Polymer-mediated synthesis of a nitrogen-doped carbon aerogel with highly dispersed Pt nanoparticles for enhanced electrocatalytic activity

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A simple chemical process for the direct synthesis of a nitrogen (N)-doped carbon aerogel (NCA) with highly dispersed Pt nanoparticles via a poly(ethyleneimine) (PEI)-assisted strategy is described. A resorcinol-formaldehyde (RF) gel was treated with water soluble cationic PEI, which mainly functions as an anchoring site for metal ions. The functionalized PEI chains on the surface of the RF gel resulted in the unique formation of chemical complexes, with PtCl₂⁻ anchored to the RF gel, and subsequent homogeneous metal nanoparticle growth. The abundant amino groups containing PEI grafted to the RF gel also allowed the nitrogen atoms to be incorporated into the carbon framework, which can directly be converted into a NCA. The spherical Pt nanoparticles in the resulting material (Pt/NCA) were highly dispersed on the surface of the NCA without any evidence of agglomeration, even after a thermal annealing at 900 °C. Compared with a Pt/CA synthesized by a conventional reduction method, the Pt/NCA showed enhanced electrochemical performance with a high electrochemically active surface area (191.1 cm² g⁻¹) and electrocatalytic activity (V₁₀₀₀ = 0.95 V vs. RHE) with respect to oxygen reduction. The superior electrocatalytic activities of the Pt/NCA can be attributed to the synergistic effect of the highly dispersed Pt nanoparticles and the N-doped carbon supports that were prepared using the PEI-assisted strategy. The findings reported herein suggest that the use of PEI can be effectively extended to broad applications that require the homogeneous deposition of metal nanoparticles.

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1. Introduction

Nanostructured synthetic carbons such as carbon aerogels (CA) are regarded as promising candidates for use in gas adsorbers, energy storage devices and catalyst supports due to their high surface area, well-developed pore structure, high electronic conductivity, as well as exhibiting rich or easily adjustable surface chemistry [1–3]. It is well known that the resorcinol-formaldehyde (RF) method is a simple and reproducible method for the synthesis of CAs with good control of its textural properties under appropriate experimental conditions including gelation temperature, pH, reaction time, and carbonization process [4–6]. Nevertheless, most CAs normally lack desirable properties owing to their chemically inert nature, which consequently hampers their use in catalysis applications.

The deposition of noble metal nanoparticles (NPs), especially Pt, onto a carbon surface, to enhance the catalytic ability of carbon materials is widely used in various areas [7,8]. Although Ptcarbon composites can be prepared by a variety of procedures, most of the currently used procedures are generally confined to the post-synthetic deposition of metal NPs on a supporting material [9–11]. Moreover, the inert nature and intrinsic hydrophobicity of the carbon surface acts as an obstacle for the impregnation of Pt NPs, resulting in undesirable loss and the uncontrollable growth of Pt NPs [10,12–14]. It should be noted that extensive modification of the carbon surface is typically needed to introduce nucleation sites for the deposition of Pt NPs on the carbon surface, which is normally accompanied by a detrimental effect on surface properties as well as being a time consuming process [14–16]. In this sense, finding a facile and mild route for the synthesis of
carbon with highly dispersed Pt NPs continues to be a challenging issue.

Polyethyleneimine (PEI), a hydrophilic cationic polymer, is widely used as a chelating agent due to the fact that it contains a large number of amine groups [17,18]. These functional groups enable PEI not only to be adsorbed on the surface of supporting materials, which can introduce highly dense and homogeneous active sites for anchoring anionic metal ion precursors over the entire surface of the support, but also to serve as electron donors for the reduction of metal ions and templates for the subsequent growth of metal NPs [19,20]. Furthermore, PEI-encapsulated metal NPs can improve their stability via steric hindrance and electrostatic repulsion, which could effectively contribute to the suppression of metal aggregate formation at high temperature during the conversion of PEI into carbon material [17,18,21]. More importantly, since PEI grafted onto a carbon surface could serve as a nitrogen source, the N-doping would be achieved by the straightforward incorporation of nitrogen atoms into the carbon framework through interactions between —NH— groups and carbon atoms during the carbonization process [14,22,23]. The presence of N species could enhance the catalytic properties including the oxygen reduction reaction (ORR) and facilitate the high dispersion and immobilization of metal NPs on the carbon support by metal-nitrogen interactions [15]. Hence, after comprehensively considering the advantages described above, we fabricated Pt/N-doped carbon aerogel (Pt/NCA) composites as high performance electrocatalysts by using the RF-gel as a carbon source. Our concept efficiently utilizes the combinative merits of stabilized metal particle growth and nitrogen incorporation simultaneously via “PEI-mediated deposition”.

