Preparation of Reduced-Graphene-Oxide-Supported CoPt and Ag Nanoparticles for the Catalytic Reduction of 4-Nitrophenol

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Abstract: Composite nanostructure materials are widely used in catalysis. They exhibit several characteristics, such as the unique structural advantage and the synergism among their components, which significantly enhances their catalytic performance. In this work, CoPt nanoparticles and reduced-graphene-oxide-based nanocomposite catalysts (rGO/CoPt, rGO/CoPt/Ag) were prepared by using a facile co-reduction strategy. The crystalline structure, morphology, composition, and optical characteristics of the CoPt nanoparticles, rGO/CoPt nanocomposite, and rGO/CoPt/Ag nanocomposite catalysts were investigated by a set of techniques. The \( I_G/I_C \) value of the rGO/CoPt/Ag nanocomposite is 1.158, higher than that of rGO/CoPt (1.042). The kinetic apparent rate constant, \( k \), of the rGO/CoPt/Ag nanocomposite against 4-nitrophenol (4-NP) reduction is 5.306 min\(^{-1}\), which is higher than that of CoPt (0.495 min\(^{-1}\)) and rGO/CoPt (1.283 min\(^{-1}\)). The normalized rate constant, \( k_{nor} \), of the rGO/CoPt/Ag nanocomposite is 56.76 min\(^{-1}\)mg\(^{-1}\), which is higher than some other catalytic materials. The rGO/CoPt/Ag nanocomposite shows a significantly enhanced catalytic performance when compared to CoPt nanoparticles and the rGO/CoPt nanocomposite, which may confirm that the novel rGO/CoPt/Ag nanocomposite is a promising catalyst for the application of catalytic fields.

Keywords: rGO/CoPt/Ag; NaBH\(_4\); catalytic reduction; 4-nitrophenol

1. Introduction

The problem of environmental pollution caused by the fast evolution of technologies in the chemical industry has triggered significant attention [1–5]. 4-nitrophenol (4-NP) is a nitroaromatic compound widely present in the environment and can negatively affect the health of both animals and humans. Several methods, including photo-degradation, chemical oxidation, and biodegradation, are used to remove or reduce the presence of 4-NP in the environment [6–9]. However, these techniques are expensive and have been proven to be only partially effective. Contrary to these methods, the reaction by NaBH\(_4\) is a low-cost technique used in a large variety of cleaning processes. 4-aminophenol (4-AP) instead, has been extensively used in many fields [10–12].

Currently, noble metal catalysts based on Pt, Pd, Ag, and Au have been widely employed in the catalytic process of organic pollutants [12–17]. However, their increasing price and limited availability restrict their application. Besides, their catalytic efficiency does not satisfy the application requirements. For these reasons, abundant and low-cost catalysts with both high catalytic efficiency and recyclability have recently attracted the attention of several researchers. Therefore, many studies have investigated the characteristics of noble metal alloys with magnetic transition metals, due to their unique natural properties and excellent catalytic activity [18–20]. Co\(_x\)Pt\(_{100-x}\) alloy catalysts are particularly promising since Co is a low-cost magnetic transition metal, and the addition of an appropriate amount of Pt significantly increases the catalytic performance. In addition, various Co\(_x\)Pt\(_{100-x}\) alloy morphologies, such as nanoparticles [21], nanoflowers [22], and...
nanotubes [23], can improve the properties of the catalyst with other metal elements. In this case, however, the catalytic performance still needs to be improved due to the low electron transfer rate and the small active surface area of the catalyst. Although these open points can be addressed by reducing the Co$_{100-x}$Pt$_x$ alloy size to increase its surface area, the aggregation process may affect the activity of the alloy. A highly efficient catalyst may depend on three factors: (1) efficient adsorption properties for both pollutants and reducing agents, (2) a superior electron-transportation ability, and (3) an ultra-large surface area. To fulfill these requirements, the catalyst can be immobilized onto a support. Graphene has been applied as a support for catalysts because of its high electrical conductivity and large surface area [24]. Despite graphene being one of the most popular carbon-based support materials, its hydrophobic surface limits its application range. One of the derivatives of graphene is reduced graphene oxide (rGO). This material consists of a hydrophilic surface and has triggered the attention of several scientists since it can be employed as a catalytic support due to its excellent adsorption properties, its good chemical stability, etc. [25–27].

