



Facile Fabrication of Nickel/Heazlewoodite@Carbon Nanosheets and their Superior Catalytic Performance of 4-Nitrophenol Reduction

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A facile molten salt method was utilized for the synthesis of carbon anchored nickel/heazlewoodite nanoparticles (Ni/Ni₃S₂@C nanosheets) with potassium humate as the carbon and sulfur source and NaCl as template. The morphology, particle size and crystallinity of the products were characterized by various techniques containing TEM, FE-SEM and XRD. Furthermore, the mesoporous Ni/Ni₃S₂@C own easy accessibility of active sites and high surface area (149.04 m²g⁻¹). Thus, the asprepared Ni/Ni₃S₂@C exhibited prominent performance for catalytic reduction of 4-nitrophenol (4-NP). Catalytic reduction

Introduction

Over the last few years, environment pollution and energy shortage have become the most serious issues that human society face. To the best of our knowledge, water is source of life, however, the fresh water is meeting an enormous contamination. What's more, heavy-metal pollution and organic pollution are the significant segments of water pollution, which have the worst effects on health. Of these pollutants, 4nitrophenol (4-NP) is a familiar organic pollutant, which is a highly hazardous and carcinogenic material. It is hard to tackle the 4-NP from environment due to its stable chemical properties and better water solubility. Although 4-NP is environmental hazardous and difficult to handle, 4-NP also has wide adhibition in industry, agriculture and pharmacy etc. So how to solve these problems is imminent. Up till now, a lot of technologies have been developed for nitrophenols (NPs) removal, such as biodegradation, adsorption, photodegradation, Fenton prog-

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of other nitrophenols (NPs) were also tested which can prove that the catalyst own selectivity on reduction of NPs. For durability, the property of the catalyst does not decrease obviously after five cycles. More significant correlations concerning effect of activation parameters ($E_a = 37.21 \text{ kJ mol}^{-1}$) on 4-NP reduction were scrutinized and discussed. Hence, we provide a facile method for fabrication of metal/metal sulfide@C which own better dispersity, small dimension and excellent catalytic performance for further studies.

ress^[1] etc. However, these methods do not make good use of and deal with 4-NP. Furthermore, 4-NP is also a precursor of 4aminophenol (4-AP) which is renewed to be an available material and related in many ways including antipyretic and analgesic drug, sulfur dye, corrosion inhibitor, photographic developer, anticorrosion lubricant and hair-dyeing agent etc. Based on these advantages, chemical reduction of 4-NP is a most efficient and potential method. However, the reaction rate is very slow without catalysts. For this reason, a method of catalytic chemical reduction^[2] comes into researchers eyes. Thus, correlated works have been done during last few decades to make effective reduction of 4-NP to 4-AP.

Usually, the precious metal-based catalysts are still extensively utilized in catalytic reduction of 4-NP, for example platinum,^[3] aurum,^[4] argentum^[5] nanocatalysts etc. However, their high cost, rapid deactivation, low reusability and low earth-abundance limit their widespread application. For the sake of solving these problems, various transition metal catalysts, especially copper-based^[6] and nickel-based^[7] nanocatalysts, which are cost-effective, own high performance and stability have aroused great attraction. And the main factors which effect the catalytic activity of catalysts are the size, shape, crystallinity, and surface state of catalyst. So, the small nanoparticles are the ideal materials. Nevertheless, small nanoparticles could aggregate irreversibly during catalytic reaction systems on account of their high surface energies that dramatically limit catalytic activity.^[8] To solve this problem, many methods have been putting forward, including core-shell nanocomposites,^[9] York-shell nanocomposites,^[10] and nanoparticles supported on various type of nanocomposites supports. In recent years, the supports such as KCC-1,^[11] SBA-15,^[12] $Al_2O_{3_1}^{[13]}$ and other carbon supports^[14] have been used which could effectively avoid aggregation of nanoparticles. However,



the above catalysts are either more expensive or the preparation process is complicated. Therefore, it is highly desirable to develop a high efficient and low-cost catalysts for the reduction of 4-NP.

In the past few years, carbon supported nanocomposites which have versatile applications in the domains of catalysis,^[15] energy storage/conversion,^[16] gas sensing,^[17] environmental remediation^[18] etc., have attracted increasing interests on account of their unique physicochemical properties. Furthermore, based on the good conductivity, thermal/mechanical stability and durability, carbon materials are utilized in versatile catalytic reactions because the electrons transfer can be accelerated. Hence, many carbon supports are synthesized to meet the huge demands, such as graphene,^[19] carbon nanotube,^[20] amorphous carbon^[21] etc. In this work, the amorphous carbon is employed as the supports. It can not only be a good two-dimensional (2D) support, but also can encapsulate the nanoparticles to form core-shell structure by using molten salt process.^[22] Hyeon T et al. applied this method for successful synthesis of carbon-encapsulated ferrite.^[23] By utilizing this method, sodium oleate and other organic materials can also be used as the carbon source to prepare 2D carbon loaded nanomaterials.^[24] However, these sources of carbon are still more expensive.

