From Ni(OH)₂/Graphene composite to Ni@Graphene core-shell: a self-catalyzed epitaxial growth and enhanced activity for nitrophenol reduction

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ABSTRACT

Two-dimensional reduced graphene oxides (RGO) decorated with well-dispersed Ni nanoparticles were facilely fabricated via low temperature annealing of Ni(OH)₂/Graphene composites in flowing H₂. Ni@Graphene core-shell nanostructures were obtained following a self-catalyzed growth mechanism. The kinetic epitaxial growth of RGO layers on Ni(111) facets originates from annealing-driving phase transition from NiO to Ni at temperature ≥ 450 °C, which was revealed by utilizing comprehensive characterizations including X-ray diffraction, X-ray photoelectron spectroscopy, as well as aberration-corrected scanning transmission electron microscopy. This distinct core-shell structure shows extraordinary catalytic activity in reduction of 4-nitrophenol with the efficiency reaching up to 45.0 L·g⁻¹·min⁻¹ at room temperature. Atom-resolved microscopy evidences disclose that such outstanding catalytic activity could be attributed to the synergetic cooperation between Ni phase and epitaxial graphene shell. This work provides general inspiration on the facile fabrication of highly active and non-noble metal-graphene catalysts.

1. Introduction

In the recent decades, great attention has been paid to graphene due to its large surface area and excellent electrical, mechanical, thermal, and optical properties.[1-4] Graphene decorated with various metal and metal oxide nanoparticles gives rise to a group of unique

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nanocomposites.[5, 6] These structures would not only inherit the excellent properties of graphene, but also enhance the properties of metal nanoparticles, which are widely applied in catalysis, batteries and supercapacitors.[7-13] In addition, the aggregation of metal nanoparticles with high surface energy, especially for the magnetic materials, can be efficiently minimized ascribed to the perfect carrier of graphene. This distinct synergy effect promises metal/graphene nanocomposites a high efficient catalyst of environmental friend and facile production for the degradation of pollutants, such as p-nitrophenol, one of the most toxic but stable pollutants. It can be successfully reduced to p-aminophenol, which is of great commercial importance as an intermediate for the manufacture of pharmaceuticals. Unfortunately, the reaction rate of this conversion is almost negligible without the help of particular catalysts. [14, 15] To date, elaborate efforts of researchers have been spent on fabrication of diverse structures for promoting the reduction efficiency of nitrophenol, including Pd particles on (Ti/Fe/Cr) films by Sarvesh,[16] Ru nanoframes by Ye,[17] $\text{Fe}_x\text{O}_y/\text{Pd}$ @mesoporous SiO_2 by Yao,[18] dendritic Pt nanoparticles (NPs) by Wang,[19] and water-soluble Au nanocages by Li.[20] In spite of progresses made in these works, development of non-noble catalyst with low cost but high activity remains a challenging task.

In this work, we report fabrication of nano-sized Ni@Graphene core-shell structure on RGO layers through annealing of $\alpha\text{-Ni}(\text{OH})_2$ /graphene nanocomposites, which was facilely synthesized in water at ambient condition. A self-catalyzed epitaxial growth mechanism was disclosed to drive the formation of such distinct core-shell configuration, which to our best knowledge, presents as the first report based on atom-resolved microscopy evidences. The as-synthesized Ni/graphene nanocomposites exhibit high efficiency up to $45.0 \text{ L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ on catalytic reduction of p-nitrophenol. Such excellent efficiency breaks most records of reported works, even surpassing noble metal based catalysts.

2. Experimental Section

2.1 Synthesis of Ni nanoparticles on RGO nanosheets

2.1.1 Materials

All these chemicals are of analytical reagent grade and used as received without further purification.