The findings reported herein demonstrate the use of PEI-mediated deposition is a facile and integrated strategy for the synthesis of N-doped carbon aerogels with highly dispersed Pt NPs. The as-synthesized Pt/NCA composite was employed as an electrocatalyst for the oxygen reduction reaction (ORR). We used the PEI-mediated deposition method to address the following questions: (1) Can a PEI-modified RF-gel be directly converted into an NCA by the pyrolysis process? (2) What is the role of the PEI in the deposition of Pt NPs and the formation of NCA? (3) Does the Pt/NCA composite exhibit high electrochemical performance as an electrocatalyst?

2. Experimental

2.1. Preparation of polyethyleneimine-modified resorcinol-formaldehyde gel (PEI-RF gel)

The resorcinol-formaldehyde (RF) gel was synthesized following a previously reported procedure [6]. An RF-gel was first prepared by the polycondensation of resorcinol (C₉H₈O₂, Sigma–Aldrich) with formaldehyde (CH₂O, Sigma–Aldrich) in aqueous solution. In this preparation, sodium carbonate (Aldrich, a basic catalyst) was mixed with the resorcinol and deionized water to accelerate dehydration of resorcinol. After stirring the solution for a few minutes, formaldehyde was slowly added to the solution to form an RF (resorcinol-formaldehyde) solution. The molar ratio of resorcinol with respect to formaldehyde was fixed at 1:2 (R/F = 1/2). The R/C (resorcinol/catalyst) ratio was fixed at 500. After stirring the RF solution, it was allowed to cure in a vial at 80 °C for 2 days to form an RF wet gel. Solvent exchange was performed with acetone (Samchun) at 50 °C for one day. Ambient drying was then done at room temperature and 50 °C for one day to give the RF-gel. For the PEI modification of the RF-gel, the as-synthesized RF-gel (0.5 g) was first dispersed in deionized water (200 mL) by sonication for 30 min, and then transferred to a three-necked round-bottomed flask. 0.05 g of PEI (Sigma–Aldrich) was added to the above solution and the resulting suspension was stirred at 60 °C for 12 h. After cooling to room temperature, the resulting dispersion was filtered and washed several times to remove excess PEI.

2.2. Preparation of Pt/N-doped carbon aerogel (Pt/NCA)

For the formation of PEI-RF gel and PtCl₄²⁻ complexes, the as-synthesized PEI-RF gel (0.5 g) was re-dispersed in water (200 mL) by sonication for 30 min. An appropriate amount of a H₂PtCl₆·6H₂O (Sigma–Aldrich) dissolved aqueous solution (50 mL g⁻¹) was added to the PEI-RF gel dispersed solution to give a nominal Pt content of 30 wt% in the final material. The mixture was stirred at room temperature for 24 h. After isolating the sample on a filter and washing with deionized water, the sample was heated at 900 °C for 2 h under a nitrogen atmosphere. The as-obtained catalyst is denoted herein as Pt/NCA.

![Fig. 1. Schematic illustration of the fabrication process for the Pt/NCA composite.](image-url)
2.3. Preparation of Pt/Carbon aerogel (Pt/CA)

RF-gel obtained from the above process was subjected to pyrolysis at 900 °C for 2 h under a nitrogen atmosphere to produce the carbon aerogel (CA). CA-supported Pt catalysts were prepared by the conventional impregnation method. The proper amount of H₂PtCl₆·6H₂O aqueous solution (50 mL g⁻¹) was added to CA (0.5 g) in deionized water (200 mL) to give a nominal Pt content of 30 wt% in the final materials. The solution was vigorously stirred for 1 h and then sonicated for 1 h. And then, 30 mL of 0.1 M sodium borohydride (Sigma–Aldrich) aqueous solution was added to the solution, followed by stirring for 12 h in order to reduce the Pt ion. The dispersion was filtered and dried in air at room temperature for 24 h. Pt loading was achieved for the supported CA materials, namely Pt/CA.