In this work, potassium humate, a chemical raw material from weathered coal, is used for the first time in the synthesis of carbon loaded nanomaterials. Because potassium humate comes from coal, it contains a certain amount of sulfur, which may contribute to the generation of sulfides. In accordance with the aforementioned, we envision that the fabrication of carbon anchored nickel/heazlewoodite nanoparticles 2-dimensional (2D) material via facile pyrolysis of solid precursor at 600 °C, 700 °C and 800 °C, respectively under argon atmosphere. For debating overall formation process for Ni/Ni₃S₂@C nanocomposites, we systematically investigated synthesis process via one-step pyrolysis with the temperature range from 400 °C to 800 °C. Hereon, we found that throughout the pyrolysis, when the temperature was low, the sulfidation of NiO by the sulfide source from potassium humate. While the temperature increase, the carbon as the reductant to reduce the Ni²⁺ which was complexation with humic acid. In addition, these 2D nanocomposites with open structure, rapid electron transfer and accessible active sites exhibit superior catalytic reduction of 4-NP, and showed better performance ($K/m = 166.8 \text{ s}^{-1}\text{g}^{-1}$). Therefore, this work provides a novel method for the synthesis of Ni/Ni₃S₂@C nanocomposites without the need for additional sulfur source, which is also of great reference for the synthesis of other sulfides.

Results and Discussion

Process for Fabrication of Ni/Ni₃S₂@C

Potassium humate as chemical raw material from weathered coal and natural organic matters are used as the carbon and sulfur source in this work. The FT-IR analysis is further carried



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Figure 1. (a) FT-IR spectra of the potassium humate. (b) TGA (red curve) and DTA (left) measurements of precursor under Ar atmosphere.

400

Temperture (°C)

500

600

300

700

800

200

100

A

out to verify the potassium humate in fabrication of the Ni²⁺ /precursor. As shown in Figure 1(a), a large amount of peaks appears in the spectrum. Peaks at 3695 cm⁻¹ could be ascribed to the N-H bond. And peaks at 3378 cm⁻¹ is attributed to O-H which is combined by hydrogen bond. The adsorption bands at the 1870 cm⁻¹ and 1375 cm⁻¹ could be due to carbonyl vibrations of carboxyl and ketone groups. Similarly, the conjugation of C=C in the aromatic structure, the frame vibration in aromatic ring, and the telescopic shock in C-C bond peaked at 1578 cm⁻¹,1876 cm⁻¹ and 1102 cm⁻¹, respectively. And peaks at 617 cm^{-1} , 534 cm^{-1} and 469 cm^{-1} could be attributed to sulfhydryl and disulfide bond. Because of these organic groups, the potassium humate is also acted as the sulfur source. And the element analysis of the potassium humate in the Table S1 also illustrates that the sulfide content is around 0.88%.

As illustrated in Scheme 1, the synthetic strategy of 2D Ni/ $Ni_3S_2@C$ nanosheets principally consist of the following processes:

- (1) synthesis of precursor;
- (2) carbonization;
- (3) sulfuration;
- (4) carbon-thermal reduction.

The process of fabricating samples is followed by these steps. First of all, in synthesis of precursor, the potassium





Scheme 1. Synthetic scheme of nickel/heazlewoodite nanoparticles supported on amorphous carbon sheet.

humate was dispersed in the deionized water and stirring at 70°C, which the potassium humate can be sufficient hydrogenation to obtain humic acid with the pH value between 8 to 9, and this can be expressed as Equation (1). Moreover, nickel chlorite concentration was transferred into the above suspension, and with stirring at the same temperature so that the ions could interact with humic acid by complexation and chelation. After the reaction, the suspension was cooled to room temperature, with the pH value of 4.2 [Eq. (2)]. The Ni(OH)₂ obtained by hydrolysis was also adsorbed by humic acid. Hence, humic acid played a significant role in this work. The second step is synthesis of the samples. For the fabrication of Ni/Ni₃S₂ nanoparticles homogeneously disperse on carbon nanosheets, the precursor was mixed with sodium chlorite which utilized as the template to prevent the aggregation of the carbon sheet, and make the carbon sheet uniform. whereupon, in-site the precursor was uniformly coated on the outside surface of sodium chlorite which possess the face-centered cubic structure. This mixture was calcined under inert gas (argon) atmosphere and successfully annealing at argon. To optimize the calcination temperature, the TGA analysis was used. Figure 1(b) showed the TGA and DTG curves of the precursor which was treated from room temperature to 800 °C under argon atmosphere. The first loss (~8.7%) below about 100°C could be ascribed to the removal of the physically adsorbed water of the precursor. The subsequent loss (~6.9%) ranged from 100°C to 150°C was attributed to water of hydration in the precursor. And then the humic acid was carbonized from 150 $^{\circ}$ C to 360 $^{\circ}$ C [Eq. (3)]. When the temperature was range from 360 °C to 450 °C, Ni(OH)₂ transferred to NiO. And at the same time, the obtained NiO nucleus was spread, and it guickly combined with sulfide to generate Ni_3S_{2r} , as expressed by Equation (4) and (5). The sample calcinated at 400° C also demonstrated this procedure. As shown in Figure S1(b), the XRD pattern illustrates that the sample contents NiOOH, NiO and Ni₃S₂. Because of the intricate reaction, the nanoparticles were aggregated, obviously showed in Figure S1(a). While the temperature raised to 500 °C, the NiO was all transferred to Ni₃S₂, as displayed in the Figure S2(b). The TEM image Figure S2(a), also showed the nanoparticles uniformly disperse on the carbon nanosheets. Then, when the temperature raised to 600 °C, Ni²⁺, which was complexation and chelation with humic

