Photon-induced Synthesis of Ultrafine Metal Nanoparticles on Graphene as Electrocatalysts: Impact of Functionalization and Doping

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ARTICLE

Photon-induced Synthesis of Ultrafine Metal Nanoparticles on Graphene as Electrocatalysts: Impact of Functionalization and Doping

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Utilizing reducing species generated by high-energy photons offers an alternative strategy to prepare metal nanoparticles (NPs) in the absence of foreign reductant. However, fine control of NP size and dispersity remains a big challenge. Herein, we report that by properly selecting the solvent, precursor concentration and carbon support, ultrafine palladium (Pd) NPs with an average size of 3.0 nm uniformly distributed on nitrogen-doped graphene (NG) are radiolytically prepared. Control experiments demonstrate that ethylene glycol with moderate reducibility is superior to water. Among four graphene-based supports with distinct functionalization or doping, nitrogen dopants outperform oxygen functional groups in anchoring the NPs and controlling the size and dispersity. Pd/NG also affords the lowest η_{10} (overpotential at a current density of 10 mA·cm⁻²) toward hydrogen evolution reaction (HER). Comparison of Pd/NG with varied Pd loadings indicates that the HER activity nearly reaches a plateau once the loading increases to 2.6 wt %, which is limited by the nitrogen content of NG. X-ray photoelectron spectroscopy unambiguously reveals the electron transfer from electron-rich Pd to electron-deficient nitrogen, especially the graphitic nitrogen, corroborating the decisive role of doped nitrogen in stabilizing the Pd NPs on NG. Extending the synthesis to platinum (Pt) yields Pt/NG that presents even lower η_{10} than the commercial 10 wt % Pt/carbon black due to the smaller NP size. These results collectively highlight the potential of high-energy photons for green, versatile and scalable synthesis of heterogeneous nanostructures.

Introduction

Green, versatile and scalable synthesis of nanomaterials lays the foundation for the industrial real-world implementation of nanotechnology. The existing synthetic methodologies are deemed as either top-down or bottom-up strategies, which set the stage for the birth of multitudinous nanomaterials. As a bottom-up method, wet-chemical reduction has been prevalently employed for preparing metal-based nanostructures.¹⁻⁴ However, harsh reaction conditions (high temperature and/or pressure), troublesome surfactants and excess reductants are often required to steer the synthesis, resulting in high cost input and environmental footprint. These deficiencies thus necessitate the development of alternative green and cost-effective synthetic method.

Radiation inclusive of electromagnetic, acoustic and particulate is ubiquitous. Since the pioneering work by Yamazaki and colleagues in 1960s⁵, considerable attempts have been made in exploring the utilization of radiation to prepare nanostructured materials. For instance, Duan and co-workers reported the

synthesis of graphene-supported single atomic metals with the aid of microwave.⁶ Photochemical reduction, induced by ultraviolet and visible light, has also been utilized to prepare Ag⁷⁻¹⁰, Au¹¹⁻¹³, Pt¹⁴⁻¹⁶, and Pd^{17, 18} nanostructures. Nonetheless, such radiolytic methods are often kinetically inefficient and thus entail elevated temperature, presence of semiconductor (photoelectron generator) and/or long reaction time. Compared to these non-ionizing radiation, ionizing radiation, such as gamma and X-ray radiation, features high photon energy to more efficiently ionize atoms and break chemical bonds. Therefore, ionizing radiation constitutes a potential powerful method for advanced nanomaterial preparation.

As a highly penetrative electromagnetic wave with the highest photon energy, gamma radiation has been attempted in the wet-chemical preparation of metal¹⁹⁻²¹, oxide²²⁻²⁵ and carbon-based materials²⁶⁻²⁸. When the solution concentration is low, solvent is the dominating species that interacts with gamma rays. Radiation chemistry of the corresponding solvents thereby dictates the reaction mechanism. By far, the most frequently studied is the aqueous system.²⁰ The radiolytic reaction of water is described in eq 1.^{20, 21}

The reaction proceeds so efficiently that the radiolysis can be conducted at room temperature and ambient pressure.²⁹ Essentially, the species of e_{aq}^- and H^* with low redox potentials serve as in-situ reductants, while the oxidative OH^* radical is

