

# Synthesis and Application of Nanocarbon Materials Using Plasma Technology

Fan Yang and Yongfeng Li

**Abstract**—We report an environmentally friendly approach to the synthesis of ultrasmall monodispersed Au, Ag, Pt, Pd nanoparticles (NPs) and Pd, Au NPs functionalized oxidation carbon nanotubes (Pd-CNTs, Au-CNTs) by gas-liquid ionic plasma (GLIP) method. Furthermore, the synthesized nanocarbon hybrid materials were characterized by Transmission electron microscopy (TEM) and X-ray diffraction (XRD). The synthesized Pd-CNTs can be applicable for the catalyst in the Suzuki reaction, showing the good reactivity, stability and recyclability, and the Au-CNTs catalyst exhibited much more remarkable catalytic activity in the oxidation of various organosilanes by using water as the solvent compared with other organic solvents (for example THF, ethyl acetate, and acetone), which is very important for organic synthesis from both the standpoint of practical reasons and an economic perspective.

**Index Terms**—Nanocarbon materials, plasma, nanoparticle, molecule transformation reactions.

## I. INTRODUCTION

Liquid-related plasmas have recently attracted much attention because of their unique properties such as ultra-high density, high reactivity, high process rate, and preparing nanomaterial at large scale, the plasma technology has been widely utilized for applications in environmental, biomedical, and nanomaterial process fields. On the other hand, this methodology is especially advantageous in avoiding use of toxic stabilizers and reducing agents, and the continuous synthesis, reaction at room temperature and no need to stir during the nanoparticle formation process [1]-[3]. It has been recently a subject of considerable research focused on nanoparticle synthesis by a gas-liquid interfacial plasmas (GLIP) method, including various kinds of nanoparticles such as Au, Ag, Pt, Pd and Cu [4]-[7]. However, there still exists a problem that the size distribution and the morphology of the synthesized metal nanoparticles are not controllable, which therefore limits their potential applications. Recently, much effort has been paid to solve these difficulties, such as by using carbon nanotubes, polyvinylpyrrolidone (PVP) or DNA to stabilize the metal nanoparticles. Therefore, it is desirable to develop an efficient and inexpensive synthetic approach for

the synthesis of metal nanoparticle hybrid materials with controlled morphology, narrow size distribution and wide range of potential applications.

Catalysis using metal nanoparticles has attracted increasing interest due to their potentially green and sustainable catalytic properties. It has been reported that metal NPs supported on various metal oxide surfaces, such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> with controllable shape, exhibit unprecedented catalytic activities for transformation of organic substrates. CNTs have many properties for example large chemically active surface, unique physical properties, inherent size, hollow geometry and stability at high temperatures [8], and graphene is a novel two-dimensional material with atoms arranged in a honeycomb lattice, which has exhibited fascinating exceptional electronic, mechanical, and chemical properties due to its unique physical structure and dimensions [9]. Considering these characters, such nanocarbon materials have been normally used as an ideal support for the dispersion and stabilization of metal nanoparticle (NPs).

Based on this background, here we report the synthesis of ultrasmall monodispersed metal NPs (Au NPs, Ag NPs and Pd NPs) and metal NPs functionalized nanocarbon materials by an environmentally-friendly GLIP method. Furthermore, the new catalyst based on nanocarbon materials has been proved to be stable and high catalytic performance in organic molecule transformation reactions [8]-[10].