acid, was reduced by carbon that act as reductant at high temperature as illustrated by Equation (6). After that, 2D carbon anchored Ni/Ni₃S₂ nanoparticles structure is fabricated. At length, with the increase of temperature, the crystallinity of the nanoparticles was better, as exhibited in Figure 4. Finally, the catalysts were separated by dissolved sodium chloride particles in deionized water.

1	tassium humate + $H_2O \rightarrow$ humic acid + OH^- (1))
	(i	1

$$Ni^{2+} + H_2O \rightarrow Ni(OH)_2 + H^+$$
 (2)

humic acid
$$\xrightarrow{\Delta, Ar}$$
 C + CO + CO₂ + H₂O (3)

$$Ni(OH)_2 \xrightarrow{d, Ar} NiO + H_2O$$
 (4)

$$NiO + sulfide \xrightarrow{\Delta, Ar} Ni_3S_2$$
(5)

$$Ni^{2+} + C \xrightarrow{\Delta, Ar} Ni(6)$$
 (6)

Characterized of Ni/Ni₃S₂@C Nanosheets

The morphology of carbon anchored nickel/heazlewoodite nanosheets were characterized by transmission electron microscopy (TEM), and Field-emission scanning electron microscopy (FE-SEM). TEM analysis found that the nickel/heazlewoodite nanoparticles in the Ni/Ni₃S₂@C samples are anchored with uniformly dispersion, as shown in Figure 2(a), (d), (g). As can be seen from Figure 2(a) and (c), the Ni/Ni₃S₂ nanoparticles in S₁-600 were not uniform in size which were in range from 5 to 18 nm. In more details, the TEM image in Figure 2(f) and (i) shown that the Ni/Ni₃S₂ nanoparticles in S₁-700 and S₁-800 are about 6 nm and 20 nm, respectively. Field-emission SEM exhibits the morphology of the carbon sheets. Figure 2(b), (e), (h) shown FE-SEM images of S₁-600, S₁-700 and S₁-800, respectively. And the carbon sheets like a flower experienced flower bud, bursting into bloom and withering throughout this process. This is because when the temperature increased, the carbon sheet becomes thinner and thinner so that it tends to aggregate. When it coated on the sodium chloride, this can avoid aggregation, but while the sodium chloride is molten, the carbon sheet tends aggregation. Meanwhile, the elemental mapping images illustrate that amorphous carbon, Ni, S, and O were homogeneously dispersed in the whole product S1-700 [Figure S5(a~e)], whereas the results also indicated that Ni/ Ni₃S₂ nanoparticles were anchored on the carbon sheets. EDS spectra shows that the weight percentage of different elements, as given in Figure S4.

The crystal phase of carbon anchored nickel/heazlewoodite nanosheets were further confirmed by X-ray diffraction (XRD). The XRD pattern in the Figure 3 showed the Ni/Ni₃S₂@C structural information. The pattern for Ni has three prominent peaks that could be well-indexed to nickel which was face-centered cubic structure (JCPDS no. 04-0850). And the diffraction pattern exhibits three peaks at 44.5°, 51.8°, and 76.4°, corresponding to (111), (200), and (220) crystal face, respectively. Furthermore, other peaks appearing in the pattern



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Figure 2. TEM image of Ni/Ni₃S₂@C nanosheets: (a) S₁-600; (d) S₁-700; (g) S₁-800, and their relative particles size distribution of Ni/Ni₃S₂@C nanosheets: (c) S₁-600; (f) S₁-700; (i) S₁-800. FE-SEM image of Ni/Ni₃S₂@C nanosheets: (b) S₁-600; (e) S₁-700; (h) S₁-800.



Figure 3. XRD patterns of the as-prepared S_1 -600, S_1 -700 and S_1 -800.

could be indexed to heazlewoodite (JCPDS no. 44-1418). Similarly, the X-ray diffraction showed the $2\theta = 21.7^{\circ}$, 31.1° , 37.8° , 44.3° , 49.7° , 50.1° , 54.6° , and 55.1° which were characteristic of the crystal face (101), (110), (003), (202), (113), (211), (104), and (122) respectively, of heazlewoodite. And the characteristic peak of carbon was observed at about $2\theta = 23^{\circ}$,

as shown in Figure S3. In addition, by using Scherer equation,^[25] the results of Ni/Ni₃S₂ nanoparticles are shown in Table 1. This compare with the above TEM consequence in Table 1, the nanoparticles were aggregated to the larger agglomerates on the carbon sheet.

