One-pot synthesis of graphene/carbon nanospheres/graphene sandwich supported Pt$_3$Ni nanoparticles with enhanced electrocatalytic activity in methanol oxidation

Wenhan Niu a, Ligui Lia, Xiaojun Liu a, Weijia Zhou a, Wei Li a, Jia Lu a, Shaowei Chen a,b,*

a New Energy Research Institute, College of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, China
b Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, CA 95064, United States

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Abstract

A facile method was demonstrated for the preparation of Pt$_3$Ni alloy nanoparticles supported on a sandwich-like graphene sheets/carbon nanospheres/graphene sheets substrate (Pt$_3$Ni–C/rGO) through a one-pot solvothermal process in N,N-dimethylformamide without the addition of reducing agents and surfactants. Transmission electron microscopic measurements showed that carbon nanospheres were homogeneously dispersed in the matrix of exfoliated graphene sheets, and Pt$_3$Ni nanoparticles were distributed on the graphene surfaces without apparent agglomeration, where the average core size was estimated to be 12.6 ± 2.4 nm. X-ray photoelectron spectroscopic studies demonstrated that electron transfer likely occurred from the Pt$_3$Ni alloy nanoparticles to the graphene sheets. Electrochemical measurements showed that the mass activity of the Pt$_3$Ni–C/rGO catalysts in methanol oxidation was 1.7-times higher than that of Pt$_3$Ni nanoparticles supported on reduced graphene oxide alone (Pt$_3$Ni/rGO), and 1.3-times higher than that of commercial Pt/C (20 wt%). Additionally, CO tolerance and durability were also remarkably enhanced. These superior electrocatalytic activities were attributed to the following major factors: (i) the insertion of carbon nanospheres into the graphene matrix prevented restacking/refolding of the graphene sheets, leading to an increasing number of accessible active sites as well as transport channels for mass and charges; and (ii) the synergetic effect between Pt$_3$Ni nanoparticles and rGO weakened the bonding interactions with reactant species, as manifested by the enhanced kinetics of methanol oxidation and CO oxidative desorption.

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Introduction

Direct methanol fuel cells (DMFCs) have been attracting considerable attention for their potential applications in vehicle power supplies and portable electronic devices. Platinum has been used extensively as anode materials in DMFCs due to its high electrocatalytic activity for direct methanol oxidation [1–4]. However, the limited reserves and high costs of platinum have been the main bottlenecks that hamper the widespread commercialization of DMFCs [5–9]. Preparation Pt-based alloy nanoparticles with non-precious metals (e.g., Fe, Ni, Co, Sn, etc.) is a judicious strategy which can not only reduce the amount of Pt used, but also lead to substantial enhancement of the electrocatalytic activity resulting from the synergetic effect between Pt and non-precious metals [10–16]. More importantly, alloy nanoparticles may display stronger resistance to CO poisoning thanks to deliberate tuning of the d-electron density of Pt [17,18]. Among the alloy electrocatalysts, Pt3Ni is of great interest, as it has been reported by Stamenkovic et al. that the Pt3Ni(111) surface is 10 times more active for oxygen reduction reaction (ORR) than the corresponding Pt(111) surface [19] and 90 times more active than leading commercial Pt/C catalysts [20–24]. Theoretical simulation has also shown that phase separation that generally lead to Pt surface enrichment is unlikely to occur in the Pt–Ni alloy system [14,25,26]. In addition, with a nickel hydroxide passivated surface as well as enhanced stability of Ni in the Pt lattice, Ni in Pt–Ni alloys is much more difficult to dissolve in typical fuel cell electrolytes than Ru in the extensively used PtRu alloys in the potential range of methanol oxidation [14].

In practical applications, nanoparticle catalysts are usually dispersed on supporting substrates of high surface areas or protected by organic surfactants to prevent aggregation and hence enhance accessibility [27–29]. From the viewpoint of both academic research and practical applications, carbon-based materials have been one of the most commonly used supporting substrates, such as carbon black [30], carbon nanotubes [31], and graphene [32–34]. This is mainly due to their low costs, high conductivity, and remarkable chemical inertness that may facilitate electron-transfer reactions on the electrode surface and concurrently improve catalyst stability and durability. Of the carbon-based materials, graphene derivatives have attracted worldwide attention in fuel cell electrocatalysis [27]. Currently, graphene (oxide) is mostly prepared by the Hummers method, which is then subjected to chemical reduction with strong reducing agents, such as hydrazine and NaBH₄, to (partly) restore the Csp² hybridization. Unfortunately, the resulting reduced graphene oxide (rGO) sheets might refold/restack because of strong π–π interactions, thus compromising the even dispersion and ready accessibility of supported metal nanoparticle catalysts.

