

Research Article

Room-Temperature Polyol Synthesis of Ag/SiO₂ Nanocomposite as a Catalyst for 4-Nitrophenol Reduction

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We prepared silver nanoparticles (AgNP) embedded in SiO₂ using a green polyol approach by conducting the synthesis at ambient temperature and pH. Glycerol solutions of SiO₂ and silver nitrate were stirred overnight at room temperature. UV-vis spectra and TEM images of the reaction dispersion and XRD patterns of the centrifuged solid confirmed formation of AgNP (6 ± 2 nm) were embedded in SiO₂. AAS showed that, about 50% of initial silver was deposited on SiO₂. The presence of SiO₂ enhanced the formation of AgNP and the stability of Ag/SiO₂ in glycerol. The reason for these findings was probably the ultrasonic-probe dispersion of SiO₂ in glycerol, which caused chemical interactions between glycerol and SiO₂. Compared to bare AgNP, the AgNP/SiO₂ demonstrated higher catalytic activity toward 4-nitrophenol reduction by NaBH₄. The highest apparent rate constant was approximately $1.1 \times 10^{-4} \text{ s}^{-1}$, comparable with Ag/SiO₂ catalysts prepared using other methods. This study proposes a greener polyol method to synthesize SiO₂-supported AgNP catalyst that does not require heating or regulating pH of the reaction mixture. This nanocomposite can be used in catalytic, antimicrobial, sensing, and other applications that are using AgNP/SiO₂ synthesized by conventional methods.

1. Introduction

Nitrophenols are organic pollutants widely present in agricultural and industrial wastewater [1]. These compounds are highly toxic and environmentally harmful, which were included in the top 114 toxic chemicals [2]. For example, 4-nitrophenol (4-NP) adversely affects the kidney, liver, and central nervous system, transforming haemoglobin into methemoglobin in human and animal blood to cause severe hypoxia [3, 4]. Therefore, eliminating nitrophenols from wastewater has a crucial positive impact on the environment. One of the most simple and efficient ways to remove nitrophenols is the reduction with sodium borohydride (NaBH₄), a commercially available and inexpensive reducing agent. Moreover, the aminophenol products from these reactions are useful and important in many applications. For example, 4-aminophenol, the

product of 4-NP reduction, is an intermediate in the synthesis of pharmaceuticals, such as analgesic and antipyretic drugs. It is also used as a corrosion inhibitor, photographic developer, and hair-dyeing agent [1, 5, 6].

A common and highly efficient strategy to assist the reduction of 4-NP is to use metal nanoparticles (NP), such as Ag [7], Au [8], Pd [9], and Pt [10]. Among these NP, AgNP is the most promising due to several advantages: easy control of catalytic activity by regulating the shape and size of particles [11, 12], relatively low price (about 1/50 of Au, Pt and 1/25 of Pd), and relatively low toxicity for the environment [13]. AgNP can be synthesized using physical or chemical methods, such as reducing silver ions in solution [14], thermal decomposition of silver compounds [15], or reactions in reverse micelles [16]. Among these methods, the chemical reduction is the most common, using reducing

agents such as hydrazine [17], NaBH_4 [18], ascorbic acid [19], or polyols [20, 21]. The polyol method is considered the greenest because polyols, such as glycerol, ethylene glycol, polyvinyl alcohol, and saccharides, are nontoxic, biodegradable, and inexpensive compounds that can play the roles of a reducing agent, capping agent, and solvent in the synthesis of AgNP. Most AgNP syntheses using the polyol approach require high temperatures, ultraviolet irradiation, or alkaline medium [22–24]. Very few studies use the polyol synthesis at ambient pH and temperature, which are desirable conditions for green processes [25].

The nanoscale sizes of nanoparticles result in high specific surface areas and consequently high catalytic activities. However, the high specific surface areas of NP also lead to their tendency to agglomerate into larger particles. To overcome this disadvantage, nanoparticles are usually embedded in solid supports such as polymers, carbon materials, and oxides [26, 27]. SiO_2 is the most common oxide support for AgNP due to its low cost, high surface area, high chemical and thermal stability, and ability of surface modification.

In this study, we used a greener-than-conventional polyol method to produce AgNP embedded in SiO_2 by conducting the polyol synthesis at room temperature (RT) and neutral pH using glycerol as the multifunctional reducing agent, capping agent, and solvent, silver nitrate as the AgNP precursor, and SiO_2 as a catalyst support. The synthesized nanocomposite was characterized and successfully used as a catalyst for 4-NP reduction using NaBH_4 as the reducing agent.