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scavenged by common alcohol additives, such as isopropanol and ethanol. Starting from this principle, Zhao and co-workers reported the synthesis of monodispersed Ag nanoparticles (NPs)/graphene nanocomposites using gamma radiation.³⁰ Pt NPs-decorated reduced graphene oxide (rGO) was similarly fabricated as a counter electrode.³¹ Ag NPs on rGO and titania nanotube arrays were also prepared as photocatalysts.³² These trials however fail to deliver surfactant-free NP surface, ultrafine NP size, narrow size distribution, and/or uniform NP dispersity, which unfortunately are paramount attributes for heterogeneous catalysts. Given the three components of the irradiated system (metal precursor, solvent and support), the improvement of radiolytic synthesis thus calls for appropriate selection of the solvent and support materials. Recently, metal-organic frameworks have been used to confine the noble metal (Pd, Pt and Au) NPs by utilizing gamma rays with high penetration, yielding an active catalyst for 4-nitrophenol reduction.³³ Using ethylene glycol (EG) as a solvent, Zhai and co-workers synthesized amorphous MoS_x/C composites by gamma-ray radiation as efficient electrocatalysts for hydrogen evolution.³⁴ These studies rationalize the significance of beyond-water solvent and adequate support in the radiolytic synthesis of heterogeneous catalysts.

Despite the benefits of avoiding foreign reductant, mitigating harsh reaction conditions and high versatility in the NP synthesis using high-energy photons, a systematic study to address issues in controlling the size and dispersity, especially in the absence of surfactants, is still lacking. To this end, we hereby conduct a comprehensive investigation on the effect of solvent, support and metal precursor concentration on the gamma radiolytic synthesis of supported NPs. Instructed by the classical nucleation and growth mechanism, we first justify that EG with mild reducibility and high viscosity is a superior solvent to water. Four graphene materials, including graphene oxide (GO), rGO, nitrogen-doped graphene (NG), and in-house electrochemically exfoliated graphene (G), are scrutinized as potential supports for Pd NPs to reveal the impact of graphene functionalization and doping on support effect. Among them, NG is found to yield an ultrafine Pd NP size with high dispersity and Pd/NG displays the lowest overpotential for the acidic hydrogen evolution reaction (HER). By tuning the Pd loading, we find that the HER activity of Pd/NG levels off once the loading reaches 2.6 wt %. Mechanistic analysis is thus provided to identify the critical role of nitrogen dopants, especially the graphitic nitrogen, in anchoring and stabilizing the formed Pd NPs by electronic interaction. When replacing Pd with Pt, Pt/NG presents even better HER activity than the commercial 10 wt % Pt/CB catalyst.

Experimental

Chemicals

All chemicals were purchased unless otherwise indicated and used as received without further treatment. Chemicals including graphene oxide (GO, sheets), reduced graphene oxide (rGO, chemically reduced by hydrazine), nitrogen-doped

graphene (NG, ≥4% nitrogen content), palladium acetylacetonate (Pd(acac)₂, 99%), chloroplatinic acid hydrate (H₂PtCl₆·xH₂O, ≥99.9%), ethylene glycol (EG, anhydrous, 99.8%), 2-propanol (IPA, ≥99.5%), and ethanol (absolute, ≥99.8%) were purchased from Sigma-Aldrich. Platinum on carbon black (nominally 10 wt % Pt/CB, HiSPEC 2000) was supplied by Thermo Fisher Scientific. Electrochemically exfoliated graphene (G) was provided by collaborators and the detailed procedures were described in previous work.³⁵ Deionized (DI) water (18.2 MΩ·cm) was used in all the experiments.

Synthesis of Supported NP Catalysts

Synthesis of the composites was conducted by exposing the materials to a Cobalt-60 gamma irradiator at Dalton Cumbrian Facility, The University of Manchester. Figure 1 schematically illustrates the one-step radiolytic synthesis. Taking the 2.6 wt % Pd/NG sample as an example, a 20 mL headspace vial containing 16 mL of 0.25 M Pd(acac)₂ in EG solution and 16 mg of NG was sufficiently sonicated (≥ 24h) to obtain a homogeneous suspension. After deaeration with argon (N5.0, BOC gas) for 20 min to remove oxygen, the sealed vial was placed inside the irradiator at room temperature and ambient pressure. The radiation was held for 2h. The total dose was controlled to ~42 kGy at a dose rate of ~300 Gy min⁻¹. Afterwards, the Pd/NG was separated by centrifugation (Sigma 2-16KL centrifuge) at 15000 rpm for 5 min and washed with a mixture of ethanol and DI water. After washing for another three times, the composite was dried at 40 °C in a vacuum oven overnight.

Figure 1. Pictorial illustration of the radiolytic synthesis of graphene-based materials supported Pd NPs in EG.