2.1.2 Preparation of Reduced graphene oxides (RGO)

Graphite oxides (GO) were synthesized through Hummer's method.[21] In a typical reaction, concentrated H_2SO_4 (20 mL) was added to a mixture of graphite flakes (0.5 g) and NaNO_3 (0.5 g) in an ice water bath. KMnO_4 (3.0 g) was added slowly in order to weaken the increase of temperature. Then, the system was heated to 35 °C and stirred for 60 min. Subsequently, 40 mL deionized water was added slowly, while the temperature was raised to 95 °C. After stirred for 30 min, additional water (100 mL) and 30% H_2O_2 (3 mL) was added. GO were collected with filtration and centrifugation with enough water. In order to get RGO powder, GO aqueous solution (1 mg/mL), dispersed by sonication, was reduced by hydrazine hydrate (50 wt%) at 95 °C with oil bath for 12 h and then dried in vacuum at 60 °C after washed with ethanol.

2.1.3 Preparation of Ni/graphene samples

Typically, 25 mg of as-prepared RGO was dispersed in 15 mL of deionized water by stirring for 10 min and sonication for 1 h, then 15 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added by sonication for another hour. Freshly prepared aqueous solution of NaBH_4 (0.4 mL, 1 M) was added dropwise to get composite precursor. After stirring and aging of mixture solution at room temperature for 2 h, the products were collected by centrifuge and washed with deionized water and ethanol several times, and recorded as initial sample. Then, initial products were dried in a blasting drying trunk at 60 °C and followed by the annealing treatment in a tube furnace under 2% H_2 (in Ar) flow of 200 sccm for 1 h at 350 °C, 450 °C, 550 °C and 770 °C respectively to yield different types of Ni/RGO nanocomposites.

2.2 Characterizations

The morphology and structure were investigated by field-emission scanning electron microscopy (FE-SEM) (INSPECT F50), and scanning transmission electron microscopy (STEM) mode (JEOL JEM 2100F 200kV, equipped with a CEOS GmbH probe corrector) through high angle annual dark-field (HAADF) and bright-field (BF) imaging. A powder X-ray diffraction (XRD) was conducted to determine the phase of the as-synthesized products on a DX 2700, with measurements taken using $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on Kratos AXIS Ultra DLD instrument using monochromated $\text{Al K}\alpha$ X-rays as the excitation source. UV-vis spectra of the samples were measured on a Shimadzu UV-2550 ultraviolet visible spectrophotometer. Raman experiments were conducted with a Jobin Yvon Labram HR800 spectrometer.

2.3 Catalytic activity test on reduction of 4-Nitrophenol

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was used as a model reaction to test the catalytic activity of Ni/graphene nanostructures. Typically, 1 mg of Ni/RGO nanocomposites were dispersed in 100 ml deionized water by sonication for 5 min. Then 2 ml of 4-NP aqueous solution (5.0 mM) was added into the solution with color turning into light yellow. After 2 ml freshly prepared NaBH₄ aqueous solution (1 M) was added, the color of the mixture solution changed from light yellow to yellow green and then gradually faded as the reaction proceeded under magnetic stirring. During entire reaction process, about 3.0 mL of reaction solution was withdrawn at a given time interval, which was immediately recorded in the Shimadzu UV2550 spectrophotometer over the scanning range from 260 to 500 nm at 25 °C. In order to compare the catalytic activity of different catalysts, reactions catalyzed by Ni nanoparticles, NiAu bimetallic nanoparticles, raw RGO and α -Ni(OH)₂ were also investigated under the same condition.

3. Results and Discussions

3.1 Microstructure Evolution of Ni/RGO Nanocomposites

In this reaction, series of Ni/RGO nanostructures were synthesized through two steps. In brief, the procedure involves transformation of Ni(NO₃)₂·6H₂O to initial Ni precursor by adding NaBH₄ to RGO suspension, and then further reduction of initial samples to final products through annealing treatment at different temperatures.