## II. EXPERIMENTAL

### A. Typical Procedure for the Formation of Metal NPs

The experimental configuration of ionic liquid introduced plasma, which is used for the synthesis of the metal NPs, is similar to the previous work [8]-[10]. The glow discharge plasma was generated between the top flat stainless steel (SUS) and bottom ionic liquid electrode by using a DC power source (KIKUSUI PMC 500-0.1A). Ar gas was introduced and used as the plasma forming gas, the chamber was a stainless steel with inner diameter of 70 mm and four glass windows, and the gap between electrodes is 4 mm. A direct current (DC) power source with voltage  $V_{DC} = 220-250$  V is applied to a stainless steel electrode in gas phase for the generation of an Ar plasma, where the discharge current  $I = 0.02$  A is fixed, and the Ar gas is introduced up to a pressure  $P_{gas} = 290$  Pa. Oleylamine was dissolved in butyl-3-methylimidazolium tetrafluoroborate by sonication for 15 min, metal salt was added to the mixture sonication for 5 min. The solution was transferred to the stainless steel cell of the experimental setup. The inter-electrode gap is 4 mm. The gas pressure of Ar in the chamber was evacuated to 290 Pa by a

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vacuum pump. The discharge current was 0.02 A, and the voltage was in the range of 220-250 V. The plasma was kept steady at this situation for 20 min. The synthesized metal NPs in the ionic liquid were precipitated out by adding the ethanol and centrifugation at 4000 rpm for 10 min, and then the product was washed for four times and dispersed in methylene chloride.

### B. Synthesis of the Pd-CNTs Hybrid Materials

50 mg oxidation CNTs were dispersed in ethanol by sonicated for 15 min. After that, Pd(OAc)<sub>2</sub> ethanol solution were added to the dispersed CNTs in ethanol solution, then the ethanol was evaporated at 40-50 °C. As a result, the Pd compounds were well dispersed on the surface of oxidation CNTs. The obtained oxidation CNTs decorated with the Pd compounds were dispersed in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF<sub>4</sub>). For the formation of Pd NPs, electrons were irradiated toward the ionic liquid for *t* = 10 min, then the mixture were sonicated in ethanol to remove the excess impurities and extracted from the ionic liquid by a centrifuge process.

### C. Catalytic Activity of the Pd-CNTs

The Pd-CNTs catalyst, corresponding to a percentage of Pd of 1 mmol% with respect to 4-Bromoacetophenone was used, and 4-Bromoacetophenone (0.5 mmol, 100 mg), phenylboronic acid (0.6 mmol, 73 mg) were mixed together in a pressure vial, then 2 mL potassium carbonate solution (2 M) and 2 mL ethanol were added, the mixture was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered through a polyvinylidene fluoride (PVDF) membrane with 0.2 μm pore size in order to isolate the catalysts which were washed with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and water (10 mL), and dried at 110 °C. The alcoholic/aqueous solution was extracted with diethylether (10 mL) for 3 times. The organic extracts were dried with anhydrous magnesium sulfate, filtered, and evaporated to dryness, allowing the isolation of pure 1-([1,1-biphenyl]-4-yl) ethanone as the reaction product.

### D. Synthesis of the Au-CNTs Hybrid Materials

The decoration of AuNPs on the oxidation CNTs catalyst was carried out by a GLIP method with HAuCl<sub>4</sub> 4H<sub>2</sub>O, oxidation CNTs and oleylamine (OA) at room temperature. 50 mg oxidation CNTs were added to the reactor, HAuCl<sub>4</sub> 4H<sub>2</sub>O were dispersed in 1-butyl-3-methylimidazolium tetra-fluoroborate ([BMIM]BF<sub>4</sub>) and OA, then the Au solution was added to the reactor, and the Au solution and CNTs mixture was left for 10 min. For the formation of AuNPs, electrons were irradiated toward the ionic liquid, and the electron irradiation for *t* = 15 min, the mixture was sonicated in ethanol to remove the excess impurities and extracted from the ionic liquid using a centrifuge.