Pd/GO, Pd/rGO and Pd/G were prepared by replacing the NG with equivalent GO, rGO and G, respectively. Using 16 mL of 0.125, 0.375 and 0.5 M Pd(acac)₂ in EG solution, Pd/NG with nominal Pd loadings of 1.3, 3.9 and 5.2 wt % were prepared, respectively. 2.6 wt % Pt/NG was obtained by replacing Pd with equivalent Pt precursor. 1 mg·mL⁻¹ of GO dispersions in EG and DI water (with 2.5 vol. % IPA) were irradiated to investigate the effect of different solvents.

Physical Characterization

The microstructure and morphology of supported composite were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F and Thermo Scientific Talos F200X, 200 kV) and scanning electron microscopy (SEM, Thermo Scientific Quanta 250 FEG, 10 kV). For the specimen preparation, one droplet of the composite suspension was dropped onto a copper grid coated with carbon film (400 mesh, TAAB) and dried in air.

X-ray powder diffraction (XRD) was performed to obtain the crystallographic information of the samples. The powder diffraction patterns were recorded on a Malvern PANalytical X-Ray diffractometer (Empyrean) using Cu K α radiation source (λ = 1.5406 Å, 45 kV and 40 mA). Scanning angles for all samples were set in the 2θ range of 10–90° with a step size of 0.01313° and time per step of 120 s. Peaks were indexed according to the database established by Joint Committee on Powder Diffraction Standards (JCPDS).

Raman spectrum was obtained using a confocal Raman microscope (SENTERRA II, Bruker) equipped with an optical microscope, a CCD camera and an argon ion laser source. The laser provided 2 mW power at a wavelength of 532 nm for the exciting line. Integration time was 60 s, number of co-addition was 4 and slit aperture size was 50×1000 μ m.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was carried out on a Bruker VERTEX 70 spectrometer by using a DigiText DLATGS detector and platinum ATR. All spectra were recorded with a resolution of 2 cm⁻¹ for 200 scans in the spectral range between $\tilde{\nu}$ =400 and 4000 cm⁻¹. The background spectrum of air was measured as a single beam and used as reference.

X-ray photoelectron spectroscopy (XPS) analysis was performed on the Nexsa X-Ray Photoelectron Spectrometer (XPS) System (Thermo Fisher Scientific) utilizing a monochromatic Al K α source (1486.69 eV). High-resolution spectra were obtained at a pass energy of 40.0 eV, a step size of 0.1 eV, and a dwell time of 50 ms per step. The analysis spot size was 100×200 μ m. All spectra were calibrated to the C 1s peak (284.5 eV). XPS peaks were deconvoluted and curve-fitted on CasaXPS software.

Electrochemical Characterization

Electrochemical measurements were conducted on an Autolab PGSTAT101 potentiostat (Metrohm U.K. Ltd.) in a standard three-electrode cell at room temperature. A glass carbon electrode (GCE, diameter of 3 mm), Ag/AgCl in 3M KCl electrode and platinum foil were used as working, reference and counter electrode, respectively. 0.5 M H₂SO₄ solution was used as the electrolyte. All the potentials were calibrated to the reversible hydrogen electrode (RHE), according to Nernst equation $E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + 0.21 + 0.0592 \times \text{pH}$. The geometric area of GCE was 0.0707 cm², which was used to calculate the current density in the linear sweep voltammetry (LSV).

Modified working electrode was fabricated via the following procedure: 5 mg of as-prepared catalyst or commercial Pt/CB was dispersed in a mixture of 600 μ L of DI water, 300 μ L of ethanol and 100 μ L of 5 wt % Nafion solution. The mixture was ultrasonically stirred for at least 2 h to obtain a homogeneous suspension. Then 3 μ L of the suspension was taken by a microsyringe and drop-casted onto a clean GCE with an overall loading of 0.212 mg·cm⁻². The modified GCE was dried naturally in air. Prior to the LSV test, the electrochemical cell was saturated with argon for at least 30 min and the modified GCE was activated by applying a cyclic voltammetry (CV) method in the potential range of 0 to 0.5 V_{RHE} for 50 cycles at a scan rate of 200 mV·s⁻¹. The LSV scan potential was set in the range of

–0.4 to 0.1 V_{RHE} and the scan rate was 5 mV·s⁻¹. All polarization curves were presented without iR compensation.