Whereas restacking of graphene sheets may be diminished by using capping ligands/surfactant agents, the capping ligands/surfactant agents also block the active sites of nanoparticle catalysts and hence decrease the catalytic activity [35–37]. Therefore, it remains highly desired to develop new graphene-based supporting substrates with unique micro/nano structures for nanoparticle catalysts so that their electrocatalytic performance can be fully achieved.

Herein, we describe a facile method to synthesize surfactant-free Pt3Ni nanoparticles supported on sandwich-like graphene/carbon sphere/graphene substrates (Pt3Ni–C/rGO) for the electrocatalytic oxidation of methanol. It was found that the obtained Pt3Ni–C/rGO composites showed much greater peak current density, remarkably higher mass and specific activity, as well as better CO tolerance and durability in methanol oxidation than the same alloy nanoparticles supported on rGO alone (Pt3Ni/rGO) and commercial Pt/C catalysts. The superior catalytic activity indicate that the insertion of carbon nanospheres into graphene sheets may be a general and effective method to minimize the aggregation of graphene nanosheets and enhance the electrocatalytic activity of nanoparticle catalysts in the anodic oxidation of methanol.

Experimental section

Chemicals

Platinum(II) 2,4-pentanedionate ([Pt(acac)₂], 97%), nickel(II) 2,4-pentanedionate ([Ni(acac)₂], 95%), graphite powders (99.998%, 8000 mesh), and Nafion (5% w/w) were purchased from Aladdin Reagents Inc. Vulcan XC-72 active carbon nanospheres were purchased from Cabot Corporation. All other reagents were of analytical grade and used without further purification.

Synthesis of nanocomposite catalysts

Pt3Ni/rGO was prepared by the following procedure. In a typical reaction, graphene oxide (GO) was first synthesized by a modified Hummers method [38], and dispersed in N,N-dimethylformamide (DMF) to form a GO solution at a concentration of 0.5 mg/mL. 1 mL of a solution containing 30 mM Pt(acac)₂ and 10 mM Ni(acac)₂ was then mixed (Pt:Ni molar feed ratio 3:1) with 16 mL of the GO solution in DMF in a sealed PTFE-lined vessel under sonication for 30 min. The resulting mixture was transferred into a furnace and heated at 180 °C for 6 h before being cooled down to room temperature. Finally, the product was sonicated for 30 min and then washed several times with an ethanol-acetone mixture to remove excessive reagents. The obtained catalysts were dried in a vacuum oven at 60 °C overnight, and denoted as Pt3Ni/rGO.

Pt3Ni–C/rGO was synthesized in a similar fashion except that graphene/carbon/graphene (GCG) sandwiched-like composite substrates were used instead, which were prepared by mixing GO and active carbon at a 3:1 mass ratio in deionized water under sonication for 30 min, before being precipitated by centrifugation and dried in a vacuum oven at 60 °C overnight.

Characterizations

Transmission electron microscopic (TEM) measurements were conducted on a Tecnai G2-F20 at an acceleration voltage...
of 100 kV, along with EDX analysis. The TEM samples were prepared by drop-casting a water solution containing the nanocomposite catalysts directly onto a copper grid coated with a high carbon film. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo Escalab 250Xi instrument. The binding energies were calibrated by using C1s (284.6 eV) as the reference energy. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-Advance diffractometer using Cu Kα radiation. Raman spectra were recorded on an RENISHAW inVia instrument with an Ar laser source of 488 nm in a macroscopic configuration.

