at 1377 and 1460 cm^{-1}. The peak at 1730 cm^{-1}, marked by an arrow, a possible indication of an ester, turns out to be the overtone (or combination) of aromatic C−H out-of-plane bending modes. The changes in the aromatic C=C stretching and C−H out-of-plane bending regions indicate the covalent nature of the interaction between graphene and Pd nanoparticles.

stretching (~1670 cm^{-1}) and phenolic O–H groups (3200–3650 cm^{-1}), unambiguously show that carboxylic, carbonyl, and phenolic groups are not necessary for Pd nanoparticles to anchor on graphene.

IR spectra further reveal that anchoring of Pd nanoparticles on graphene is of covalent nature, a conclusion predicted by theoretical calculations[4] yet never directly experimentally proven before. As shown in Figure 2, considerable changes occur in regions characteristic of aromatic C=C stretching (~1600 cm^{-1}) and C–H out-of-plane bending modes (between 700 and 1000 cm^{-1}) after the metal reduction.[13] With the intensities normalized relative to the aliphatic C–H deformation (1377 and 1460 cm^{-1}), the C=C stretching absorption reduces significantly in intensity, suggesting the chemical interaction between the π-electrons in the graphene and the Pd particles. However, no obvious shift in the C=C stretching frequency is observed, indicating the little disturbance in the C=C bonds, consistent with the small changes in the electronic transitions of QD **1** shown in Figure 1. The chemical interaction between the graphene QDs and the Pd nanoparticles is further confirmed by the spectral changes between 700 and 1000 cm^{-1} where many new peaks appear and the original peaks in **1** reduce in intensity. Considering the small difference between the electronegativity of Pd and carbon, we exclude the possibility of ionic interaction and conclude that the Pd-graphene interaction must be covalent in nature. This has been predicted by density functional theory (DFT) calculations,[4] for which our studies for the first time provide direct experimental evidence.

Identification of the covalent interaction between the Pd particles and graphene provides important insights regarding the possible mechanisms of carbon-supported Pd particles for various applications. To understand the Ohmic behavior between Pd contacts and carbon nanotubes or graphene, DFT calculations of Pd atoms or clusters adsorbed on graphene[4] have shown significant mixing between the Pd 4d orbitals and the π-orbitals of graphene through electron donation and back-donation. More specifically, graphene donates electron (density) to the Pd $4d_{xz}$, 4 d_{yz} orbitals that form the antibonding orbitals of Pd–Pd bonds and meanwhile Pd $4d_{z^2}$ orbitals back-donate electron to graphene.[4b] The same interactions could also explain the high affinity between the Pd nanoparticles and the graphene QDs we observed, as well as the stability of sandwich compounds of palladium sheets between aromatic hydrocarbons that were previously reported.[14] According to the calculations, the graphene/metal interaction simultaneously involves multiple metal atoms, different from normal Pd–C bonds that involve a single Pd atom.[15] Interestingly, the calculations also indicated that the electron donation from graphene to Pd significantly weakens the Pd–Pd bonds and increases Pd reactivity. It opens interesting possibilities to tune the reactivity of Pd, and possibly other transition metal nanoparticles as well, by controlling the electron transfer from the graphene to the metals. This is being investigated with graphene QDs with tunable redox potentials due to various covalently attached functional groups.[16]

In summary, herein we demonstrate the use of colloidal graphene QDs as a model system for more complex carbon materials to study metal–carbon interaction. We show that Pd nanoparticles can form on the graphene QDs with high stability, for the first time confirming the covalent interaction between Pd nanoparticles and graphene. The graphene QDs, with well-defined structures and properties, provide a unique tool to understand the mechanisms of carbon-supported metal particles for various applications, and allow us to systematically investigate the role of the carbon supports in these functions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and more spectroscopic characterization. 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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