Raman spectroscopy excited by 532.17 nm laser was adopted to provide general structural status of RGO sample as shown in **Figure 1a**. The spectra are performed in wavenumber range from 500 to 3500 cm⁻¹, covering both first and second order bands. The weak 2D peak at ~2600 cm⁻¹ suggests the nature of a few layered graphene for all these samples.[22] The D peak is associated with structural imperfections created by oxygen-containing functional groups at graphene edges and amorphous carbon (Csp³ species).[23, 24] The full width at half maximum (FWHM) of D peak is chosen as a parameter to define the degree of reduction, while the FWHM of D peak decreases linearly as GO is further reduced and the percentage of Csp² rises.[25] The FWHMs of D peak (fitting in lorentzian style) are 216, 226, 199, 223, 165 cm⁻¹ respectively for initial, 350C, 450C, 550C, 770°C sample. Except 770°C sample, no obvious change can be recognized comparing with pure RGO with D peak width of 213 cm⁻¹. According to the D peak, no doubt that the 770°C sample is further reduced with higher annealing temperature in H₂/N₂ atmosphere which means the increasing percentage of Csp². Moreover, the intensity ratio of the D and G bands (I_D/I_G) can index the abundance of modification or defects in carbon component.[26]

Following the above principles, the initial sample and ones after annealing at 350 °C, 450 °C and 550 °C exhibits slight decrease trend of I_D/I_G ratio from ~0.9, ~0.88, ~0.88 to ~0.86, respectively. This implies that under higher temperature annealing, oxygen functional groups are easier to be reduced by H_2 while disorder seems decrease. However, a sharp increase of I_D/I_G ratio occurred for sample annealed at 770 °C (~1.03). This suggests that more disorders are induced due to the drastic removal of oxygen functional groups under temperature as high as 770 °C. The removal of oxygen functional groups as well as the arrangement of carbon atoms may lead to not only the formation of perfect graphene, but also a higher possibility of aggregation of graphene layers to stacked graphite or even the formation of amorphous carbon. The Raman spectrum of as-prepared pure RGO (**Figure S1a**) presents lowest I_D/I_G ratio (~0.66), indicating more oxygen-containing functions in raw materials. However, the obviously higher 2D peak suggests better single-layered status in raw materials compared to as-synthesized Ni/graphene samples.[27]

Figure 1. (a) Raman spectra and (b) XRD patterns of Ni/RGO before and after different temperature of annealing treatment.

The structure changes as revealed by above Raman spectroscopy are further confirmed by XRD results shown in Figure 1b. Since the peak at $2\theta = \sim 10^\circ$ is regarded as the evidence of graphene oxides,[28, 29] the absence of this diffraction peak for RGO product (Figure S1b) proves that the raw materials have been fully reduced. The peak between 20° and 30° is mainly contributed by RGO interlayer (002). As the temperature increases, this peak shows a right shift, indicating the decrease of the interlayer spacing of graphene. In addition, RGO also contributes to the peak at $2\theta = \sim 43.2^\circ$ due to the second order diffraction. Meanwhile, the diffraction pattern of initial sample (Figure 1a) exhibits peaks at about $2\theta = 33.7^\circ$ and 60° , corresponding to the (101) and (311) planes of α -Ni(OH)₂ (JCPDS 38-0715).[30] To further evidence the Ni element status in initial sample, a XRD pattern of standard α -Ni(OH)₂ sample without adding RGO were collected under the same condition. As is shown in Figure S1b, it fits well with the XRD pattern of α -Ni(OH)₂. As illustrated in Figure 1b, with the increase of annealing temperature, the intensity

of peaks of α -Ni(OH)₂ gradually decreases. On the contrary, the diffraction peaks at 44.1°, 51.5° and 75.9° rise with promoting temperature, corresponding to the (111), (200) and (220) planes of metallic Ni (JCPDS 01–1260). This trend reveals that α -Ni(OH)₂ is gradually converted to face center cubic nickel through annealing treatment. As can be seen in Figure 1b, a weak peak at 44.1° corresponding to Ni(111) starts to appear after annealing at 350 °C, indicating the initiation of phase conversion. At the annealing temperature of 770 °C, no α -Ni(OH)₂ peak can be recognized suggesting total conversion of Ni elements into metallic Ni.