In this work, the CoPt, rGO/CoPt, and rGO/CoPt/Ag catalysts were synthesized by employing a simple, effective co-reduction process. The effects of the composition-dependent catalytic performance were thoroughly investigated. Their excellent magnetic response enables their magnetic separation from a mixture for recycling purposes. Due to the unique structural advantage, rGO/CoPt/Ag has excellent catalytic performance in 4-NP reduction. The results of this work demonstrate that this nanocomposite is a promising catalyst, exhibiting an enhanced catalytic performance, which can be used to improve the durability of several catalytic processes.

2. Results and Discussion

2.1. Characterization and Properties of CoPt, GO, rGO, rGO/CoPt, and rGO/CoPt/Ag

The crystallite structures of the samples were acquired via XRD. Figure 1a displays XRD patterns of GO and rGO. The peak located at $2\theta = 10.6^\circ$ can be attributed to the existence of the (002) plane of GO in Figure 1a [28]. Moreover, the GO diffraction peak disappears, and peak (002) appears at $2\theta = 23.1^\circ$, confirming that GO was reduced to rGO (Figure 1a) [29]. This result confirms that the hydrazine hydrate can efficiently reduce GO into rGO. Figure 1b displays XRD patterns of CoPt nanoparticles (NPs), rGO/CoPt, and rGO/CoPt/Ag nanocomposites. The broad peak at $2\theta = 41.85^\circ$ corresponds to the plane of the face-centered tetragonal (FCT) CoPt (111) [30]. Figure 1b displays that the rGO/CoPt peak at $2\theta = 41.86^\circ$ indicates the presence of CoPt NPs, confirming the formation of the rGO/CoPt nanocomposite. For rGO/CoPt/Ag, the peaks located at $2\theta = 38.15^\circ$, 44.31$^\circ$, 64.43$^\circ$, and 77.42$^\circ$ demonstrate that Ag ions can be effectively reduced into Ag NPs [31]. Moreover, the absence of the characteristic peak at $2\theta = 10.6^\circ$ of the (002) plane of GO is due to the GO reduction during the formation of rGO/CoPt and rGO/CoPt/Ag nanocomposites [32]. Furthermore, the characteristic diffraction peaks of rGO are not obvious in both rGO/CoPt and rGO/CoPt/Ag. This phenomenon may be due to the lower content of rGO and weaker diffraction peak intensity of rGO compared to CoPt and Ag [33].

Raman spectra were applied to analyze the structural properties of samples. Figure 2 displays Raman spectra of CoPt, GO, rGO, rGO/CoPt, and rGO/CoPt/Ag. Figure 2 shows that two prominent peaks appear in the 1200–1600 cm$^{-1}$ range, corresponding to the characteristic peaks (D and G bands) of graphene-based materials. The two peaks may indicate that rGO is included in the rGO/CoPt and rGO/CoPt/Ag since the two peaks (D and G bands) usually represent the nature of carbon materials [34]. The D peak is assigned to the disorder and defects, and the G peak represents the ordered vibrational sp$^2$-bonded carbon atoms [35,36]. The peak intensity ratio ($I_D/I_G$) can provide an estimate of the defect intensity in graphene-based materials [37]. The values of $I_D/I_G$ for GO, rGO, rGO/CoPt, and rGO/CoPt/Ag are about 0.843, 1.018, 1.042, and 1.158, which indicate that the highest concentration of defects is present in rGO/CoPt/Ag [38]. Such a high $I_D/I_G$ value of rGO/CoPt/Ag is due to the significantly high number of defects and the
disorder of the rGO sheets during the formation of the nanocomposite [39]. Furthermore, the catalytic activity of rGO/CoPt/Ag can be enhanced by these defects, which can maybe serve as active sites [40].