Results and discussion

Effect of Solvent and Precursor Concentration

According to the classical nucleation and growth theory³⁶, in a homogeneous system, metal cations are first reduced to give a high supersaturation of monomers, which leads to a burst of nuclei. Competition between bulk energy and surface energy then drives either the dissolution of nuclei back to monomers or the growth of nuclei into larger sizes. Lastly, the Ostwald ripening occurs due to the minimization of the overall surface energy. However, graphene supports in the raw solution can adsorb the metal nuclei or nanoparticles to reduce the surface energy and hinder the monomer diffusion. Therefore, in the radiolytic synthesis, the final size and distribution of Pd NPs shall mainly be determined by the nucleation and growth.

From the expression of critical nucleus radius r_c , as detailed in Note S1, we see that r_c is dependent on the supersaturation S . A relatively large r_c is preferred to prevent nuclei from easily overcoming the energy barrier and growing into large-sized particles. This strategy has been applied to prepare even single atomic catalyst.³⁷ Upon gamma radiation, reducing species are generated from the solvent by high-energy photons to rapidly convert Pd ions into monomers. It is thus speculated that the generation rate of reducing species from the solvent and the metal precursor concentration play a critical role in triggering and controlling the nucleation and growth of Pd NPs.

We first compare the reducibility of two common solvents, H₂O and EG, in the radiolytic reduction of GO. 1 mg·mL⁻¹ of GO dispersed in H₂O-IPA (v/v=39/1) or EG are prepared by mechanical sonication and stirring, and subsequently irradiated under gamma rays for 6 h with a total dose of ~120 kGy. Figure 2 shows the ATR-FTIR and Raman spectra of pristine and irradiated GO. In Figure 2a, typical functional groups are observed for the pristine GO. When GO is irradiated in H₂O, these functional groups are substantially removed, indicating the efficient reduction. Whereas, GO irradiated in EG shows no major changes in these functional groups. Figure 2b presents their Raman spectra. Two distinct peaks appearing at 1345 and 1588 cm⁻¹ for all the GO samples are discerned, representing the D and G peaks, respectively. The D band stems from vibrational modes of carbon atoms around the edges and defects, manifesting the presence of structural disorder. The G band originates from the in-plane vibrational modes of sp²-hybridized carbon atoms in the graphene layer.^{38, 39} The band intensity ratio (I_D/I_G) is often used as a descriptor of the graphitization degree of carbon materials. There are two opposing effects that cause the change of I_D/I_G ratio of GO. Mechanical sonication and stirring break the graphene sheets into smaller pieces with more edges, resulting in a decrease in the average size of the in-plane sp² domains and thus an increase of I_D/I_G ratio. On the contrary, reduction of GO by irradiation remove the oxygen groups and sp³-hybridized carbon atoms turn into sp² carbon, leading to a decrease of I_D/I_G

ratio. Figure 2c shows that GO irradiated in H₂O has a higher I_D/I_G ratio (1.08) than pristine GO (0.92), whereas GO irradiated in EG has an I_D/I_G ratio (1.00) close to pristine GO. The increased I_D/I_G ratios of both irradiated GO can be attributed to the dominant effect of mechanical breakage of GO on the I_D/I_G ratio. This is confirmed by their SEM images in Figure S1, in which we can see flat and large-sized GO changes to fluffy sheets with more edges after radiation. Meanwhile, despite that GO irradiated in H₂O is significantly reduced, the mechanical fracture shall be more intense to compensate the restoration for GO in H₂O than GO in EG, which should be attributed to the different dispersity of GO in H₂O and EG. These results indicate that EG has a relatively moderate reducibility and is a more appropriate solvent than H₂O for preparing metal NPs by gamma radiation. Therefore EG is selected as the solvent throughout the remainder of this study.

Figure 2. ATR-FTIR spectra (a), Raman spectra (b), and I_D/I_G ratios of pristine GO, GO in H₂O, and GO in EG after gamma radiation.

Effect of metal precursor concentration on NP size is also roughly explored by irradiating 1 and 2 mM Pd(acac)₂ in EG containing 1 mg·mL⁻¹ of GO as support. No external surfactant is added. Figure S2 shows the representative SEM images of Pd/GO samples. According to the SEM principle, secondary electrons are the most common signals, which closely correlate to the sample conductivity.⁴⁰ The bright area is attributed to the formed Pd metal with high conductivity while the dark area should be the GO with poor conductivity. We can see the formation of micron-sized Pd aggregates when using 2 mM Pd(acac)₂ (Figure S2a). Despite lowering the concentration to 1 mM Pd(acac)₂ effectively reduces the aggregation, small amount of micron particles are still observed (Figure S2b). In light of this, the metal precursor concentration should be kept below 1 mM to avoid severe segregation when no surfactant is present.