Figure 2. (a~e) SEM and (f~j) STEM-ADF images of initial, 350 °C, 450 °C, 550 °C and 770 °C annealed samples, respectively. (k) Elemental distribution maps of initial sample obtained by STEM-EDS. (l~o) Size distributions of corresponding samples.

To explore the annealing driving evolution of Ni/RGO nanocomposites in aspects of morphologies and microstructures, SEM as well as STEM-HAADF imaging was utilized with results shown in **Figure 2**. Initial sample without annealing treatment presents homogenous contrast similar to raw graphene and no particle features can be observed in SEM image (Figure 2a) as well as STEM-ADF image (Figure 2f). The elemental mapping via X-ray energy dispersive spectroscopy (EDS) confirms the uniform loading of α -Ni(OH)₂ on graphene layers in initial sample proved by the homogenous distribution of carbon, nickel and oxygen elements (Figure 2k). Whereas, small nanoparticles emerge and grow with promoted temperatures (350~550 °C) for the samples subjected to annealing. Combined with XRD results, these nanoparticles should be metallic Ni. The detailed particle size distributions of Ni nanoparticles are illustrated in Figure 2l~2o. Their mean sizes increase from ~6 nm to 30 nm as the annealing temperature rises from

350 to 550 °C. All these isolated Ni nanoparticles are well dispersed on RGO nanosheets. Except for size, the particle morphology also evolves gradually from irregular asymmetry to regular shape (ellipsoidal or spherical). Nevertheless, it is totally different for the sample annealed at 770 °C. The mean particle size (~25 nm) does not increase as expected compared with sample annealed at 550 °C. A broad size distribution appears instead and SEM image (Figure 2e) discloses that Ni particles are encapsulated by carbon contrast, which implies the crystal growth of Ni particles have been blocked by the aggravated reformation of surrounding RGO (as indicated by XRD results). These results suggest that annealing at 770 °C is too high to facilitate controlled reconstruction of Ni/RGO nanostructures and graphene layers can be severely destroyed (**Figure S2a**).

Table 1. Atomic percentages of carbon, oxygen and nickel elements calculated on the basis of XPS spectra.

Samples	Initial	350 °C	450 °C	550 °C	770 °C
C% (atom %)	78.97	80.66	87.76	90.08	98.27
O% (atom %)	18.54	16.80	11.19	9.17	1.71
Ni% (atom %)	2.50	2.54	0.95	0.75	0.02

XPS and high resolution HR-STEM approaches were performed to investigate the surface states and microstructure of Ni/RGO nanocomposites in **Figure 3** and **S3**. Figure 3a demonstrates the full range of XPS spectra of five samples ranging from 0 to 1000 eV. The atomic percentages of carbon, oxygen and nickel at the surface of each sample are listed in **Table 1**. Herein, taking the carbon signal as the normalized reference, the atomic ratios of oxygen and carbon atom (O/C) are ~0.234, ~0.208, ~0.127, ~0.102 and ~0.017 for initial, 350, 450, 550 and 770 °C sample, respectively, indicating the gradually removal of oxygen-containing functional groups and adsorbed oxygen among graphene layers during annealing. In addition, the phase conversion from Ni(OH)₂ to Ni also attributes to the decrease of O/C ratio. More intriguingly, the ratios between nickel and carbon (Ni/C) are ~0.032, ~0.031, ~0.011, ~0.008 and ~0.001 for the five Ni/RGO samples. The content of nickel element gradually decreases while the annealing temperature rises, even nearly no nickel element can be detected for 770 °C sample, which seems to be an apparent contradiction with above XRD and STEM results.