2.4. Characterization

The surface morphology and composition of the samples were examined by scanning electron microscopy (SEM, Carl Zeiss, SUPRA 55VP), transmission electron microscopy (TEM, JEOL, JEM-3010), and energy dispersive spectrometer (EDS, Bruker, XFlash5030 detector). X-ray photoelectron spectroscopy (XPS, Kratos, Axis-HSi) and X-ray diffraction (XRD, Rigaku, D/max-2200) were used to examine the composite structure and the surface composition. The amount of platinum loaded was determined by inductively coupled plasma with atomic emission spectrometry (ICP-AES, Shimadzu, JP/IPS-7500). BET surface area and N₂ adsorption–desorption isotherm were measured with an ASAP 2010 instrument (Micromeritics).

2.5. Electrochemical measurements

Electrochemical characterization was performed at room temperature in a single compartment glass cell with a standard three-electrode configuration using a rotating disc electrode (RDE, Princeton Applied Research, 616RDE). An Ag/AgCl electrode and a platinum mesh were used as a reference and a counter electrode, respectively. A catalyst loaded glassy carbon electrode with a diameter of 5 mm was used as the working electrode. In this study all potentials are with reference to the reversible hydrogen electrode (RHE). Homogeneous catalysts ink was prepared by dispersing a sample of the synthesized catalyst (10 mg) in water (20.0 μL), 5% Nafion (57.2 μL), and isopropyl alcohol (0.8 mL) with repeated stirring and sonication for at least 30 min. Finally, the catalyst ink (7.0 μL) was transferred to a polished glassy carbon electrode and allowed to dry, resulting in the formation of a catalyst layer. Cyclic voltammetry experiments were carried out repeatedly between 0.0 and 1.2 V (vs. RHE) using a potentiostat (Iviumstat, Ivium) in a N₂ saturated 0.1 M HClO₄ aqueous solution at a scan rate of 50 mV/s. The polarization curves were obtained in the potential range of 0.2–1.2 V (vs. RHE) with scanning rate 5 mV/s in O₂-saturated 0.1 M HClO₄ aqueous solution at a rotation rate of 1600 rpm. The cycle stability and methanol crossover effect were evaluated by using a chronoamperometric method at 0.7 V (vs. RHE) in an O₂-saturated 0.1 M HClO₄ solution at a rotation rate of 1600 rpm. For methanol oxidation reaction, 0.5 M CH₃OH was added to the electrolyte.

3. Results and discussion

A schematic diagram for the synthesis of NCA with highly dispersed Pt NPs using the PEI-assisted strategy is shown in Fig. 1. The suspension of an RF-gel was easily achieved owing to easy ionization of the hydroxymethyl and hydroxyl groups present on its surface [24]. Typically, their functional groups can covalently be linked to the water-soluble PEI via the formation of amide bonds [17,18]. The hydrophilic functionalization of PEI on the surface of the RF-gel induces electrostatic and steric stabilization, resulting in a higher level of dispersion of the RF-gels in the solution [17,25–27].

![Fig. 2. SEM images and EDS atomic analysis results of (a) PEI-coated RF-gel and (b) Pt/NCA.](image)}
Furthermore, the water-soluble polymer chains can effectively introduce highly dense and homogeneous functional sites for the adsorption of metal precursor ions within the interconnected gel structures [28]. As the PEI-modified RF-gel suspension was mixed with the negatively charged Pt precursors in the solution, the large amount of amino groups from the PEI form stable complexes by combining with PtCl₆²⁻ ions via electrostatic attraction. The PEI chains that are grafted on the surface serve as both a template for Pt NP growth without agglomeration and a source of electrons for the reduction of metal ions. The presence of PEI reduces the nucleation energy barrier, critical nucleus size, and interfacial energy, which consequently contributes to the narrow size distribution and high dispersion of Pt NPs on the surface of the RF-gel [17,25–27]. In addition, a large amount of radicals can be created from the amino groups, which allows the electron transfer from the radicals of PEI to the Pt ions during the heat treatment, followed by the formation of Pt NPs [29]. More importantly, the simultaneous carbonization of both the PEI and RF-gel leads to the formation of the NCA by the in-situ direct-doping route via the rearrangement of nitrogen and carbon atoms at high temperatures. As a result, highly dispersed Pt/NCA composites with enhanced catalytic properties can be easily produced using the PEI-assisted strategy.