![Figure 1. XRD patterns of (a) GO and rGO, (b) CoPt, rGO/CoPt, and rGO/CoPt/Ag.](image)

![Figure 2. Raman spectra of CoPt, GO, rGO, rGO/CoPt, and rGO/CoPt/Ag.](image)

To verify the effective reduction of GO, and the formation of rGO/CoPt and rGO/CoPt/Ag nanocomposites, the FT-IR spectroscopy of all the samples was studied. Figure 3 displays absorption peaks of CoPt at about 879, 1049, 1087, 2923, and 2971 cm\(^{-1}\) assigned to the C-H, C-O, C-N, and C-H groups, which may be a residue produced during the CoPt NPs' formation process. The GO peaks are located at about 3422, 1732, 1625, 1397, and 1051 cm\(^{-1}\), corresponding to O-H, C=O, and skeletal vibrations of the graphitic domains, C-OH and C-O, respectively [41,42]. It is well-known that the peaks of oxygen-containing groups would become weak or disappear when the GO is reduced into rGO [33,43]. However, compared to GO, the relative peak intensities of those oxygen-containing groups (3422, 1397, and 1051 cm\(^{-1}\)) increase in rGO/CoPt and rGO/CoPt/Ag, which may be due to the presence of CoPt NPs, and this result may confirm the formation of the composites.
XPS in the 30–900 eV range was measured to prove the composition of rGO/CoPt/Ag. XPS survey spectra of GO and rGO/CoPt/Ag are shown in Figure 4a. Figure 4a confirms that Pt, C, Ag, O, and Co elements are present in rGO/CoPt/Ag. To further study the chemical valence of all samples, the high-resolution XPS spectra of C1s, Pt4f, Ag3d, and Co2p were collected. The results are shown in Figure 4b–f. As shown in Figure 4b, the peaks of C1s of GO located at 284.8, 287.1, and 288.5 eV confirm the existence of C=C, C=O, and C=O. However, only two peaks can be observed in Figure 4c, and they accord with C=C and C=O of C1s. The C=O peak disappears, and the intensity of the C-O peak significantly decreases due to the formation of rGO. These results are in agreement with the results of FT-IR and Raman spectroscopy. Figure 4d shows the Co2p spectrum of rGO/CoPt/Ag, and there are four peaks. The peaks in the 778–783 and 792–800 eV range accord with Co⁰ and Co⁵⁺, which confirms the oxidation of the surface of the alloy NPs [44,45]. Figure 4e shows the spectra of Pt4f, and the two peaks at 71.6 and 74.8 eV correspond to Pt4f₇/₂ and Pt4f₅/₂, respectively. Figure 4f shows that the peaks at 367.8 and 373.8 eV in the Ag3d spectrum accord with Ag3d₅/₂ and Ag3d₃/₂, respectively [46].

High-angle annular dark-field scanning TEM (HAADF-STEM) and EDS mapping were applied to study the elemental distribution of rGO/CoPt/Ag. The results are shown in Figure 5a–e: C, Ag, Co, and Pt elements are evenly distributed in the sample, proving the formation of rGO/CoPt/Ag. The elemental composition of rGO/CoPt/Ag was analyzed via EDX. Figure 5f shows that rGO/CoPt/Ag comprises C, Ag, Co, and Pt elements. Supplementary Figure S1 shows the high-resolution TEM image of rGO/CoPt/Ag, and it confirms the presence of CoPt NPs and Ag NPs in rGO/CoPt/Ag. These results are in accordance with the results of XRD, FT-IR, and XPS.