Figure 3. (a) The XPS survey spectra and b) high-resolution Ni 2p spectra of initial sample and samples annealed at 350, 450, 550 and 770 °C, respectively. (c~e) High resolution STEM-HAADF and STEM-BF images of Ni/RGO nanocomposites after annealing treatment at 350, 450, and 550 °C, respectively (The enlarged image of red square in (d) is embedded). (f) Schematic illustration of annealing driving phase evolution from Ni(OH)₂, NiO, Ni@NiO to Ni@Graphene core-shell structures.

This phenomenon can be well interpreted on the basis of annealing driving core-shell reconstruction as evidenced by the HR-STEM results (Figure 3d~3e). The encapsulation of graphene layers around Ni nanoparticles accounts for the decreased detectability of Ni signal in XPS due to the limited probe depth (≤ 3 nm for Nickel 2p edges) of instruments suffering from the inelastic scattering of photon electrons. After annealing at ≥ 450 °C, RGO shells of multilayers formed in thickness of ≥ 3 nm, already blocking most XPS signal of metallic Ni core. Therefore, the XPS signals of Ni 2p for samples annealed at 450 °C or higher could be only attributed to the divalent Ni²⁺ from either residual Ni(OH)₂ or transformed NiO on the RGO surface. We could

also deduce that the absence of Ni signal in the 770 °C annealed sample proves the complete conversion of α -Ni(OH)₂ to metallic Ni and being encapsulated by the reformed carbon components. The above discovery coincides with the clues of both XRD and STEM results. Specially, for the sample annealed at 350 °C, no RGO shell is found according to STEM-BF image (inset Figure 3c), while only NiO clusters dominate besides a few Ni@NiO particles noting that those NiO shells also prevent metallic Ni from detection of XPS. Additional information on valence state of elements were obtained via high-resolution XPS analyze as demonstrated in Figure 3b and S3b. The Ni 2p region is composed of four peaks, Ni2p_{3/2} and Ni2p_{1/2} main peaks and their satellites. No apparent peaks for metallic nickel are detected for all these samples, which serve as direct evidence supporting the Ni/RGO core-shell reconstruction. Besides, it should be noticed in Figure 3b that the Ni2p_{1/2} peak constitutes with 2 peaks at ~854.4 eV and ~856.0 eV corresponding to NiO[31] and Ni(OH)₂[32] for the initial, 350 and 450 °C annealed samples (Figure 3b). Meanwhile, only one peak of Ni(OH)₂ appears at 856.0 eV for 550 °C sample. This suggests that the existence of NiO phase provides a critical intermediate during the phase evolution from Ni(OH)₂ to final Ni@Graphene following the annealing driving reconstruction mechanism. The sharp drop of Ni2p_{1/2} sub-peak for NiO phase from 350 °C to 450 °C annealing treatment manifests that the metallic Ni phase is reduced from the NiO rather than directly from Ni(OH)₂ phase, since the decrease of NiO occurs spontaneously with the formation of Ni/RGO core-shell at 450 °C annealing. This point is also confirmed by the HR-STEM image of Figure 3c, where apparent Ni/NiO heterostructures form at 350 °C without initiation of growth of RGO shell. Furthermore, for sample annealed at temperatures higher than 450 °C, the HR-STEM images (Figure 3d and 3e) offer strong evidences of self-catalyzed epitaxial growth of graphene layers around Ni particles accompanied with kinetic phase transition from α -Ni(OH)₂, NiO to Ni. It needs to be noted that graphene layers only grow along Ni(111) due to the lattice symmetry,[33, 34] resulting in the broken of graphene layers at the corners indexed to be (200) and (220) of Ni-core (red circled areas in Figure 3d), where the NiO clusters locate serving as growth source of Ni particles. However, these shell breaks gradually disappears with the further growth of graphene layers. As is shown in the blue circled area in Figure 3e, no NiO cluster is observed and two pieces of graphene layers from adjacent Ni(111) facets begin to form a complete piece enclosing outside Ni-core, which prevents the further growth of Ni particle. Especially for 770 °C sample, the higher reconstruction rate of carbon atoms on the particle surface leads to the smaller particle mean size compared to 550 °C sample.