### E. Catalytic Activity of the Au-CNTs

The organosilanes in water solution (0.25 M, 2 mL) and Au-CNTs (0.1 mol%, 1.3 mg) were added to PhMe<sub>2</sub>SiH (78mL, 0.5 mmol) at room temperature. The reaction mixture was stirred at room temperature for 40 min and monitored by thin layer chromatography (TLC) analysis. The mixture was filtered through a polyvinylidene fluoride (PVDF) membrane with 0.2μm pore size in order to isolate the catalysts which

were washed with water (10 mL) and acetone (10 mL), and dried at 110 C. The filtrate was extracted with diethylether three times. The organic extracts were dried with anhydrous magnesium sulfate, filtered, and evaporated to dryness. After concentration, the residue was purified by silica gel chromatography to afford PhMe<sub>2</sub>SiOH (75.6 mg, 99%) as yellowish oil.

## III. RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) images for Au, Ag, Pt and Pd NPs stabilized by OA prepared with GLIP are shown in Figs. 1(a)-(d), indicating that the monodispersed Au, Ag, Pt and Pd NPs were formed, the size distribution of the Au, Ag, Pt and Pd NPs were 2.4, 2.9, 2.0 and 2.7 nm, respectively. High-resolution transmission electron microscopy (HRTEM) images of each kinds of metal NPs are shown in Fig. 1(e)-(h), in which the interfinger distance are measured, and it was corresponding to the (111) of the face centered cubic Au, Ag, Pt and Pd, respectively.

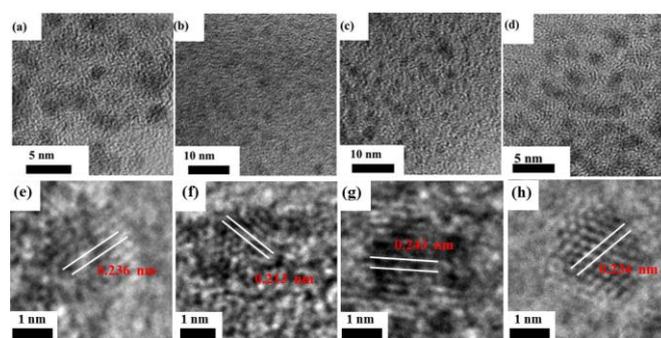


Fig. 1. TEM images of Ag (a), Pt (b), Pd (c), Au (d), and HRTEM images of Ag (e), Pt (f), Pd (g), Au (h).

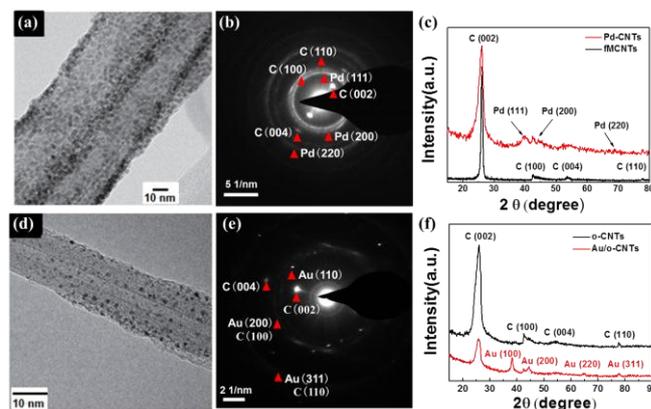


Fig. 2. TEM image of Pd-CNTs (a), SEAD image of Pd-CNTs (b), XRD image of Pd-CNTs (c), TEM image of Au-CNTs (d), SEAD image of Au-CNTs (e), XRD image of Au-CNTs (f).

Furthermore, metal NPs supported on nanocarbon materials have been synthesized by the GLIP method, for example, oxidation CNTs supporting Pd NPs (Pd-CNTs) and Au NPs (Au-CNTs). Their corresponding TEM images are summarized in Fig. 2(a) and Fig. 2(d), and the results demonstrate that all synthesized nanocarbon materials exhibit uniform morphologies and the particle diameters of Pd-CNTs, Au-CNTs are 3 nm, 1.2 nm, respectively. Moreover, the samples are characterized by SEAD, XRD as indicated in Figs. 2(b), 2(c), 2(e), 2(f), showing the characteristic diffraction

peaks at 25.9 °; 42.8 °; 54.3 ° and 77.7 °; corresponding to (002), (100), (004), and (110) reflections of graphite, respectively. Diffraction peaks were also observed at 40.1 °; 46.7 °; and 68.7 °; which could be indexed as the (111), (200), and (220) reflections of crystalline Pd (0), respectively. The peaks at 38.1 °; 44.4 °; 64.5 °; and 77.6 ° correspond to (111), (200), (220), and (311) reflections of crystalline Au (0), respectively.