Electrochemistry

Electrochemical measurements were performed on a CHI 750E electrochemical workstation (CH Instruments, Chenhua Co., China) in a conventional three-electrode cell, with a platinum wire as the counter electrode, a reversible hydrogen electrode (RHE) as the reference electrode, and a catalysts-modified glassy carbon electrode as the working electrode. To prepare the catalysts-modified electrode, 1 mg of the catalysts was added into a solution containing water, isopropanol and NaFon (5%) at a volume ratio of 4:1:0.025 to form a homogeneous suspension at a catalyst concentration of 1 mg/mL. A calculated amount (20 μL for the Pt/C 20 wt% catalyst; 10 μL for the Pt3Ni/rGO and Pt3Ni–C/rGO catalysts) of the suspension was then evenly cast on the clean glassy carbon electrode (GCE) with a syringe and dried in air, corresponding to a Pt loading of each catalyst at 20.4 μg/cm².

CO-stripping voltammograms were recorded by oxidizing pre-adsorbed CO (COad) in 0.1 M HClO4 at a potential scan rate of 50 mV/s. CO was purged into 0.1 M HClO4 for 40 min to allow the Pt3Ni/rGO and Pt3Ni loading of each catalyst at 20.4 μg/cm². CO-stripping voltammograms were recorded by oxidizing pre-adsorbed CO (COad) in 0.1 M HClO4 at a potential scan rate of 50 mV/s. CO was purged into 0.1 M HClO4 for 40 min to allow the equilibrium adsorption of CO on the deposited catalyst surfaces.

Results and discussion

Fig. 1 shows the representative TEM micrographs of Pt3Ni nanoparticles supported on ([A] to [C]) rGO and ([D] to [F]) GCG, respectively. For the Pt3Ni/rGO sample, in panel (A), one can see that a number of Pt3Ni alloy nanoparticles, the dark-contrast objects, were dispersed rather evenly on a low-contrast sheet-like background of rGO. Higher-magnification images in panels (B) and (C) showed that the nanoparticles exhibited clearly-defined lattice fringes with an interlayer spacing of 1.96 Å and 2.24 Å (insets to panels (C) and (F)) that are consistent with the (200) and (111) crystallographic planes of face-centered cubic (fcc) Pt3Ni alloy, respectively [17,31]. This suggests that DMF serves as an effective reducing agent in the solvothermal synthesis of the Pt3Ni/rGO nanocomposites, as observed previously [39,40]. Similar structural characteristics can be seen with Pt3Ni–C/rGO, as manifested in panels (D) to (F). Note that the respective average diameter of the Pt3Ni nanoparticles is rather consistent at 12.7 ± 2.5 nm and 12.6 ± 2.4 nm, based on statistical analysis of more than 100 nanoparticles in each sample, as manifested in the core size histograms (insets to panels (A) and (D)); and a large portion of the nanoparticles displayed a polyhedron-like shape, as highlighted by the red-dashed boxes in panels (B) and (E). Nevertheless, there is one apparent difference between Pt3Ni–C/rGO and Pt3Ni/rGO. In contrast to the rather uniform gray background in panel (A) of Pt3Ni/rGO, the background of Pt3Ni–C/rGO in panel (D) is rather uneven, with dark-gray globular objects (diameters range from 100 nm down to a few tens of nm) embedded in a light-gray background of reduced graphene oxide sheets. These were most likely carbon nanospheres that are embedded in the graphene nanosheet matrix (more TEM images in Fig. S1 in the Supporting Information).

The relative contents of Pt and Ni in Pt3Ni/rGO and Pt3Ni–C/rGO nanoparticles were then quantified by energy-dispersive X-ray spectroscopic (EDX) measurements. From the EDX spectra in the insets to panels (B) and (E), the molar ratio of Pt to Ni was estimated to be 2.9:1 and 3:0:1, respectively, consistent with the initial feed ratio of 3:1.

The crystalline structures of the Pt3Ni/rGO and Pt3Ni–C/rGO nanocomposites were then characterized by XRD measurements. From Fig. 2, one can see that both Pt3Ni–C/rGO (curve a) and Pt3Ni/rGO (curve b) exhibited four major peaks at 20 = 39.9°, 46.3°, 68.1°, 81.6° and 85.7°, which are somewhat greater than those anticipated for the (111), (200), (220), (311) and (222) crystalline planes of fcc Pt (blue bars, PDF No. 65-2865), suggesting lattice shrinkage because of alloying with nickel in the nanoparticles [41]. From the width of the (111) diffraction peak, the size of the Pt3Ni nanoparticles was estimated by the Scherrer equation to be 10.5 ± 0.2 nm for Pt3Ni–C/rGO and 11.1 ± 0.3 nm for Pt3Ni/rGO, respectively, in excellent agreement with the TEM results shown in Fig. 1. Furthermore, the absence of nickel diffraction features (brown bars, PDF No. 65-2865) indicates that no pure metallic nickel nanoparticles were formed in the samples.