Fig. 3. TEM images of as-synthesized samples. (a) CA, (b) NCA, (c and d) Pt/CA, and (d and e) Pt/NCA.
To confirm the presence of the amino groups on the surface of the RF-gels after the PEI modification and its successful conversion into the N-doped carbon (NCA) even after the Pt loading, scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) were employed, as shown in Fig. 2. Fig. 2(a) proves that the large amount of nitrogen species within amino groups induced from PEI chains was homogeneously grafted onto the surface of RF-gels, which could give rise to sequential complexation between RF-gels and PtCl₆²⁻ ions. Furthermore, after the thermal annealing treatment of the PEI-modified RF-gels/PtCl₆²⁻ complex, nitrogen and Pt components were uniformly distributed on the entire surface of carbon aerogel, as shown in Fig. 2(b). From the above results, it was demonstrated that the RF-gels were successfully functionalized with nitrogen species by introducing the PEI chains. In addition, the PEI could play an important role in both the formation of nitrogen-doped carbon material and the growth of highly dispersed Pt NPs.

The overall morphologies of the as-synthesized materials after heat treatment were primarily studied by transmission electron microscopy (TEM) as shown in Fig. 3. The morphology of the as-synthesized CA (without PEI functionalization) showed the typical features of an aerogel with an interconnected mesoporous structure (Fig. 3(a)) [6]. The formation of pores (white dots) for the CA and the results of HR-TEM are the evidence. In the case of the NCA, it can be seen easily that the relatively larger pores had disappeared, and thereby only the relatively small pores were produced. These changes may be attributed to the PEI coating layer by blocking the developed pores. Fig. 3(c–d) and 3(e–f) show the features of the dispersed Pt NPs on the CA and the NCA, respectively. The Pt NPs appear to form larger particles by agglomeration at certain locations in the case of the Pt/CA, while the Pt NPs for the Pt/NCA are highly dispersed across the entire surface of the NCA. Due to the chemically inert nature of carbon materials, the surface of the CA normally lacks desirable nucleation sites to facilitate a high dispersion of Pt NPs, which consequently results in a broad size distribution with aggregation of the Pt NPs for the Pt/CA. In contrast, the fact that no obvious Pt NPs agglomeration for the Pt/NCA is seen clearly demonstrates that the Pt NPs were electrostatically stabilized by the effect of PEI encapsulation during the heating process. The average sizes of the Pt NPs for Pt/CA and Pt/NCA were estimated to be 4.7 nm and 3.5 nm, respectively. It should be noted that the ICP analyses confirmed that the Pt contents for the Pt/CA and Pt/NCA were 29.1 and 29.7 wt%, respectively, which are in good agreement with the expected from the nominal composition. Based on the above results, it is confirmed that the presence of PEI facilitates uniform active sites for the growth of metal NPs, thereby leading to a higher dispersion and smaller size of Pt NPs for Pt/NCA than those for Pt/CA.

The crystalline properties of the as-prepared samples were investigated for basal characterization by using XRD spectroscopy as shown in Fig. 4(a). For both the CA and the NCA, no pronounced peaks for the crystalline carbon structure were observed, indicating that these carbon materials consist typically of an amorphous phase. The XRD patterns for all of the formed Pt NPs were identical, and the three major diffraction lines near 2θ = 40°, 46° and 67° can be indexed to the characteristic reflections of face-centered cubic crystalline Pt (JCPDS, Card No. 04-080002), namely, (1 1 1), (2 0 0), and (2 2 0) [28]. The average sizes of Pt NPs were calculated from the full width at half-maximum (FWHM) of the Pt (2 2 0) peak using the Scherrer formula and were found to be 4.6 and 3.6 nm for Pt/CA and Pt/NCA, respectively. These results are well integrated with the results of HR-TEM analyses.