The graphite sheets in the S_1 -600, S_1 -700 and S_1 -800 were also confirmed with Raman spectrum as shown in Figure 4. Two apparent peaks corresponding to the D peak and G peak were observed clearly at 1340 cm⁻¹ and 1590 cm⁻¹, respectively. Herein, the I_D/I_G ratio from the Raman spectrum was used to further characterize the average size of sp² domains.^[26] Hence, the higher ratio of I_D/I_G means the smaller size sp² domains.^[15a] From Figure 5, the ratio of I_D/I_G for S_1 -600, S_1 -700 and S_1 -800 were 0.806, 0.922 and 0.933, respectively. It is reasonable that the I_D/I_G ratio of S_1 -700 is higher than the I_D/I_G ratio of S_1 -600. It can be seen from TEM image the size of nanoparticles is smaller in size of S₁-700, and the amount of Ni/Ni₃S₂ nanoparticles are more adequate on the carbon sheet. And the smaller particles might decorate the surface of the carbon sheet. The reason for I_D/I_G ratio of S₁-800 is higher than S₁-700 is that the aggregation of the carbon sheet.



Table 1. BET surface area, pore volume, pore diameter, crystallite size^[a] and TEM crystallite size of Ni/Ni₃S₂@C and the corresponding catalysts of S₁-600, S₁-700 and S₁-800, respectively.

Catalysts	S_{BET} $[m^2g^{-1}]$	Pore volume [cm ³ g ⁻¹]	Pore diameter [nm]	Crysta size [nm]	llite	TEM crystallite size [nm]	
				Ni	Ni_3S_2		
S ₁ -600	116.05	0.3425	3.85	2.45	1.56	11	
S ₁ -700	149.04	0.3225	3.93	2.39	1.11	6	
S ₁ -800	68.88	0.3989	3.98	2.85	6.21	21	
[a] Crystallite size calculate from XRD using the Scherer equation							

[a] Crystallite size calculate from XRD using the Scherer equation.



Figure 4. Raman spectra of S_1 -600, S_1 -700 and S_1 -800.



Figure 5. XPS spectra of Ni/Ni₃S₂@C: (a) full survey spectrum of S₁-600, S₁-700 and S₁-800; high resolution (b) Ni 2p peaks of S₁-600, S₁-700 and S₁-800; (c) S 2p peaks; (d) C 1s peaks.

For further acknowledged the catalysts, X-ray photoelectron spectroscopy (XPS) was utilized to analyze the surface composition and bonding state of the Ni/Ni₃S₂@C as shown in the Figure 5. And the XPS survey spectrum of Ni/Ni₃S₂@C illustrated that Ni, S, C, O were present in the composition as shown in the Figure 5(a). Two distinct peaks shown in the Figure 5(b) that were obtained in the core level spectrum are Ni 2p at about

856.28 eV and 873.88 eV that corresponded to Ni 2p_{3/2} and 2p_{1/} 2, respectively with the spin-orbit splitting of 17.6 eV, which revealed that the stronger Ni-S bonding. And this also confirm that Ni₃S₂ is formed. The satellite peaks at around 879.78 eV and 861.98 eV could be attributed to Ni $2p_{1/2}$ and $2p_{3/2}$ respectively. Additionally, Figure 5(c) displays the HRXPS spectra of the S-2p binding energy of Ni₃S₂. The obvious peaks at 163.48 eV and 164.58 eV were due to the S $2p_{3/2}$ and $2p_{1/2}$ binding energies, respectively. And the peaks at around 168.3 eV and 169.6 eV would be attributed to the other inconsequential $Ni_x S_v^{[28]}$ Figure 5(d) shows HR-XPS of C in the S1-600, S1-700 and S1-800, respectively. The XPS spectrum illustrated the characteristic peaks of carbon at C-C (at 284.78 eV), C-O-C (at 286.68 eV), C=O (at 288.78 eV) and O= C-O (at 290.48 eV). These peaks could be ascribed to the functional groups in humic acid.

For further investigate the surface property, the N₂ adsorption/desorption isotherm of Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size were utilized to characterize the catalysts. And the result of surface area and pore diameter are shown in Table 1. Each isotherm could be corresponded to a type-IV isotherm with a small hysteresis loop which indicate the presence of mesopores in the catalysts, (Figure 6). Compared with these three catalysts, S₁-700 possesses the largest BET surface area about 149.04 $m^2 g^{-1}$, and the smaller pore diameter about 3.93 nm. This indicate that it could adsorb more molecules. Furthermore, the pore volume of S_1 -700 was 0.3225 m³g⁻¹, the smallest pore volume in three catalysts, which could be attributed to the decoration of the nanoparticles. And it may also suggest that it can accommodate fewer molecules, and the product could easily desorb on the surface.