One may also see that both Pt3Ni/rGO and Pt3Ni–C/rGO nanocomposites exhibited a broad peak centered at around 24.7°. This may be ascribed to diffraction from the graphite (002) crystalline planes. It should be noted that a similar feature can be observed with rGO (curve c), in contrast to GO that displayed only a diffraction peak at a much lower 20 angle of 12.5° (curve d), implying that the graphene oxide sheets were mostly converted to highly conductive graphene after the solvothermal treatment.

The elemental compositions and charge states of the Pt3Ni/rGO and Pt3Ni–C/rGO nanocomposites were then examined by XPS measurements. As illustrated in the panels (A) and (D) of Fig. 3, the Pt4f electrons in both nanocomposites exhibited two pairs of peaks, one at 71.59 and 74.95 eV that may be attributed to the 4f7/2 and 4f5/2 electrons of metallic Pt, and the other at 71.98 and 75.38 eV that are consistent with PtO and PtOH species, respectively. For the Ni2p electrons in panels (B) and (E), deconvolution yields a major peak at 853.23 eV and a satellite at 860.83 eV that are consistent with metallic Ni, as well as two additional peaks centered at 854.63 eV and 856.63 eV that may be attributed to NiO and Ni(OH)2, respectively. Note that the presence of metal oxides has been suggested to not only facilitate the formation of surface hydroxyl species and transport of protons and electrons that are essential in methanol oxidation but also prevent the catalysts from corrosion [42]. For the C1s electrons in panels (C) and (F), three main peaks were identified at 284.73 eV, 285.58 eV and...
288.07 eV that may be assigned to carbons in C—C/C=C—C, C—O, and C=O, respectively, at an atomic ratio of 2.01:1.23:1. One may also notice that the binding energies of the Pt4f and Ni2p electrons in Pt3Ni are somewhat higher than those of standard Pt(0) (71.3 eV and 74.4 eV) and Ni(0) (852.70 eV), suggesting electron transfer likely occurred from Pt3Ni nanoparticles to graphene oxide [43-45]. This may lead to reduced binding energy of Pt—CO and hence weakened the adsorption of CO on Pt3Ni nanoparticle surfaces [46-50], as manifested in electrochemical measurements below.

Raman measurements were then carried out to further examine the carbon supporting substrates, as depicted in Fig. 4. It can be seen that GO, rGO, Pt3Ni/rGO, and Pt3Ni—C/rGO all exhibited a pair of peaks at 1585 cm⁻¹ and 1348 cm⁻¹. The former may be assigned to the G band that is related to the vibration of sp²-bonded carbon atoms, whereas the latter is known as the D band, which usually originates from vibrations of carbon atoms with dangling bonds defects and staging disorder in the plane of graphene sheets. Furthermore, the ratio between the D and G band intensity (ID/IG) for the Pt3Ni—C/rGO catalysts was estimated to be 1.07, somewhat greater than those for Pt3Ni/rGO (1.01), rGO (0.98) and GO (0.96), suggesting enhanced disordering with the insertion of carbon nanospheres into the rGO sheets.