The magnetic property of rGO/CoPt/Ag was investigated via SQUID. Figure 6 shows that the Ms is about 29.97 emu/g, and the rGO/CoPt/Ag nanocomposite exhibits a strong magnetic response (inset of Figure 6). The magnetic response property of the nanocomposite makes it easily separable from its mixture by applying an external magnetic field for recycling purposes.
Figure 4. (a) Survey XPS spectra of GO and rGO/CoPt/Ag, (b) XPS spectra of C1s of GO, (c) C1s, (d) Co2p, (e) Pt4f, and (f) Ag3d of rGO/CoPt/Ag.

2.2. Catalytic Applications of CoPt, rGO/CoPt, and rGO/CoPt/Ag Catalysts

The CoPt, rGO/CoPt, and rGO/CoPt/Ag were applied to the 4-NP reduction with NaBH₄ at normal temperature. The catalytic performances of CoPt, rGO/CoPt, and rGO/CoPt/Ag were monitored via UV-Vis in the 250–500 nm range. Although the 4-NP reduction reaction with NaBH₄ is thermodynamically advantageous based on the standard electrode potential, its kinetics almost limit the reaction in the absence of a catalyst [47]. Moreover, after adding the NaBH₄ aqueous solution, the peak shifts to 400 nm, confirming that 4-NP anions were formed [48]. The peak intensity remains constant with time, and the catalytic reduction reaction does not proceed further without a catalyst. As soon as there is an addition of catalysts, the intensity of the absorption peak decreases. Furthermore, the peak of 4-AP appears at 300 nm. Figure 7a–c displays the time-dependent UV-Vis spectra of the reduction reaction with NaBH₄ by CoPt, rGO/CoPt, and rGO/CoPt/Ag catalysts. Figure 7a–c displays that rGO/CoPt/Ag exhibits the highest catalytic performance among the investigated catalysts, completing the reduction reaction in 1 min under the same experimental conditions. This is followed by rGO/CoPt (4 min) and CoPt (8 min). Combining these results makes it possible to confirm that the better
catalytic performance of rGO/CoPt/Ag compared to other catalysts may originate from the synergy among its components.

Figure 5. (a) HAADF-STEM image, (b–e) EDS mapping, and (f) EDX spectrum of rGO/CoPt/Ag.

Figure 6. Hysteresis loop of rGO/CoPt/Ag at room temperature.
To investigate the reduction kinetics of 4-NP, the concentration of NaBH<sub>4</sub> was higher than that of 4-NP during the catalytic reaction. Therefore, the catalytic system accords with the pseudo-first-order reaction kinetics, which can be described as follows [49,50]:

\[
\ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = -kt
\]

where \(A_0\) and \(A_t\) are the ratio of absorbance at an initial and certain time, respectively. The parameter \(k\) is an apparent rate constant, whereas \(t\) is the reaction time. In Equation (1), the value of \(k\) can be obtained by assuming a linear correlation between the time \(t\) and \(\ln(\frac{A_t}{A_0})\). The rate of the catalytic reduction exhibits a positive correlation with the value of \(k\). Figure 8a–c displays that \(k\) of rGO/CoPt/Ag is 5.306 min<sup>−1</sup>, which is higher than that of rGO/CoPt (1.283 min<sup>−1</sup>) and CoPt (0.495 min<sup>−1</sup>), indicating that rGO/CoPt/Ag possesses an excellent catalytic performance.

Furthermore, the normalized rate constant \((k_{\text{norm}} = k/m)\) was studied to display the catalytic reduction performance of the rGO/CoPt/Ag catalyst. Herein, thermogravimetric analysis (TGA) was performed (Figure 9). TGA shows that the CoPt and Ag loading was about 77.9 wt.% in the rGO/CoPt/Ag catalyst, and the weight loss may be due to the existence of moisture, rGO, etc. [51]. Table 1 shows the values of \(k_{\text{norm}}\) and other parameters. As shown in Table 1, the catalytic activity of rGO/CoPt/Ag is comparable to or better than that of other catalytic materials [52–55]. In order to investigate the reusability of the rGO/CoPt/Ag nanocomposite, the catalyst was separated from the reaction mixture after each run by using an external magnet, and then the sample was washed with deionized...
water for the next cycle under the same conditions. Figure 10 shows the reusability of rGO/CoPt/Ag for 4-NP reduction. The catalyst can be recycled four times, confirming the stability of rGO/CoPt/Ag during the catalytic reaction.