Catalytic Reaction of 4-NP to 4-AP

For detecting the catalytic performance of the carbon anchored nickel/heazlewoodite nanoparticles\, the catalytic reduction of 4-NP to 4-AP with an excessive amount of sodium borohydride was selected as a model reaction. And all the reactions which were determined by UV-vis spectrophotometry were performed in aqueous solution with no magnetic string. As is known, the reduction of 4-NP to 4-AP at ambient condition is favorable thermodynamically with borohydride which is a strong reductant, because the difference of their standard electrode $(\Delta E_0 = E_0 (4 - NP/4 - AP) - E_0 (H_3 BO_3 / BH^{4-}) =$ potentials -0.76-(-1.33)=0.67 V) is higher than zero.^[29] But the challenge of this reaction is kinetic barrier. With kinetic barrier, the process of this reaction is very slow. Significantly, the UV-vis spectrum indicates that 4-NP aqueous solution shows a strong peak at 317 nm before addition of NaBH₄, and after adding the excessive sodium borohydride, the solution is changed to alkaline condition which suggest that the absorption peak of 4-NP red-shifts from 317 nm to 400 nm immediately as shown in Figure 7 (a), and accompanied with the color of the solution change from light yellow to bright yellow as illustrated in Scheme 2, because of the formation of 4-nitrophenolate anions.



Figure 6. N_2 adsorption-desorption isotherms of (a) S_1 -600), (b) S_1 -700 and (c) S_1 -800; the corresponding BJH desorption pore size distributions curve (inset) and the magnified pore size distributions range from 0–20 nm.



Figure 7. (a) UV-vis spectra of 4-NP before, 1 s after and 24 h after addition of NaBH₄ solution. (b)–(d) UV- vis spectra of 4-NP ions at different time; (b) S₁-600, (c) S₁-700, (d) S₁-800. The plots of (e) C_t/C_0 and (f) $\ln C_t/C_0$ versus reaction time.



Scheme 2. Schematic diagram for 4-NP reduction.

Before detecting the catalytic reduction of 4-NP to 4-AP of the catalyst it must be check: (1) the effect of self-hydrolysis of sodium borohydride reduce the 4-NP; (2) whether the support can be used as the catalyst. Hence, without addition of the catalyst, the adsorption peak at 400 nm have not very noticeable change last for 24 h in the Figure 8(a). Accordingly, there isn't any apparent adsorption peak related to the product of 4-AP after adding S1-700 (C) as Figure S7 shows, this might indicate that the 4-nitrophenolate anions were just adsorbed on carbon sheets, and carbon sheets were inactive for the reaction. After addition of Ni/Ni₃S₂@C to bright solution, the color of the solution fades up which resulted in the decrease in the adsorption peaks of 4-nitrophnolate anions with a new peak appeared at 300 nm [Figure 8(b)] of 4-AP. Moreover, the isosbestic point demonstrates that single product is formation.^[30] Kinetic traces [Figure 8(b), (c), and (d)] show the UV-vis absorption spectra of 4-NP with the reaction time in the



Figure 8. The plots of C_t/C_0 (a) and ln (C_t/C_0) (b) versus reaction time using S_1 -700 catalyst.

presence of S1-600, S₁-700, and S₁-800, respectively. After addition of catalysts, the suspension become colorless, gradually within 360 s. The equilibrium conversion rate of 4-NP was calculated to be 99.9% as summarized in Table 2 when S₁-700 is

Table 2. Reduction of 4-NP by using different catalysts. ^[a]					
$ \begin{array}{c c} \mbox{Catalysts} & \mbox{Amount of} & \mbox{K_{app}} & \mbox{K/m} & \mbox{Conve} \\ & \mbox{catalyst} & [s^{-1}] & [s^{-1}g^{-1}] & [\%] \\ & \mbox{$[\mu g]$} \end{array} $					
S ₁ -500 S ₁ -600 S ₁ -700 S ₁ -800	50 50 50 50	82.8 122.4 166.8 64.0	75.6 89.0 99.9 65.2		
[a] Reduction conditions: temperature (298.15 K), 4-NP (2.95 mL, 0.12 mM), catalysts (50 μ L, 1 mgmL ⁻¹), NaBH ₄ (0.28 mmol), and reaction time (360 s).					

utilized as a catalyst. And while the catalyst was present in the reaction system, there was a rapid decrease with the order of $S_1-700 > S_1-600 > S_1-500 > S_1-800$. In all these cases, S_1-700 proves to be the most efficient among the other catalysts tested.

The kinetic studies of this reaction were carried out by using Langmuir-Hinshelwood equation. With the excess sodium borohydride, this reaction is a pseudo-first-order reaction. So, a plot of the experimental data according to Equation (7) for the different catalysts could give a linear relationship [Figure 8(f)], which can correspond to pseudo-first-order kinetics. In the Equation (7) where C_0 and C_t are the initial concentrations of 4-NP and concentrations of 4-NP at time t, respectively. And K_{app} can represent the apparent rate constant. For comparing the performance of different catalyst, we choose K/m as the standard.

$$ln\left(\frac{C_t}{C_0}\right) = K_{app} \cdot t \tag{7}$$

Catalytic Performance of S₁-700 Catalyst with Different Amount of Sodium Borohydride