Pd NPs on Different Supports

When support materials are present in the solution, the nucleation and growth is energetically favored at structural inhomogeneities, such as support edges and defective sites.⁴¹ Benefiting from the high conductivity, large surface area and flexible surface chemistry, graphene materials, either functionalized by oxidation or doped with heteroatom, are widely used supports.⁴²⁻⁴⁴ Nitrogen dopants in NG have been disclosed to stably anchor the metal NPs, even at atomic scale as M-N₄-C moieties.^{45, 46} It is thus interesting to investigate the effect of NG on controlling the size and dispersion during

radiolytic synthesis of metal NPs. Besides, electrostatic interaction between the support and precursor ions should be considered.^{47, 48} To this end, GO, rGO and G are utilized as comparison since the zeta potential of these supports varies from negative to positive.

Figure 3 shows the XRD patterns of four pristine supports and 0.25 mM Pd(acac)₂ and 1 mg·mL⁻¹ of support in EG. The nominal Pd loading is 2.6 wt % provided the support remain intact after radiation. For the GO support, the (001) peak at 2 theta of ~10° is still present while (002) peak at 2 theta of ~22° shifts to ~25° after gamma irradiation, indicating GO is slightly reduced and a small amount of functional groups are removed. Meanwhile, five characteristic peaks at 2 theta of 40, 46, 68, 82, and 86° are indexed to JCPDS card No. 87-0643, corresponding to (111), (200), (220), (311), and (222) crystal planes of metallic Pd. On the contrary, no obvious variations are observed for the rGO, G and NG supports before and after radiation, manifesting their high structural stability. In addition, relatively small diffraction peaks of Pd are detected for Pd/rGO, Pd/G and Pd/NG. The broad diffraction peak suggests small crystalline domains or amorphous nature of the Pd, as shown in Table S1 for the average crystallite sizes, which is expected since the radiation is performed at room temperature. Heat transfer resulted from the gamma radiation for 2 h is tested to be negligible.

Figure 3. XRD patterns of the pristine supports and corresponding Pd supported composites: (top left) Pd/GO and GO, (top right) Pd/rGO and rGO, (bottom left) Pd/G and G, and (bottom right) Pd/NG and NG.

XPS technique is used to acquire elemental and compositional information of the supported composites and pristine supports. Full survey XPS spectra in Figure S3 confirms their elemental compositions of C, O, N, and/or Pd. Figure 4 compares their high-resolution XPS spectra of the C 1s region. The deconvoluted peaks in different colors indicate the distinct oxygen functionalization and nitrogen doping. For instance, GO contains sp² hybridized C, C-O, C=O, O-C=O, and C-H. After radiation, C-H species is removed and C-O species of Pd/GO is dramatically reduced. rGO has much less O-containing groups relative to GO and no major difference is observed compared to Pd/rGO. Note that rGO is prepared by hydrazine reduction

according to the description of the supplier. During the reduction, hydrazine reacts with carbonyl groups to form hydrazone but barely reacts with hydroxyl or carboxyl groups.⁴⁹⁻⁵¹ rGO thus shall contain residual oxygen groups and incorporated nitrogen atoms. These nitrogen species exist as functional groups (amino and imine groups) mostly at the graphene edges instead of being randomly doped into the basal plane of graphene. G and NG contain mostly sp^2 hybridized C except the C–N peak in NG. Both of them also remain largely identical after being irradiated. Table S2 details the atomic and weight percentage of C, N, O, and Pd for the pristine supports and supported composites. It is confirmed that O content of GO is substantially reduced while rGO, G and NG remain mostly unchanged after radiation. However, the Pd content varies from 1.1 wt % for Pd/GO and Pd/rGO to 10.1 wt % for Pd/NG, as shown in Figure S4 in reference to the nominal value of 2.6 wt %. This unexpected result can be explained by the immobilization of Pd NPs on the outmost surface of support and the nature of XPS analysis. XPS only determines elemental compositions from the outmost surface up to a depth of several nanometers of the sample. It is rational to have higher Pd content on the surface than the nominal value that takes Pd and support as an integrity. Meanwhile, for Pd/GO and Pd/rGO, Pd(II) could be partially reduced and loaded on the supports, giving lower Pd loadings. It also demonstrates that N-containing groups (amino and imine groups) in rGO are less competitive than doped nitrogen species in anchoring the Pd NPs when comparing Pd/rGO and Pd/NG. In light of this, the O-containing groups on functionalized graphene should hold accountable because of the potential re-oxidation/dissolution of Pd by O-containing groups and/or adverse electrostatic interaction between the negatively charged support and Pd NPs.^{52, 53}

Figure 4. High-resolution XPS spectra of C 1s region for the pristine supports and corresponding Pd supported composites: (top left) Pd/GO and GO, (top right) Pd/rGO and rGO, (bottom left) Pd/G and G, and (bottom right) Pd/NG and NG.