On the basis of microscopy evidences demonstrated above, a schematic illustration is established to describe the whole formation process of Ni@Graphene in Figure 3f. With

annealing treatment, the NiO particles transformed from Ni(OH)₂ clusters on RGO surface are further reduced to form Ni core, while unreduced NiO clusters automatically aggregate to Ni core to form Ni/NiO heterostructures. For annealing temperature higher than 450 °C, self-catalyzed epitaxial growth of graphene layers occurs along the Ni(111) facets accompanied with kinetic phase transition from α -Ni(OH)₂, NiO to Ni. Such phase transformation process continues under the feeding of NiO source from the shell breaches at the (200) and (220) facets until these breaches close due to further growth of graphene layers.

From the aforementioned analysis, the sample annealed at 450 °C is verified to be the most representative stage during the entire annealing driving core-shell reconstruction procedures. Therefore, atom-resolved STEM characterizations have been performed for putting insights into this distinct evolution behavior of Ni/RGO nanocomposites as shown in **Figure 4**. The low-magnified STEM-HAADF image (Figure 4a) reveals that Ni particles do not exhibit regular uniform morphology. The enlarged image (Figure. 4b) shows an individual particle enclosed with small facets of both high index (e.g. Ni200, Ni220) and low index (typical as Ni111) crystal facets. The HR-STEM images of Figure 4c~4f give the quantitative demonstration of atomic steps on the surface of Ni-core and NiO cluster adsorbates. Figure 4d and 4e demonstrate atomic steps along Ni (111) stacking, yielding large amount of low-coordinated atoms on the surface. Meanwhile, the graphene layers with the interlayer distance of ~0.338 nm bridge together over the (200) facet from adjacent Ni(111) facets forming wrinkled incompact multilayer stacking outside the Ni surface(Figure 4c). In addition, the HAADF image of Figure 4f further proves that NiO clusters at the edge serve as the growth source of Ni particles where no graphene layers exist. NiO clusters transported by thermal decomposition of Ni(OH)₂ can migrate from adjacent area, feeding the growth of Ni particles from only several nanometres (e.g. 450 °C) to tens of nanometres (e.g. 550 °C).

Figure 4. (a) Low magnification STEM-ADF image of the sample after 450 °C thermal reduction. Atom-resolved STEM-BF (b~d) and STEM-HAADF (f) images of an individual Ni/RGO particle. (e) Reconstructed atomic model of (d)

3.2 Catalytic activity on reduction of 4-Nitrophenol

It is widely accepted that special surface area plays an important role in the catalyst activity, while controlling the shape and size of particles will surely affect the specific surface area of catalyst.[35, 36] The irregularly shaped polyhedron morphology would increase the specific surface area of the catalyst via forming more low-coordinated atomic steps/facets, thus promising higher catalytic activity. It is of great significance to realize that graphene layers are catalyzed to grow only along Ni(111) leaving those higher indexed facets with high activity exposed. This distinct behaviour is believed to facilitate core-shell nanostructure with potentials of both high catalytic efficiency and structural stability with aggregation being protected by RGO shells. Therefore, the reduction reaction of 4-NP by NaBH_4 was conducted at room temperature to explore the catalytic activity of the as-synthesized Ni/RGO nanocomposites.

Figure 5. (a) Process of the conversion from 4-NP to 4-AP; (b) UV-vis spectra of 4-NP, 4-NPI and 4-AP.

Theoretically, this process actually involves two steps as shown in **Figure 5**. At first, 4-NP interacts rapidly with the hydroxyl ion induced by the hydrolysis of sodium borohydride, when 4-NP is converted to 4-nitrophenolate ions (4-NPI) immediately accompanied by a characteristic red shift of photon absorbance. Secondly, 4-nitrophenolate ion is reduced by NaBH_4 and 4-aminophenol (4-AP) comes into being. Such process is consistent with the UV-vis absorption spectra in Figure 5. The 4-NP shows an absorbance peak at ~ 317 nm, while red shift to 400 nm in the presence of NaBH_4 due to the formation of 4-NPI in the alkaline environment caused by the hydrolysis of NaBH_4 (Figure 5b).