![TGA thermogram of the rGO/CoPt/Ag catalyst.](image)

Table 1. Comparison of catalytic activity for the 4-nitrophenol reduction by different catalysts.

| Catalysts       | Mass (µg) | k (min⁻¹) | k\textsubscript{nor} (min⁻¹mg⁻¹) * | Reference |
|-----------------|-----------|-----------|-----------------------------------|-----------|
| Ag NPs          | 32        | 0.36      | 11.25                             | [52]      |
| Fe₃O₄@SiO₂@Ag   | 2         | 0.14      | 70                                | [53]      |
| MSAg-50         | 50        | 1.18      | 23.6                              | [54]      |
| Cu₂O@CuO(Au-Pd) | 84.5      | 1.158     | 13.7                              | [55]      |
| rGO/CoPt/Ag     | 93.48     | 5.306     | 56.76                             | This work |

*\textit{k\textsubscript{nor} = k/m} (k: apparent rate constant, m: the quantity of catalysts).

2.3. Possible Catalytic Mechanism

The enhanced catalytic activity of the rGO/CoPt/Ag catalyst, when compared to the other catalysts, is perhaps due to the following factors: (1) an unusual morphology of the rGO/CoPt/Ag nanocomposite catalyst provides the high adsorption capacity, which decreases the induction time [56,57], and (2) the synergistic effects among its components strongly enhance its catalytic activity [58]. Figure 11 displays the probable mechanism for 4-NP reduction with the rGO/CoPt/Ag nanocomposite by NaBH₄: BH₄⁻ ions act as both the hydrogen source and the electron donor, and it is provided by the ionization of NaBH₄ in water. However, without rGO/CoPt/Ag, the catalytic reduction reaction cannot proceed. As the catalyst is added into the system, the BH₄⁻ ions and 4-NP are adsorbed by rGO/CoPt/Ag, due to its layered wrinkle structure, which provides a very strong adsorption capacity. The electrons transfer to rGO/CoPt/Ag from BH₄⁻ ions, the active hydrogen species are formed, and then the active hydrogen species reduce 4-NP into 4-AP [51,59]. Lastly, 4-AP is desorbed from rGO/CoPt/Ag.
The rGO/CoPt/Ag nanocomposite catalyst was obtained. The rGO/CoPt catalyst was prepared by employing a similar strategy without adding AgNO₃ in the aqueous solution. The two solutions were then mixed and mechanically stirred for 10 min. The temperature was then raised to 320 °C for 60 min. The two solutions were then mixed and mechanically stirred for 10 min to form nanoparticles of CoPt. The mixture was sonicated for 10 min, then dried at 60 °C overnight. After complete drying, the rGO/CoPt/Ag nanocomposite catalyst was obtained. The rGO/CoPt catalyst was prepared by a modified Hummers' method from graphite powder. Possible catalytic mechanism for conversion of 4-NP into 4-AP [51,59]. Lastly, 4-AP is desorbed from rGO/CoPt/Ag.

Figure 10. Reusability of the rGO/CoPt/Ag nanocomposite catalyst for the 4-NP reduction.

Figure 11. Possible catalytic mechanism for conversion of 4-NP into 4-AP upon the addition of the rGO/CoPt/Ag nanocomposite catalyst with NaBH₄.