To visually observe the size and distribution of Pd on NG support, TEM analysis of Pd/NG is conducted. Figure 5a shows a representative bright field TEM image of the Pd/NG. Uniform distribution of Pd NPs immobilized on the surface of NG is discerned. Based on a statistic count of particle size (>500 counts) and subsequent Gauss fit (Figure 5b), an ultrafine average particle size (APS) of 3.0 ± 0.6 nm is determined and a narrow particle size distribution (PSD) is confirmed. TEM images and the corresponding PSDs of Pd NPs on GO, rGO and G are presented in Figure S5. The larger APS than average crystallite size (Table S1) for each composite signifies the multicrystalline nature of all Pd NPs. In contrast to Pd/NG, Pd NPs are either sparsely anchored on GO and rGO with a relatively small quantity, or severely aggregated on G, conforming well to the elemental percentage by XPS analysis. These results indicate the superior role of NG to the other supports in size controlling and uniform loading of Pd NPs. Comparison of solvent, surfactant and APS in the radiolytic synthesis of Pd/NG in this study and results in the literature is detailed in Table S3 and plotted in Figure S6. We clearly see that the APS and PSD of Pd NPs on NG are superior to most of the other metal particles and among the best when no surfactant is employed, highlighting the merits of our synthetic method. Although H_2O has been prevalently used as the solvent, the ultrafine Pd NPs on Pd/NG demonstrate that EG can be more competitive in the control of size and dispersity of NPs. SEM images of pristine supports and the composites are shown in Figure S7. Severe fracture is again observed for GO after radiation, whereas no obvious variation is discerned for rGO, G and NG supports.

Figure 5. Representative bright field TEM image (a) and corresponding particle size distribution curve (b) of the Pd/NG based on statistical counts.

Raman spectra of the supports and supported composites are examined for further structural information. Figure 6 presents the Raman spectra and calculated I_D/I_G ratios before and after the radiation. The D and G bands are clearly shown for all the graphene-based materials. For the G and Pd/G, a strong 2D band is observed, indicating the small layer number of G. However, the other GO, rGO and NG show no appreciable 2D band, which suggests the stacking of graphene sheets with relatively large layer numbers.³⁹ The quality of commercial graphene-based materials has also been questioned

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previously.⁵⁴ Moreover, the I_D/I_G ratios largely remain consistent for the GO, rGO and NG supports, whereas GO exhibits a slight increase in I_D/I_G ratio after radiation, which agrees with the results in Figure 2b and 2c.

Figure 6. Raman spectra of the pristine supports and corresponding Pd supported composites (a), and comparison of the derived I_D/I_G ratios (b).

When 0.25 mM Pd(acac)₂ is fully reduced and loaded on 1 mg·mL⁻¹ of support in EG, a composite with a nominal Pd loading of 2.6 wt % is yielded. This metal loading is much lower than many commercial carbon supported noble metal catalysts with loadings of 10–40 wt %. HER has been demonstrated a highly responsive reaction for even atomic scale noble metal-based electrocatalysts.^{55, 56} Therefore, we choose the HER to probe the electrocatalytic activity of the as-prepared Pd supported composites in 0.5 M H₂SO₄. Figure 7a displays the LSV polarization curves with the four composite catalysts. As a common practice, the overpotentials at a current density of 10 mA·cm⁻² (η_{10}) are compared in Figure 7b. We can see that Pd/NG exhibits the smallest η_{10} of 199 mV, which is lower than Pd/GO (273 mV), Pd/rGO (358 mV) and Pd/G (218 mV). Based on the preceding structural characterizations, the highest HER activity of Pd/NG should be ascribed to the ultrafine Pd NP size and uniform size distribution, and potential metal-support interaction. Tafel analysis is further performed to provide mechanistic insight of the reaction pathway. The Tafel plots and Tafel slopes of fitted lines for the four composites are presented in Figure 7c and 7b, respectively. Tafel slopes of the composites fall in the range of 80–140 mV·dec⁻¹, suggesting that the initial Volmer step ($H_3O^+ + e^- + * \rightleftharpoons H^* + H_2O$, 120 mV·dec⁻¹) is the rate-determining step for the Pd-based catalysts.⁵⁷ The Volmer step involves hydrated proton adsorption and electron transfer. The more conductive G and NG thus facilitate the electron transfer for hydrogen adsorption and present smaller Tafel slopes than Pd/GO and Pd/rGO. These results again demonstrate the positive role of NG support in attaining an efficient heterostructured catalyst.