Figure 6 demonstrates the reduction of 4-NP into 4-AP catalyzed by Ni/RGO sample series. Originally, an absorption maximum at 400 nm can be observed in aqueous solution. As shown in Figure 6a~6e, the absorption peak of 4-NPI at 400 nm gradually decreases with the increase of reaction time accompanied by the absorbance enhancement of a new peak at 300 nm, corresponding to the formation of 4-AP.[37] An isosbestic point exists between two absorption bands, indicating that only two principal species exist. As a contrast, the catalytic activity of none-catalytic, raw RGO, pure $\alpha\text{-Ni}(\text{OH})_2$, Ni nanoparticles, and NiAu nanoparticles[38, 39] (**Figure S4**) were also tested under same condition. For pure $\alpha\text{-Ni}(\text{OH})_2$, Ni and NiAu nanoparticles, the similar decrease occurred at the absorption peak of 400 nm (**Figure S5c~5e**). However, the decrease of the peak at 400 nm is almost indiscernible by using RGO as the catalyst (Figure S5b), indicating that metal nanoparticles actually act as catalysts for 4-NP reduction. Without introducing these metallic catalysts, the reaction can hardly be recognized (Figure S5a).

Figure 6. Successive UV-vis spectra for the reduction reaction of 4-nitrophenol by NaBH₄ with Ni/RGO before and after different temperature of annealing treatment as a catalyst, (a) initial sample; (b) 350 °C; (c) 450 °C; (d) 550 °C; (e) 770 °C. (f) Plots of $\ln(A_t/A_0)$ of 4-nitrophenolate ions versus reaction time for the nanocomposites.

In considering that the reaction follows the pseudo-first order kinetics[40] with respect to the concentration of 4-NP when excess NaBH₄ is used. In our reaction system, the apparent rate constant (k_{app}) is calculated by plotting the negative logarithm of the ratio of absorbance (A_t/A_0 at $\lambda = 400$ nm) with respect to time as shown in Figure 6f and Figure S5f. The kinetic equation of the reduction reaction could be given as follows:[26]

$$k_{app}t = \ln C_0 - \ln C_t = \ln A_0 - \ln A_t = -\ln\left(\frac{A_t}{A_0}\right) \quad (1)$$

Where C_t and C_0 are the concentration of 4-NP at time t and $t = 0$, respectively; A_t and A_0 represent for the absorbance of the mixture solution at time t and $t = 0$, respectively. Meanwhile, since k_{app} shows linear relationship with the concentration of catalyst,[24, 41] a new parameter K is introduced to better exhibit the catalytic activity, which is defined as follow:

$$K = \frac{k_{app}}{m/V} \quad (2)$$

Where m is the mass of catalysts added in the catalysis, and V is the volume of the total catalytic system, while k_{app} is the apparent rate constant calculated through equation (1). An induction period exists for this reaction when 4-NP is rapidly converted to 4-NPI and then absorbed onto the surface of RGO so that the Ni nanoparticles and α -Ni(OH)₂ attached to RGO could begin the catalytic reaction. Therefore, the data of few minutes at the beginning are not taken into account in order to get more accurate k_{app} .

Table 2. The rate constants for the reduction reaction of 4-nitrophenol under different catalysts and the correlation coefficient for $\ln(A_t/A_0) - t$ plots.