For investigating the effect for the amount of sodium borohydride on the catalytic reaction, we do some experiments with different amount of sodium borohydride under other conditions unchanged. It could be seen that the apparent rate constant tends to increase with amount of sodium borohydride increase as shown in Figure S8. In addition, from our work, the synergistic effect about nickel sulfide and metallic nickel nanoparticles is also discussed. Table 3 is summary of K_{app} and

Table 3. Catalytic reduction of 4-NP.						
Catalysts	Amount of catalyst [mg]	NaBH₄ [mmol]	<i>K</i> _{app} [s ⁻¹]×10 ⁻³	<i>K/m</i> [s ⁻¹ g ⁻¹]	R ²	Ref.
S ₁ -700 S ₁ -700 S ₁ -700 S ₁ -500 Ni _{0.22} /CB NCMSS-4 CNFs@Au Pt black Au NCs/rGO Ni@PtNi NCs- rGO Ni ₃ S ₂ @C Ni@Pd/KCC-1	0.05 0.05 0.05 0.05 1.00 7.00 0.15 0.05 0.15 0.40	0.14 0.21 0.28 0.28 2.64 0.30 3.00 0.50 0.50 0.25 0.05 0.25	3.69 7.43 8.34 4.14 9.95 2.82 5.42 0.70 6.18 4.50 0.90 20.4	73.8 148.6 166.8 82.8 9.95 0.41 54.2 15.0 123.6 257.0 6.00 51.0	0.94 0.97 0.99 0.98 0.99 - - - - - - - - - - - - 0.99	# ^[a] # ^[a] # ^[a] [31] [32] [33] [34] [35] [11] [36]
Ag/c-0.05 2.00 0.35 5.32 2.00 -						

K/m values about different catalysts and amount of NaBH₄. With the listed datum, the performance of Ni/Ni₃S₂@C was better than single nickel sulfide and metallic nickel nanoparticles supported on carbon sheets. What's more, our catalytic performance is better than that of many noble nanoparticles catalyst.



Catalytic Performance of S₁-700 Catalyst for the Reduction of Various Nitrophenols

In this work, we choose catalytic reduction of 4-NP as the reaction model, to optimized reaction conditions. The results revealed that with the same condition, the catalytic reduction of 4-NP (360 s) was faster than 4-nitroaniline (480 s) shown in Figure S9(b). Because when –OH connected with benzene ring, the benzene ring could be activated. The consideration of the consumption graphs given in Figure 8 revealed that the initial rate of S₁-700 catalytic reduction of nitrophenols^[37] at same condition followed the sequence of 2,4,6-trinitrophenol > 2,4-dinitrophenol > 4-nitrophenol > 2,6-dinitrophenol > 2-nitrophenol. The results indicate that the catalyst has better selectivity. And the UV-vis spectrum of these nitrophenols are given in the Figure S9 (a), (c), (d), (e). As shown in Table 4, a variety of

Table 4. Reduction of nitrophenols by using S1-700. ^[a]					
Amount of catalysts [µg]	Substrates	K_{app} [s ⁻¹]	<i>K/m</i> [s ⁻¹ g ⁻¹]	Conversion [%]	
50	NO ₂ OH	8.34×10 ⁻³	166.8	99.9	
50	OH NO ₂	3.37	67.4	70.0	
50	NH ₂ NO ₂	5.62	112.4	88.0	
50		9.61	192.2	99.9	
50	OH O ₂ N NO ₂	5.80	116.0	88.1	
50		16.94	338.8	99.9	

nitrophenols could be selectively reduced under these optimized conditions in the presence of S_1 -700 catalyst, and the results are listed on it.

The Activation Parameters for ${\rm S_1}\mathchar`-700$ Catalyzed Reduction of 4-NP

The effect of temperature on the catalytic reaction of 4-NP was investigated via preparing a series of experiments for 4-NP under same condition with the temperature range from 298.15 K to 323.15 K [Figure 9(a)]. The apparent rate constants of catalytic reaction at different temperature are summarized in the Table 5. The activation parameters contain activation

Table 5. [a] Reduction conditions: nitrophenols (2.95 mL, 0.12 mM), S ₁ -700 catalyst (50 μ L, 1 mgmL ⁻¹), NaBH ₄ (0.28 mmol), temperature (298.15 K) and reaction time (360 s).Table 5 Reduction of 4-NP by using S ₁ -700 at different temperature. ^[a]					
Amount of Temperature [K] K_{app} [s ⁻¹] R^2 catalysts [µg]					
50	298.15	8.34×10 ⁻³	0.9921		
50	303.15	13.10×10^{-3}	0.9840		
50	308.15	18.54×10^{-3}	0.9912		
50	313.15	23.18×10^{-3}	0.9857		
50	318.15	25.25×10^{-3}	0.9907		
50 323.15 30.00×10 ⁻³ 0.9884					
[a] 4-NP (2.95 mL, 0.12 mM), $S_1\mbox{-}700$ catalyst (50 $\mu\mbox{L},$ 1 mg mL $^{-1}\mbox{)},$ NaBH $_4$ (0.28 mmol).					