Figure 7. Polarization curves (a), overpotentials at 10 mA·cm⁻² and Tafel slopes (b), and Tafel plots (c) of Pd supported on four graphene-based supports in argon-saturated 0.5 M H₂SO₄.

Pd/NG with Different Loadings

Reducing the noble metal usage while maintaining its catalytic performance is important for developing cost-effective catalysts. To explore the size-dependent activity of Pd NPs for HER, we irradiated 1 mg·mL⁻¹ of NG in EG solutions with different Pd concentrations of 0.125, 0.25, 0.375, and 0.5 mM. The nominal Pd loadings of Pd/NG are 1.3, 2.6, 3.9, and 5.2 wt %. The corresponding composites are designated as x-Pd/NG, x is the metal loading.

Figure 8a shows the XRD patterns of the pristine NG and four Pd/NG composites. Apart from the characteristic peaks of NG, new diffraction peaks assigned to Pd phase are observed for all the Pd/NG. With increasing Pd loadings, intensity of these peaks strengthens and peak shape narrows down. Figure S8 displays the bright-field TEM images of Pd/NG of different loadings and their corresponding PSDs. With increasing Pd loadings comes also larger crystallite size (Table S1), APS and severer NP aggregation, underscoring the importance in the optimization of Pd content on Pd/NG. SEM images of the four composites are displayed in Figure S9, in which similar surface morphology featuring fluffy graphene sheets is confirmed for all samples. In addition, Raman spectra of the pristine NG and four Pd/NG composites are presented in Figure 8b. Their I_D/I_G ratios in Figure 8c are found to be almost unchanged, indicating the high structural stability of NG during dispersion and radiation.

Figure 8. XRD patterns (a) and Raman spectra (b) of the pristine NG and Pd/NG with four Pd loadings of 1.3, 2.6, 3.9, and 5.2 wt %, and comparison of the derived I_D/I_G ratios (c).

HER activities of the pristine NG and four Pd/NG composites are further tested. Figure 9a presents the LSV polarization curves in argon-saturated 0.5 M H₂SO₄. The η_{10} data is taken and plotted in Figure 9b. Compared to NG with a large η_{10} , 1.3-Pd/NG and 2.6-Pd/NG yield significantly reduced η_{10} of 286 and 199 mV, respectively, which conforms to the intuition that more metal endows with higher activity. Surprisingly, when further increasing the Pd loading, no substantial variation of the η_{10} is observed for 3.9-Pd/NG (218 mV) and 5.2-Pd/NG (218 mV).

Given that only surface and/or subsurface Pd atoms participate in the HER catalysis, this counter-intuitive observation should be attributed to the similar content of catalytically active Pd atoms for 2.6-Pd/NG, 3.9-Pd/NG and 5.2-Pd/NG. According to the Tafel plots in Figure 9c, the Tafel slopes are presented in Figure 9b. We can see that the four Pd/NG catalysts have similar Tafel slopes in the range of 100–140 mV·dec⁻¹, signifying that the Volmer step is the rate-determining step for all of the catalysts.

Figure 9. Polarization curves (a), overpotentials at 10 mA·cm⁻² and Tafel slopes (b), and Tafel plots (c) of NG and Pd/NG with four Pd loadings in argon-saturated 0.5 M H₂SO₄.

To deepen the understanding of the role of NG in stabilizing Pd NPs, we analyze the chemical speciation and composition of Pd and N elements of Pd/NG using XPS. Full survey XPS spectra in Figure S10 corroborates the elemental composition. Figure 10a shows the XPS spectra of Pd 3d region for four Pd/NG composites. Through proper deconvolution and fitting, the Pd 3d spectra can be resolved into two Pd species of dominant zero-valence Pd₀ and minor slightly oxidized Pd_{ox}. Each species consists of two spin-orbit doublets, that is, Pd 3d_{5/2} and Pd 3d_{3/2}. Under identical testing conditions, it is found that the XPS peak intensity increases progressively with the increase of Pd loading. The peaks at binding energies of 335.6 and 340.9 eV belong to Pd₀ 3d_{5/2} and Pd₀ 3d_{3/2}, respectively. Shift of the binding energy is not observed for different composites, indicating the similar chemical environment of Pd.