The pore characteristics of the resulting electrocatalysts were examined by nitrogen adsorption-desorption isotherms and the results are shown in Fig. 4(b) and (c). The results show that the isotherms for the CA, NCA, Pt/CA and the Pt/NCA exhibited a type-IV isotherm with the BET surface areas of 826 m² g⁻¹, 430 m² g⁻¹, 756 m² g⁻¹ and 363 m² g⁻¹, respectively [30]. Typically, the deposition of metal NPs on porous carbon materials leads to a reduction in total surface area by means of the pore filling, which is in good agreement with the decrease of surface areas for the Pt/CA and Pt/NCA compared to those for CA and NCA. Moreover, it was observed that the surface areas for NCA and Pt/NCA are smaller than those for the CA and Pt/CA. This is because the coated PEI chains on the RF gel can partially clog the developed pores thus reducing the pore sizes of the RF gel before the carbonization process, which also results in a reduction of the overall surface area and volume determined via adsorbed N₂ molecules. In particular, the mesoporous ratios for the CA, NCA, Pt/CA, and Pt/NCA in the total surface area were estimated to be 44.3%, 9.3%, 31.0% and
of the supports [13,25–27]. Furthermore, the heat treatment of the PEI-RF gel at 900 °C under a nitrogen atmosphere could lead to direct Pt-N interactions, which can be attributed to the role of nitrogen functional groups as electron donors for the reduction of metal precursor ions and as templates for the growth of Pt NPs. As expected, the Pt 4f spectrum of the Pt/NCA clearly indicated that the Pt particles were successfully reduced from Pt ions as shown in Fig. 5(b). Moreover, it was confirmed that the nitrogen functional groups were incorporated into the carbon structure as shown in Fig. 5(b). The high-resolution N 1s spectrum indicated the presence of three categories of nitrogen bonding status, which are namely pyridinic N (398.5 eV), pyrrolic N (400.6 eV), and quaternary N (402.1 eV) [32,33]. These groups have been shown to serve as catalytically active sites for oxygen reduction [34]. In addition, the C 1s spectrum can be well-fitted into three individual component peaks, representing C–C bonds at 284.5 eV, C–O and/or C–N bonds at 285.7 eV, and C–N or/and C–N bonds at around 288.3 eV, respectively [15,33]. These results imply that the PEI-modified RF-gels can readily be converted into NCA, which is a key factor for ensuring the high distribution of Pt NPs by metal-nitrogen interaction and the enhanced electrocatalytic activity toward ORR.

To evaluate the influence of the coexistence of N-doping and highly dispersed Pt NPs and their expected synergistic effects as an electrocatalyst, the electrochemical active surface areas (EASA) of the as-synthesized samples were examined by cyclic voltammetry (CV) in a N2-saturated 0.1 M HClO4 aqueous solution at 50 mV s−1 in a potential window from 0.0 to 1.2 V vs. reversible hydrogen electrode (RHE), as shown in Fig. 6(a). The CV curves for the CA and NCA show a quasi-rectangular shape, attributable to electrical double-layer capacitance of the NCA compared to that of the CA is due to the fact that this material has a lower surface area than that for the CA. In contrast, well-defined CV curves, including the expected behaviors of the Pt electrocatalysts in acidic media, were obtained for Pt/CA and Pt/NCA. Typically, the cathodic and anodic peaks located between 0.0 and 0.3 V are assigned to the adsorption and desorption of the protons on the Pt surface, respectively. The EASA was calculated by integrating the area of H-adsorption [35]. The calculated EASA for the Pt/CA was 87.4 cm2 g−1, 54.3% smaller than that of Pt/NCA (191.1 cm2 g−1).