2. Materials and Methods

2.1. Chemicals. Silver nitrate was purchased from Fisher Scientific (USA), sodium borohydride from Merck Millipore (USA), and glycerol, fumed silica, and 4-nitrophenol from Xilong Scientific (China).

2.2. Preparation of Ag/SiO₂ Catalyst. A stock dispersion of SiO_2 (2 g/L) was prepared by dispersing 100 mg of SiO_2 in 50 mL of glycerol and ultrasonication (UIP 1000 HD probe, 1000 W, 20 kHz, Hielscher, Germany) at 60% maximum intensity for 5 min. A stock solution of AgNO_3 (0.100 M) was prepared by dissolving 170 mg of AgNO_3 in 10 mL of deionized (DI) water. AgNP was synthesized by adding 100 μL of the AgNO_3 solution to 10 mL of the SiO_2 dispersion in a glass vial wrapped with aluminium foil and stirred for 24 h at room temperature. The reaction mixture was then 4-fold diluted using DI water to decrease the viscosity and centrifuged at 1400 rpm for 15 min to obtain the Ag/SiO₂ solid. The solid was washed three times with DI water and oven-dried at 100°C for 8 h.

2.3. Characterization of Ag/SiO₂. The Ag/SiO₂ dispersion was observed using a transmission electron microscope (TEM) JEM-1400 (JEOL, USA). XRD spectrum of the Ag/SiO₂ solid was obtained with 2θ from 10° to 80° on a D2Phaser (Bruker, Germany).

The supernatant after centrifugation was analyzed for silver concentration using atomic absorption spectroscopy (AAS) technique. The solid Ag/SiO₂ obtained after drying was digested with concentrated HNO_3 and subsequently used for determination of silver content.

2.4. Ag/SiO₂-Catalysed Reduction of 4-NP with NaBH₄. In a beaker containing 8.80 mL of DI water under continuous stirring, 200 μL of 10-fold diluted Ag/SiO₂ dispersion, 500 μL of 4-NP 1.25 mM solution, and 500 μL of NaBH_4 165 mM solution were successively added. The reaction was monitored by recording UV-vis spectra of the mixture over time (UV-Vis-NIR-V670, Jasco, Japan).

To evaluate the apparent rate constants of the catalytic reactions, the pseudo-first-order reaction model was applied for the time after the induction period and before the plateau of the absorbance [11].

To investigate the catalytic stability of Ag/SiO₂, after 4-NP was completely reduced, the reaction mixture was left 2 h for complete decomposition of NaBH_4 . Then, 500 μL of 1.25 mM 4-NP and 500 μL of 165 mM NaBH_4 solutions were added to repeat the catalytic reaction on the same used catalyst. The reaction progress was again monitored by recording UV-vis spectra of the reactive mixture. This procedure was repeated until the catalyst showed no activity.

3. Results and Discussion

3.1. Synthesis of Ag/SiO₂ Nanocomposite

3.1.1. Formation of AgNP. The SiO_2 dispersion containing AgNO_3 was initially muddy white but turned brown-yellow after 2 h of stirring (Figure 1 inset).

UV-vis spectrum of SiO_2 dispersion shows strong absorption in the UV region due to the presence of SiO_2 . The spectrum of the reaction mixture after 2 h shows a broad peak developing at 400 nm, indicating the formation of AgNP [25].

After 24 h at room temperature, colours of the control AgNO_3 and SiO_2 solutions in glycerol were unchanged, while the AgNO_3 - SiO_2 solution turned brown-yellow and gradually developed to orange, which associated with a clear peak at 410 nm (Figure 2). The increase in the absorbance of Ag/SiO₂ after 24 h indicates that the formation of AgNP continued at RT after 2 h of reaction.

A typical TEM image of the Ag/SiO₂ solution (Figure 3(a)) demonstrates clusters of SiO_2 with AgNP embedded in the SiO_2 matrix. We used ImageJ software to measure the sizes of these AgNP and expressed their size distribution in Figure 3(b). The result shows an average size of 6 ± 2 nm (mean \pm standard deviation) of the synthesized AgNP.

In Figure 3(a), the places with high densities of material absorbed most of the electrons emitted from the electron microscope, thus resulting in a dark colour. Despite being small in sizes, AgNP are found as black particles because silver has an atomic number ($Z=47$) much higher than those of silicon ($Z=14$) and oxygen ($Z=8$).