energy, activation enthalpy, activation entropy, etc. And the activation energy which is a critical kinetic parameter for heterogeneous catalytic reaction is calculated by using the Arrhenius equation [Eq. (8)]. From the Equation (8), the E_a is activation energy, and where A is pre-exponential factor. Hence, we could calculate the activation energy (E_a) is 39.79 kJ mol⁻¹, which is between 8.368 and 41.84 kJ mol⁻¹ for the surface catalytic reaction.^[38] What's more, the activation parameters, activation enthalpy (ΔH^{\pm}) and activation entropy (ΔS^{\pm}) are calculated via the Eyring equation [Eq. (9)]. From the equation, where k_B and h are Boltzmann constant and Planck constant, respectively. And we also calculated the ΔH^{\pm} is 37.21 kJ mol⁻¹, and ΔS^{\pm} is $-158.73 \text{ Jmol}^{-1}$ (h). With obtained ΔH^{\pm} and ΔS^{\pm}



Figure 9. The plots of (a) ln (C_t/C_0) versus reaction time, (b) ln K versus 1/T and (c) ln (K_{app}/T) versus 1/T using S₁-700 catalyst.

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values, the calculated $\Delta G^{*}_{(298.15 \text{ K})}$ is 84.54 kJ mol⁻¹ which demonstrates that the reaction requires energy. It states that the reaction is feasible in the presence of the S₁-700 in this experiment.

$$ln(K_{app}) = -\frac{E_a}{RT} + lnA(8)$$
(8)

$$ln\left(\frac{K_{app}}{T}\right) = -\frac{\Delta H^{\#}}{RT} + ln\frac{k_{B}}{h} + \frac{\Delta S^{\#}}{R}$$
(9)

Mechanism for the Reaction of 4-NP

On the basis of our experimental results and related literature,^[31,39] the mechanism for the catalytic reaction of 4-NP by means of Ni/Ni₃S₂@C is proposed on account of Langmuir-Hinshelwood mechanism. To start with, the borohydride anion (BH_4^{-}) react with H₂O which root in the concentration, to fabricate metaborate (BO2-) and hydrogen on the surface of nickel/heazlewoodite nanoparticles, as shown by Equation (10) and a large proportion of hydrogen is adsorbed on the surface of the nanoparticles, inducing a nanoparticles hydride complex to be the active reductant. At the same time, 4-nitrophenolate anions are adsorbed onto the amorphous carbon sheets via electrostatic interaction, for example hydrogen bond with -COOH which exist in the amorphous carbon. This can put the substrate close approximately to the active reductant. And then, the active reductant is oxidized with the charge lost. The lost electron is quickly transferred through the carbon sheet to 4-nitrophelate anions. Stepwise reduction of the nitro groups to amino products is accomplished as soon as possible. Ultimately, 4-AP desorbed from carbon sheets. The hydroxylamine intermediates are abscission from carbon sheets, quickly, which can make more nitroso close to the carbon sheets to accelerate the reaction.

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$$
 (10)

The Catalytic Durability of $\mathsf{S}_1\text{-}700$ in Reduction of 4-NP in the Presence of NaBH_4

The reusability as a crucial measure of catalytic durability is also tested for S_1 -700 catalyst in catalytic reduction of 4-NP at 298.15 K. For this purpose, after every complete catalytic reaction, S_1 -700 catalyst was washed with water and ethanol, dried in vacuum at 70 °C. And after 5 cycles as given in Figure 10, the durable performance of S_1 -700 catalyst had not very decreased apparently. The conversion of 4-NP was over 97% for every cycle. After the reaction, the S_1 -700 catalyst was characterized by XRD, and from XRD result, the phase of this catalyst was not changed (Figure S10). This proved that our catalyst has better stability for catalytic applications.

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Figure 10. Reusability of S₁-700 for reduction of 4-NP.

Conclusions

In summary, a novel catalyst nickel/heazlewoodite nanoparticles which were anchored onto amorphous carbon (Ni/Ni₃S₂@C nanosheets) were successfully fabricated by a facile molten salt method. And potassium humate, a raw material from weathered coal could be served as carbon source and sulfur source. The particle size of as-prepared catalysts could be adjusted by pyrolysis the power at different temperature. The obtained products with large surface area and accessible active sites exhibited excellent performance on catalytic reduction of 4-NP via excess sodium borohydride. In addition, other nitrophenols were also tested to indicate the selectivity of the catalyst. What's more, it's indicated that amorphous carbon sheets play an important role in catalytic activity. And the as-prepared products also have other applications to be a promising material.

Experimental Section

Reagents: The chemical reagents were used without purification after purchase. The Nickle chloride tetrahydrate (NiCl₂·4H₂O) and sodium borohydride (NaBH₄) were purchased from Tianjin Hongyan Chemical Reagent Company; potassium humate, an industrial raw material, was obtained from Xinjiang Double Dragon Humic Acid Company; 4-nitrophenol (4-NP) was purchased from Aladdin; 2-nitrophenol (2-NP), 4-nitroaniline, 2,6-dinitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenolwere from Shanghai Shanpu Chemical Co. LTD. The water that was used throughout this work was purified using a Millipore system. All other reagents were of analytical grade except potassium humate.