The above results demonstrate that the metal NPs decorated nanocarbons have been successfully prepared, and its application as new catalysts for organic molecule transformation reactions have been further explored. Fig. 3 shows the Pd-CNTs catalyzed Suzuki reactions. The reaction of aryl bromide with phenylboronic acid was carried out in the presence of Pd-CNTs of 0.1 mol%, using 2M K<sub>2</sub>CO<sub>3</sub> solution and ethanol as solvent, giving the desired product with 99% yield at 80 °C. Both aryl bromide bearing an electron-donating and electro-withdrawing aromatic bromide react with phenylboronic acid were subject to the same conditions, the excellent yields were obtained. The coupling of bromobenzene and 1-bromonaphthalene with phenylboronic acid were examined, the corresponding products were obtained in high yields.

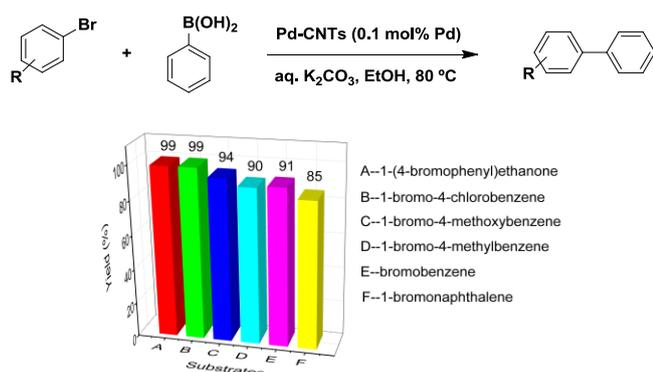


Fig. 3. Yield (%) of Suzuki-Miyaura reaction with phenylboronic acid catalyzed by Pd-CNTs.

The reusability is the most important feature for a heterogeneous catalyst, which is superior to a homogenous one. First, to confirm the reaction indeed catalyzed by solid Pd-CNTs rather than by homogenous Pd species, we first carried out the reaction, then the catalyst Pd-CNTs was removed by filtration, and the leaving solvent was evaporated and treated with nitrohydrochloric acid. The Pd content was checked by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis, and no leaching of Pd NPs was found during the reaction. To access recyclability of Pd-CNTs, multiple coupling reaction of 4-Bromoacetophenone with phenylboronic acid were carried out by filtration for the separation of the catalyst from the reaction mixture. The catalyst was repeatedly used for four times, the yields of the products were shown in Fig. 4.

Furthermore, we performed the oxidation of dimethylphenylsilane with water by using Au-CNTs as a catalyst, the reaction was proceeded smoothly, and the product was obtained in 99% yield as shown in Fig. 5. In the presence of various organic solvents, including THF, EtOAc and DMF afforded the corresponding silanols in 99% yield in

55 min, 70 min and 85 min, respectively. When using toluene as solvent, the reaction cannot proceed. In comparison, the product was surprisingly obtained in 99% yield as a single product in only 7 min in H<sub>2</sub>O. Usually, heterogeneous catalyzed oxidation of silanes to silanols was more effective by using the organic solvent compared with H<sub>2</sub>O [11].