3. Materials and Methods

3.1. Materials

Cobalt acetylacetonate [Co(acac)₂], platinum acetylacetonate [Pt(acac)₂], oleic acid (OA), oleyl amine (OAm), and dibenzyl ether (C₁₄H₁₄O) were obtained from Aladdin Biochemical Technology Co., Ltd. Silver nitrate (AgNO₃), 4-nitrophenol (4-NP), sodium...
borohydride (NaBH₄), hydrazine hydrate (H₆N₂O), graphite powder, sulfuric acid (H₂SO₄), potassium persulfate (K₂S₂O₈), phosphorus pentoxide (P₂O₅), phosphoric acid (H₃PO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), and hydrochloric acid (HCL) were obtained from Sinopharm Chemical Reagent Co., Ltd. GO was prepared by a modified Hummers’ method from graphite powder [60,61]. All the chemicals were used without further treatment.

3.2. Preparation of the CoPt Nanoparticles

A total of 0.5 mmol of Co(acac)₂ and 0.5 mmol of Pt(acac)₂ were mixed with oleic acid, oleyl amine, and dibenzyl ether. The mixture was sonicated for 15 min and then heated up to 100 °C for 60 min. The temperature was then raised to 320 °C for 60 min. Finally, the nanoparticles were washed and obtained.

3.3. Preparation of the rGO/CoPt and rGO/CoPt/Ag Nanocomposites

The preparation process of the rGO/CoPt/Ag catalyst is shown in Scheme 1. A total of 50 mg of GO was dispersed in deionized water and sonicated for 60 min. AgNO₃ (0.3 mmol) and CoPt (50 mg) were dispersed in deionized water (10 mL) and sonicated for 10 min. The two solutions were then mixed and mechanically stirred for 10 min and heated up to 90 °C. Then, 4 mL of a hydrazine hydrate was injected. The temperature was kept at 90 °C for 60 min, washed, and vacuum-dried at 60 °C overnight. After complete drying, the rGO/CoPt/Ag nanocomposite catalyst was obtained. The rGO/CoPt catalyst was prepared by employing a similar strategy without adding AgNO₃ in the aqueous solution.

Scheme 1. Schematic illustration for the synthetic process of the rGO/CoPt/Ag nanocomposite.

3.4. Catalytic Reduction of 4-Nitrophenol

The catalytic performances of the CoPt, rGO/CoPt, and rGO/CoPt/Ag catalysts were investigated by reducing 4-NP by NaBH₄. Such a catalytic reduction process has been widely used to estimate the catalytic properties of many nanomaterials. In this work, all the reactions were monitored via UV-Vis spectroscopy: 4-NP (0.1 mL, 0.005 mol/L light yellow) and deionized water (2 mL) were added to the quartz cuvette. Upon adding 1 mL of NaBH₄ (0.2 mol/L), the peak of the solution shifted to 400 nm, and the color changed to bright yellow. The reaction started after adding 60 µL of catalyst aqueous dispersion (2 mg/mL). The color changed to colorless, and the intensity of the peak located at 400 nm decreased. The characteristic peak appeared at 300 nm, confirming that 4-NP was reduced into 4-AP by the action of the catalysts. The catalytic activity of the CoPt, rGO/CoPt, and rGO/CoPt/Ag catalysts was investigated and compared.
More detailed information of the materials and methods of all the characterization techniques are offered in the Supplementary Materials.

4. Conclusions

In summary, the rGO-supported nanocomposite catalyst (rGO/CoPt and rGO/CoPt/Ag) was synthesized by a facile and robust chemical reduction method. The great values of $k$ and $k_{nor}$ for rGO/CoPt/Ag were 5.306 min$^{-1}$ and 56.76 min$^{-1}$mg$^{-1}$, indicating the superb catalytic activity for 4-NP at room temperature, which may be due to the unique structural advantage and the synergy of the rGO/CoPt/Ag nanocomposite catalyst. This work may not only present a new kind of nanocomposite catalyst for the catalytic field, but may also provide a facile route to construct desired graphene-based nanocomposite catalysts for catalytic research.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11111336/s1, Figure S1: High-resolution TEM image of rGO/CoPt/Ag.

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