Synthesis of Ni/HA Precursor: In the typical synthesis of precursor, first of all, potassium humate (5 g) was dissolved into 200 mL of deionized water, and then the brown suspension was ultrasonicated to obtain the homogeneous solution. Next, the homogeneous solution was stirred at 70 °C for 12 h. At the same time, 50 mmol of NiCl₂·4H₂O was dissolved in another 100 mL of deionized water. After stirring for 12 h, the green solution was



quickly added in the brown solution. Subsequently, the mixture was stirred at the same temperature for 24 h. And after the dispersion was cooled to the room temperature, the mixture was freeze-dried. Finally, the precursor was obtained.

*Fabrication of Ni/Ni*₃S₂@*C Catalyst:* In a typical procedure for preparation of the catalyst, the precursor was uniformly mixed with sodium chloride, with the weight ratio of precursor and NaCl (1: 15). And after that, the mixed powder was calcined at 600 °C, 700 °C and 800 °C, respectively, with the heating rate of 5 °C min⁻¹ in an airtight tube furnace under flowing argon atmosphere for 4 h. Once cooled to room temperature, the black power was harvested by centrifugation at 12000 rpm for 10 minutes, and washed several times with deionized water to remove the NaCl. And then the two-dimensional Ni/Ni₃S₂@C nanosheets were obtained. Ultimately, the as prepared samples were marked as S₁-600, S₁-700, S₁-800, respectively.

Catalytic Property towards Reduction of 4-NP: To the best of our knowledge, 4-NP is poisonous, but the products (4-AP) is practical ingredients. Thus, the catalytic reduction of nitro-compounds via NaBH₄ are chosen to be the catalytic model. In the typical procedure, 2.95 mL of aqueous 4-NP (0.12 mM) was transferred into a standard guartz cell with the path length of 1 cm. Subsequently, the sodium borohydride was added to the 4-NP solution. And then, the color of the solution changed from pale yellow to bright yellow. After that, 50 μ L of the catalyst (concentration 1 mg mL⁻¹) was added into the above bright yellow concentration, and the reduction reaction was winded up until it became colorless. At the same time, the progress of 4-NP reduction reaction was monitored from 250 nm to 500 nm by the UV-vis adsorption spectra. The conversion (%) of 4-NP could be calculated by the Equation (1). In order to test the durability of the S1-700 catalyst, the reduction reaction model was amplified 20 times which compare with the origin system. While the bright color was changed to colorless, the suspension was monitored by the UV-vis adsorption spectra. And after every cycle, the catalyst was washed with deionized water and ethanol. Then, it was dried in vacuum at 70 °C. The same procedure was repeated for 5 cycles.

Material characterization: The morphology and microstructure of the samples were characterized by transmission electron microscopy (TEM, HitachiH-600) and Field-emission scanning electron microscope (FE-SEM) equipped with Energy Dispersive Spectrometer (EDS) by using silicon wafer as basement on a Hitachi SU8010 microscope operated at 5 kV. The crystal structure of the samples was determined by a Rigaku D/max-ga X-ray diffractometer (XRD) at a scanning rate of 6° min⁻¹ with Cu Ka radiation ($\lambda = 1.54178$ Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo XPS ESCALAB 250Xi instrument with an Al K_a (1486.8 eV) X-ray source. Thermogravimetric analysis (TGA) was taken on a thermogravimetric analyzer (Netzsch TGA 409) from ambient to 800 °C with a heating rate of 10 °C min⁻¹ under Ar atmosphere. The surface area and porosity analyzer were obtained on a Micromeritics ASAP 2020 physisorption instrument by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a BRUKER VERTEX 70 with a spectral range from 400 to 4000 cm⁻¹. The UV-visible absorption spectra were recorded using a Hitachi UV-2550 spectrophotometer equipped with an integral sphere assembly.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: activation parameters \cdot catalytic reduction \cdot Ni/Ni₃S₂@C \cdot nitro compounds \cdot potassium humate

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SuperHUMATE performance: A

novel catalyst, carbon anchored

cated by facile pyrolysis of solid

nickel/heazlewoodite nanoparticles

(Ni/Ni₃S₂@C nanosheets), was fabri-

precursor with potassium humate as carbon source and sulfur source. The

Ni/Ni₃S₂@C nanocatalyst exhibited

superior catalytic performance towards 4-nitrophenol reduction with excessed sodium borohydride as reactant, which the K/m value up

to 166 $s^{-1}q^{-1}$.

Solid precursor After calcinating

X. Wang, J. Lu, Y. Zhao, X. Wang, Z. Lin, X. Liu, R. Wu, Prof. C. Yang, Prof. X. Su*

1 – 12

Facile Fabrication of Nickel/Heazlewoodite@Carbon Nanosheets and their Superior Catalytic Performance of 4-Nitrophenol Reduction Facile fabrication of nickel/heazlewoodite@carbon #nanosheets and their superior catalytic performance of 4-nitrophenol #reduction from South China University of Technology, Xinjiang University and Academy of Instrument Analysis #catalyst

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