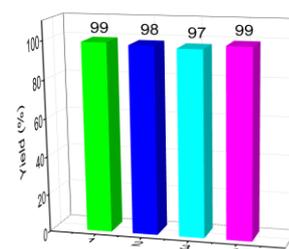


Fig. 4. Yield (%) of coupling reaction of 4'-bromoacetophenone with phenylboronic acid in subsequent runs with catalyst.

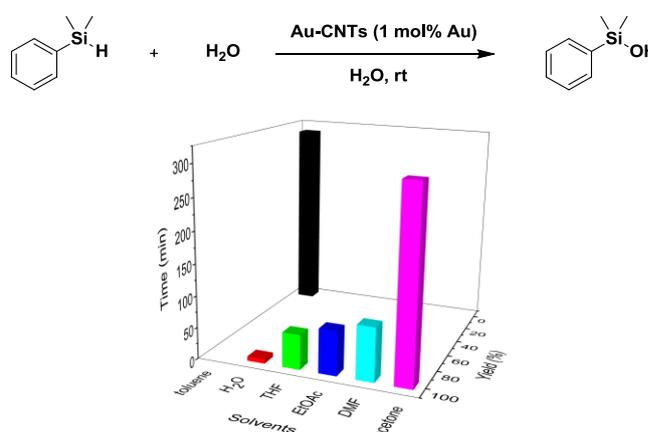


Fig. 5. Oxidation of dimethylphenylsilane with catalyst Au-CNTs in different solvents.

The catalytic oxidation reactions with a variety of organosilanes using the Au-CNTs catalyst were carried out, the results were shown in Fig. 6. First, triethylsilane exposed sterically was quantitatively oxidized to the corresponding silanol in 15 minutes without the formation of disiloxane. Next, the oxidation of two reputedly challenging substrates was examined, the corresponding silanols were obtained in high yields by increasing the catalyst loading amount and the reaction time. The Au-2 catalyst could also be used in the oxidation of diphenylsilane, and the corresponding silanol was obtained in high yield.

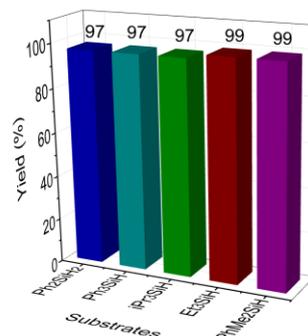


Fig. 6. Yield (%) of oxidation organosilanes in water catalyzed by Au-2.

The leaching of the AuNPs in the reaction was also examined using an ICP-OES, and no leaching of AuNPs was

detected by the ICP analysis. To assess recyclability of Au-CNTs, multiple dimethylphenylsilane oxidation cycles were carried out, and the recovery of the heterogeneous catalyst is carried out by filtration for the separation of the catalyst from the reaction mixture. The catalyst was repeatedly used four times, but no significant loss of activity was observed. The product was obtained nearly quantitatively every time as shown in Fig. 7.

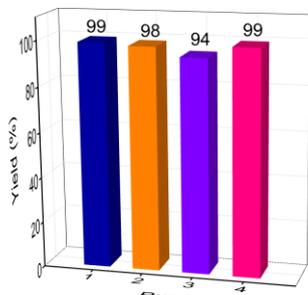


Fig. 7. Yield (%) of oxidation organosilanes in water in subsequent runs with catalyst Au-CNTs.

#### IV. CONCLUSIONS

In summary, we report the synthesis of ultrasmall monodispersed metal NPs (Au NPs, Ag NPs, Pd NPs) and metal NPs functionalized nanocarbon materials (Pd-CNTs, Au-CNTs), by an environmentally-friendly GLIP method. Furthermore, the new catalyst based on nanocarbon materials has been proved to be stable, and shows high catalytic performance in organic molecule transformation reactions. The synthesized Pd-CNTs can be applicable for the catalyst in the Suzuki reaction, showing the good reactivity, stability and recyclability, and the Au-CNTs are highly efficient heterogeneous catalysts for the selective oxidation of silanes in H<sub>2</sub>O.

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