Samples	Initial	350 °C	450 °C	550 °C	770 °C
$k_{app}(\times 10^{-3} \text{ min}^{-1})$	74.7	186.0	432.7	498.7	4.3
$K (\text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1})$	7.8	19.4	45.0	51.9	0.4
R^2	0.9956	0.9661	0.9944	0.9909	0.9974

Table 2 summarizes the k_{app} , K and R-squared of all these samples calculated from successive UV-vis spectra, providing direct judgments on the catalytic activity of each sample. The catalytic activity K increases from 7.8 $\text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ of initial Ni(OH)₂/RGO to 45.0 $\text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ of Ni@Graphene as the annealing temperature rises to 450 °C. Especially for 350 °C sample, only ~3% Ni is converted to metallic nickel (based on XPS data), while K of 350 °C sample is twice of the K of initial sample. It implies that the Ni nanoparticles dominate the contribution to catalytic activity compared with α -Ni(OH)₂. Thus an outstanding performance can be expected for the Ni@Graphene since 66% Ni is reduced according to the XPS results. It offers more evidence to prove the importance of metallic Ni particles and core-shell structure in catalysis that the catalytic activity of 550 °C increases further with lower specific surface area, attributed to the increasing size of particles[35, 42] as well as the decreasing number of terrace atoms and atomic steps.[43, 44] For Ni/RGO annealed at 770 °C, despite higher conversion of Ni phase (Figure 1b), its

catalytic activity exhibits a sharp decrease, which could be ascribed to serious structural reform of RGO component (Figure S2a) breaking the synergetic cooperation effect between Ni and RGO.

In particular, Ni@Graphene core-shell sample treated at 450 °C and 550 °C exhibit the higher catalytic activity with K reaching up to 45.0 and 51.9 L·g⁻¹·min⁻¹ respectively, which is almost six folds of initial sample (7.8 L·g⁻¹·min⁻¹) and over ten folds of pure Ni NPs (4.2 L·g⁻¹·min⁻¹) (Table S1). For this distinct core-shell configuration, only (111) facets of Ni component are encapsulated by self-catalyzed graphene layers, which not only guarantees better charge transportation via graphene layers, but also maintains high activity contributed from those exposed low-coordinated facets meanwhile exhibiting sufficient aggregation resistance benefiting from the protection of graphene layers. Comparing the k_{app} and K of α -Ni(OH)₂ with that of α -Ni(OH)₂/RGO, the synergetic cooperation effect between Ni(OH)₂ and RGO is further proved. Herein, RGO, serving as a support material with high conductivity, will not only adsorb the particles on its surface to modulate the structure of particles, but also offer a platform for reaction (adsorb 4-NP to its surface and exchange electron between catalytic agent and 4-NP) so that the samples with RGO exhibit higher catalytic performance. To have an overall glance on catalytic performance in fields of 4-NP reduction, activity data of 26 catalysts from 22 representative works have been summarized in Table S2. It is encouraging to discover that our facilely fabricated Ni@Graphene structure possesses performance superior to most of those listed catalysts, even including noble metal ones. The above facts provide convincing support on the superiority of epitaxial-grown Ni@Graphene core-shell nanostructures as facilely synthesized high efficient catalysts.

4. Conclusion

In this work, we develop facile and green fabrication of diverse Ni/RGO nanostructures following a two-steps strategy: synthesis of α -Ni(OH)₂/RGO composite in water system under ambient condition and then annealing treatment at different temperatures. A unique self-catalyzed epitaxial growth of Ni@Graphene core-shell structure is achieved following the annealing driving kinetic phase transition from α -Ni(OH)₂, NiO to Ni under temperature ≥ 450 °C. This core-shell configuration proves to be distinct to facilitate highly active catalyst benefitting for the synergetic cooperation between Ni core and epitaxial graphene shells. The efficiency for catalyzing 4-NP reduction reaches up to 45.0 and 51.9 L·g⁻¹·min⁻¹ exceeding most reported records including some noble metal based nanostructures. This work provides guideline to develop non-noble metal/graphene catalysis through a facile, environment-friendly approach.

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Notes and references

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initial

350 °C

450 °C

Ni@graphene