Electrochemical measurements were then carried out to examine the electrocatalytic activity of the nanocomposites in methanol oxidation. Fig. 5 shows the cyclic voltammograms of a glassy carbon electrode modified with a same amount of (black curve) rGO and (red curve) GCG in 0.1 M HClO₄ at a potential scan rate of 50 mV/s. It can be seen that both electrodes exhibited a pair of voltammetric peaks at ca. +0.70 V. This most likely arose from redox reactions of oxygen-containing functional groups on graphene surfaces. The markedly higher peak currents of the GCG-modified electrode suggested that the effective electrochemical surface area of GCG was greater than that of rGO. A consistent behavior can be seen with the double-layer charging currents, with a notably broader charging envelope for GCG than for rGO. These results suggest that with the insertion of carbon spheres in between the graphene sheets, the restacking and refolding of graphene sheets was minimized during the solvothermal process. This facilitated the access of the electrolyte species to the internal structures of the carbon support, leading to a dramatic increase of the electrochemically accessible surface area (ECSA) due to the unique 3D sandwich-like structure [51,52].
The electrocatalytic activity in methanol oxidation was then evaluated. Fig. 6(A) shows the cyclic voltammograms of the Pt/C, Pt$_3$Ni/rGO and Pt$_3$Ni–C/rGO catalysts loaded onto a glassy carbon electrode at a scan rate of 50 mV/s in 0.1 M HClO$_4$ + 1.0 M CH$_3$OH. It can be seen that for all nanoparticle catalysts, in the anodic scan oxidation currents started to emerge at potentials around +0.60 V, and reached the peak values at a more positive potential of around +0.93 V; in the reverse scan, a similar anodic voltammetric peak can be seen but at a less positive potential around +0.75 V, suggesting effective catalytic oxidation of methanol by these nanoparticle catalysts. Yet, a careful analysis shows that the onset potential of methanol oxidation actually increased in the order of Pt$_3$Ni–C/rGO (+0.65 V) < Pt/C (+0.68 V) < Pt$_3$Ni/rGO (+0.70 V); and the current density at +0.93 V is 360.4 mA/mg for Pt$_3$Ni–C/rGO, nearly 1.7 and 1.3 times higher than those on Pt$_3$Ni/rGO (210.7 mA/mg) and commercial Pt/C (267.8 mA/mg), respectively. In addition, it is worthy to note that in the anodic scan the Pt$_3$Ni–C/rGO catalyst also shows a somewhat lower peak potential and higher peak current density than those reported by Li et al. [41] with Pt$_3$Ni/rGO (+0.96 V, 145.8 mA/mg) and Chen et al. [8] with PtPd/rGO (+0.97 V, 198.0 mA/mg). With respect to the specific activity, in the present study, the Pt$_3$Ni–C/rGO catalyst (0.66 mA/cm$^2$) is 1.3- and 1.2-times more active than Pt$_3$N/rGO (0.51 mA/cm$^2$) and commercial Pt/C (0.54 mA/cm$^2$), respectively (Fig. 6(B)). These observations explicitly demonstrate that the Pt$_3$Ni–C/rGO displays the highest catalytic activity in the electrooxidation of methanol among the series of catalysts in the present study. Nevertheless, it should be noted that the performance of the above-mentioned Pt$_3$Ni–C/rGO is not yet as good as that of “state of the art” PtRu catalysts. However, simple addition of carbon spheres into the rGO substrates clearly enhanced the electrochemical surface area and hence the accessibility of...
nanoparticle catalyst surface, a strategy that might be exploited as a generic and effective mechanism for the further enhancement of nanoparticle electrocatalytic activity in methanol oxidation.

Note that in the above analysis, the effective electrochemical surface area (ECSA) was quantified by CO stripping measurement within the potential range of +0.6 to +1.0 V, as depicted in Fig. 7, which was observed to increase in the order of Pt3Ni/rGO (42.8 m²/g) < commercial Pt/C (50.1 m²/g) < Pt3Ni–C/rGO (52.7 m²/g). One may note that whereas the particle size of Pt3Ni in Pt3Ni/rGO and Pt3Ni–C/rGO is almost identical, the ECSA of Pt3Ni–C/rGO is markedly larger than that of Pt3Ni/rGO. This might be accounted for, again, by the insertion of carbon nanospheres into the graphene nanosheet matrix forming the GCG sandwich-like structure that likely prevented the restacking/refolding of the graphene sheets and generated an increasing number of accessible active sites as well as transport channels for mass and charges. These unique features are beneficial to the catalytic reactions. Moreover, whereas the core size of the Pt3Ni nanoparticles prepared above is markedly larger than that of commercial Pt/C (ca. 3.3 nm) [46], the ECSA of Pt3Ni–C/rGO is actually higher, as a result of the polyhedral shape of the Pt3Ni nanoparticles as well as enhanced surface accessibility by the insertion of carbon spheres into the graphene support. Similar behaviors have also been observed previously [20,53].