Linear sweep voltammetry (LSV) was also performed to investigate the oxygen reduction reaction (ORR) polarization in an O2-saturated 0.1 M HClO4 aqueous solution using a rotating disk electrode (RDE) at 1600 rpm, as shown in Fig. 6(b). It was clearly observed that the NCA exhibited a significantly enhanced ORR activity compared to the carbon aerogel CA. The onset potential (Vonset) for the NCA was 0.48 V, which is 0.09 V higher than that for the CA (0.39 V), implying that the nitrogen-doping improves the catalytic activity toward the oxygen reduction reaction [34,36]. Compared with a Pt/CA catalyst, the enhanced catalytic activity of the Pt/NCA produced via the PEI-assisted strategy is even more strongly highlighted. The half-wave potential of the Pt/CA and Pt/NCA were 0.77 and 0.81 V, respectively. The Vonset of Pt/CA (0.91 V) was ~0.04 V more negative than that of the Pt/NCA (0.95 V), which can mainly be ascribed to the severe agglomeration of Pt NPs, as evidenced by the XRD and TEM analyses. The enhancement of catalytic activity for the Pt/NCA is in good agreement with previous reports [37,38]. Zhang et al. reported that Pt on N-doped carbon black supports (Pt/NCB) prepared by NH3-treatment of pre-formed carbon support and impregnation method exhibited higher ORR electrocatalysis than undoped carbon-supported Pt catalysts (Pt/CB) [37]. The ORR half-wave potential of Pt/NCB was ~0.025 V more positive than that of Pt/ICB catalyst. Also, Shanmugam et al. developed Pt on N-doped carbon nanocapsule supports (Pt/NCNC) which exhibited enhanced ORR activity [38]. The half-wave potential of Pt/NCNC was 0.81 V, which is slightly higher than that of Pt/NCB (0.77 V). This result supports the hypothesis that the PEI-RF gel can provide a higher performance for the ORR due to the presence of nitrogen functional groups. The C 1s peak of the Pt/NCA catalyst in the XPS analysis shows two peaks at 284.5 eV and 286.1 eV, corresponding to the C=C and C–O bonds, respectively. These peaks are consistent with the presence of nitrogen functionalities in the catalyst, which can improve the ORR activity.
showed ~0.03 V more positive potential compared to Pt on carbon black support. They concluded that the enhancement in catalytic activity is attributed to the synergetic effects of the nitrogen doping in carbon supports and the uniform dispersion of Pt NPs. However, their preparation methods for Pt/N-doped carbon composites involved multiple steps, which were more complicated than those used in our method. To evaluate the practical viability for Pt-based electrocatalyst, the cyclic stability of the Pt/NCA catalyst was examined by continuous chronoamperometric measurements at 0.7 V (vs. RHE) in an O$_2$-saturated 0.1 M HClO$_4$ solution at a rotation rate of 1600 rpm. As shown in Fig. 6(c), although the current densities for both the electrodes initially decreased with time, the Pt/NCA showed higher stability (holds ~54% current density) than that of Pt/CA (holds ~31% current density) with a relatively slow decay rate in its activity during a 3000 s testing period. Moreover, the tolerance for methanol crossover was also examined, which could diminish cathodic performance through the depolarizing effect and is a crucial parameter for electrocatalysts in direct methanol fuel cells (DMFC). As shown in Fig. 6(d), it can be seen that the current densities of both catalysts immediately dropped after the injection of methanol, but the Pt/NCA exhibited higher current density, maintaining 57% of their initial current density, in respect to the Pt/CA (23%).

Based on the above results, it can be concluded that the presence of PEI chains on the surface of the RF gel provides abundant active sites for the facile formation of highly dispersed Pt NPs and induces the ready formation of N-doped carbon materials during the heating process, preventing the agglomeration of Pt NPs. The high degree of dispersion of Pt NPs is a key factor for ensuring the enhanced catalytic activity of our materials. Moreover, the substituted nitrogen atoms, especially pyridinic-N atoms, exhibit catalytic activity toward ORR, which can provide another contribution to the high performance and durability for ORR even in the presence of methanol in the electrolyte [39]. Therefore, these findings indicate that Pt/NCA is a promising material for applications in fuel cells and other energy-related devices.

4. Conclusions

Highly distributed Pt NPs were successfully deposited on an RF gel derived carbon support (Pt/NCA) using a PEI-mediated strategy. It was found that the PEI adsorbed on the RF gel not only provided active sites for the deposition of Pt ions but also served as nitrogen sources for N-doping, which prevented the classical agglomeration of Pt NPs during the thermal annealing process, consequently leading to the high EASA. Furthermore, despite the fact that the NCA has a smaller surface area than that for the CA due to the pore clogging by PEI functionalization, the NCA exhibited a higher performance toward the ORR than that for the CA by the doping of nitrogen atoms into carbon support materials. As a result, these superior physico–chemical properties of Pt/NCA compared to Pt/CA led to remarkably enhanced electrocatalytic performance toward the ORR. The findings indicate that the PEI can effectively be used in broad applications for the synthesis of homogeneous deposition of metal NPs. Further explorations regarding the application of PEI toward new synthetic approaches are currently underway.
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