XPS spectra of N 1s region for NG and four Pd/NG composites are illustrated in Figure 10b. The N 1s spectra are deciphered into three species, including pyridinic, pyrrolic and graphitic nitrogen. Pyridinic and pyrrolic nitrogen refers to the substituted nitrogen that bonds with two carbon atoms, but forms a six-membered and five-membered ring, respectively. Graphitic nitrogen is formed by direct substitution of sp² carbon. For the NG, peaks at binding energies of 398.2, 400.4 and 402.7 eV are assigned to the pyridinic, pyrrolic and graphitic nitrogen, respectively. With the increase of Pd loading, all the nitrogen species show a gradual shift of their binding energies, especially for the graphitic nitrogen. The specific binding energy is detailed in Table S4. The change of binding energy readily signifies the occurrence of electron transfer. After Pd NPs are loaded on the NG, the electrons are donated from electron-rich Pd to electron-deficient N. This electron transfer is believed to underlie the superior anchoring effect of Pd NPs on NG, emphasizing the critical role of nitrogen dopants.⁵⁸ Table S5 lists the atomic and weight percentage of C, N, O, and Pd of NG and Pd/NG. The nitrogen content of NG is found to be ~5 wt %, in line with the product specification from the supplier. Accordingly, we believe that the nitrogen content accounts for the upper limit of Pd loading. Once Pd loading exceeds this

threshold, Pd NPs would tend to grow into larger sizes instead of being stabilized by available nitrogen dopants. Besides, the Pd weight percentage is again found to be dramatically higher than the nominal values. The commercial NG is already disclosed by Raman (Figure 6a and 8b) to be rather graphite-like than single or few layer graphene-like. This result also highlights the potential of improving support quality to enhance the output of the supported catalysts.

Figure 10. High-resolution XPS spectra of Pd 3d (a) and N 1s (b) regions for the pristine NG and Pd/NG with four Pd loadings of 1.3, 2.6, 3.9, and 5.2 wt %.

Pt/NG and commercial Pt/CB

To explore the versatility of this synthetic route, we further extend to the preparation of 2.6 wt % Pt/NG by substituting Pd with Pt and compare the HER activity to commercial 10 wt % Pt/CB. Figure 11a shows the XRD patterns of pristine NG, Pt/NG and Pt/CB. Apart from the diffraction peaks of graphitic carbon, five characteristic peaks, indexed to cubic Pt phase with JCPDS card No. 89-7382, are observed for Pt/NG and Pt/CB. Comparison of the height and broadness of Pt peaks indicates a larger crystal size for Pt/CB than Pt/NG. Figure 11b presents the LSV polarization curves in argon-saturated 0.5 M H₂SO₄ together with the η_{10} data in the inset. We can see that Pt/NG yields an even smaller η_{10} of 39 mV than the commercial Pt/CB (45 mV). Based on earlier results, we attribute the superior performance of Pt/NG to the smaller Pt NP size and favorable metal-support interaction between Pt NPs and NG. Tafel plots in Figure 11c give a Tafel slope of 31 and 28 mV·dec⁻¹ for Pt/CB and Pt/NG, indicating that the HER rate is limited by the Tafel step ($2H^* \rightleftharpoons H_2 + 2^*$, 30 mV·dec⁻¹), which accords well with the known fact that hydrogen desorption is relatively slow on Pt.

Figure 11. XRD patterns of pristine NG, Pt/NG and Pt/CB (a). Polarization curves (b) and overpotentials at 10 mA·cm⁻² (inset), and Tafel plots (c) of Pd/NG and Pt/CB in argon-saturated 0.5 M H₂SO₄.

Conclusions

Utilizing in-situ generated reducing species from solvent by gamma radiation, ultrafine 3.0 nm Pd NPs with a narrow size distribution are facilely prepared and loaded on graphene-based supports in the absence of surfactants and harsh reaction conditions. Guided by classical nucleation and growth mechanism, we clarify EG is a more suitable solvent than water. Control experiments reveal that NG outperforms three other graphene-based supports in controlling the NP size and distribution, and Pd/NG exhibits the highest HER activity. The HER activity of Pd/NG is found to reach a plateau once the Pd loading increases to 2.6 wt %. The nitrogen dopants are revealed to play a contributive role in anchoring and dispersing the Pd NPs by electron transfer between Pd and doped N atoms. Further extending the synthesis to Pt metal gives Pt/NG that is even more active than the commercial Pt catalyst toward HER. This study provides useful guideline for radiation chemists to prepare advanced nanostructures.

Conflicts of interest

There are no conflicts to declare.

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