Tolerance to poisonous species is also of great importance for catalysts in practical applications. It is well known that when methanol is oxidized on Pt-based catalysts, poisonous intermediates, such as CHOads and COads, may be formed and strongly absorbed on the platinum surfaces, leading to self-poisoning of the catalysts [45]. The ratio of the oxidation peak current density in the anodic and cathodic scans (Jf/Jb) is generally used to quantitatively evaluate the tolerance strength of the catalysts to CO poisoning. A higher Jf/Jb value suggests stronger CO tolerance of the catalyst. Based on the data in Fig. 6(A), the Jf/Jb ratio of Pt3Ni–C/rGO and Pt3Ni/rGO is estimated to be 1.25 and 1.43, respectively, both markedly higher than that of Pt/C (1.11), again suggesting enhanced CO tolerance of the catalysts.

Stability is another critical factor in the assessments of nanoparticle catalysts. Fig. 6(C) shows the chronoamperometric (CA) profiles recorded at +0.85 V in 0.1 M HClO4 + 1 M CH3OH with the same catalysts-modified electrodes. Although all catalysts show a rapid decrease of the voltammetric currents (at roughly the same decay rate), the Pt3Ni–C/rGO catalysts maintained a much higher current than the other two catalysts, demonstrating remarkably enhanced electrocatalytic activity and stability. For instance, after 600 s of operation, the current density of Pt3Ni–C/rGO was 114.7 mA/mg, whereas only 20.4 mA/mg and 26.4 mA/mg were observed for Pt3Ni/rGO and commercial Pt/C, respectively.

CO stripping is another commonly used method to assess the resistance of Pt-based catalysts to CO in methanol oxidation [35]. Fig. 7 shows the cyclic voltammograms of a glassy-carbon electrode modified with (A) commercial Pt/C, (B) Pt3Ni/rGO, and (C) Pt3Ni–C/rGO catalysts that was covered with an adsorbed layer of CO in 0.1 M HClO4. Potential scan rate was 50 mV/s. Pt loading was all 20.4 μg/cm². (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
to +1.0 V, which was attributed to the oxidative removal of adsorbed CO, and consequently the hydrogen adsorption/desorption peaks were recovered in the second scans (red curves). The potential of CO oxidation is another important factor in the evaluation of CO tolerance. It can be seen from Fig. 7 that CO oxidation on (C) Pt3Ni–C/rGO peaked at ca. +0.81 V, markedly more negative than that of (A) Pt/C (+0.83 V) and (B) Pt3Ni/rGO (+0.82 V). Additionally, the onset potential of CO oxidation on Pt3Ni–C/rGO is +0.65 V, which is also lower than those of commercial Pt/C (+0.71 V) and Pt3Ni/rGO (+0.68 V). These results further highlight the excellent CO tolerance ability of Pt3Ni–C/rGO catalysts, which is likely due to the relatively weak bonding of Pt–CO resulting from electron transfer from Pt3Ni to reduced graphene oxide as manifested in XPS measurements (Fig. 3). The observation is consistent with the chronoamperometric profiles shown in Fig. 6(C), where the decay rate of Pt3Ni–C/rGO was the lowest among the series (Table S1).

One may notice that in contrast to Pt/C in panel (A), both Pt3Ni catalysts in panels (B) and (C) actually exhibited two voltammetric peaks. This may be attributed to the complexity of adsorption sites of CO on the surfaces of Pt3Ni alloy nanoparticles, where the peak at the lower potential is likely due to the oxidation of CO adsorbed on Pt (110) planes or edge sites of the Pt (111) planes, while the peak at the higher potential to the oxidation of CO adsorbed on Pt (111) planes [54].

Conclusions

In summary, a facile strategy was described for the synthesis of Pt3Ni alloy nanoparticles supported on graphene/carbon nanospheres sandwich-like substrates (Pt3Ni–C/rGO). The resulting nanocomposites exhibited markedly enhanced electrocatalytic activity and much improved durability in methanol oxidation reaction as compared to commercial Pt/C catalysts and Pt3Ni nanoparticles supported on graphene nanosheets alone (Pt3Ni/rGO). Experimental measurements showed that the superior catalytic activity might be attributed to the unique sandwich-like structure of the supporting substrate that increased the effective electrochemical surface area of Pt3Ni nanoparticles and hence the transport of electrolyte ions and reactant/product molecules. Mechanistically, the markedly enhanced CO tolerance of Pt3Ni–C/rGO was likely due to a decreased electron density of the Pt3Ni nanoparticles with partial electron transfer to graphene sheets that weakened the interactions with CO. Such a strategy might be exploited as an effective mechanism in the design and engineering of nanoparticle catalysts for enhanced performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2015.02.095.

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