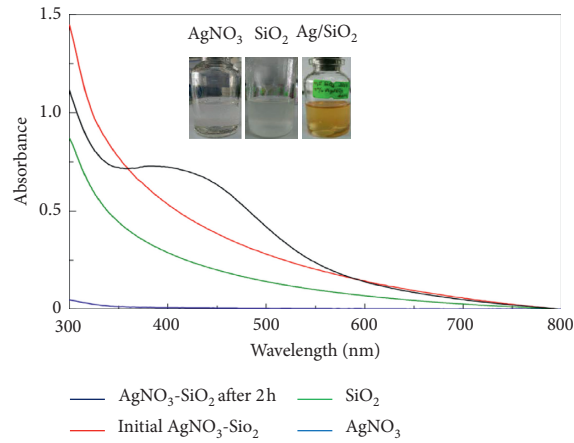


FIGURE 1: UV-vis absorption spectra of the solutions of AgNO₃, SiO₂, initial AgNO₃-SiO₂, and AgNO₃-SiO₂ after 2 h.

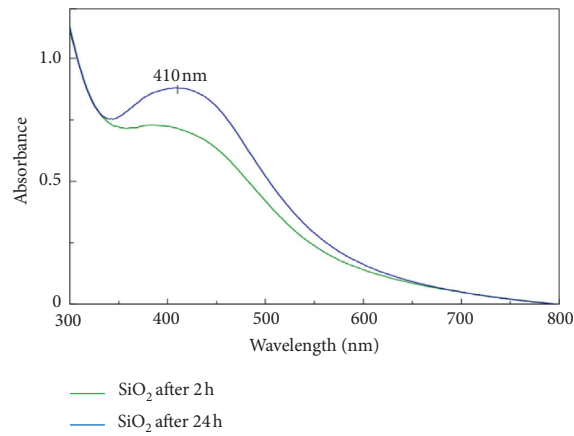


FIGURE 2: UV-vis absorption spectra of the solution AgNO₃-SiO₂ after 2 h and 24 h.

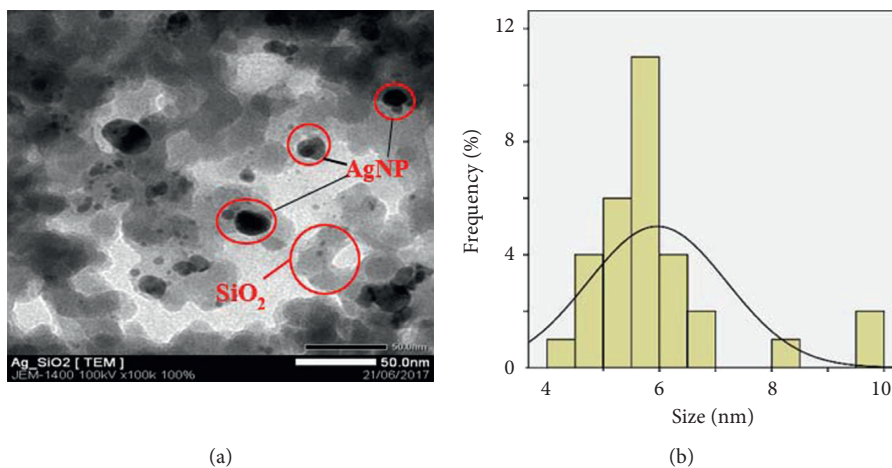


FIGURE 3: (a) a typical TEM image of the Ag/SiO₂ nanocomposite and (b) size distribution of AgNP from TEM images.

There have been many studies on the synthesis of AgNP in glycerol. However, most of them require harsh conditions, such as high temperatures, UV irradiation, or alkaline medium. Our literature survey found only one

published comprehensive research dealing with the polyol synthesis of AgNP at RT and pH [25]. The authors concluded that there can be two possible reducing species in glycerol: (i) glyceraldehyde in old glycerol, which produced

a grey solution with large and polydispersed AgNP (94 ± 36 nm) and (ii) free radicals in new glycerol, which produced a yellow solution with small and monodispersed AgNP (24 ± 11 nm). Based on the yellow colour of our solutions and the small sizes of our AgNP (6 ± 2 nm), we suggest that free radicals were responsible for the reduction of silver ions in our study. However, while the sources of these radicals in the study mentioned above can be the light and temperature, we think the main source of radicals in our system was the ultrasonic agitation during the dispersion of SiO₂ due to its high energy. Further studies are necessary to confirm this hypothesis.

To test for the formation of AgNP in the centrifuged Ag/SiO₂ nanocomposite, its XRD spectrum was compared with that of pure SiO₂ (Figure 4).

XRD pattern of pure SiO₂ (Figure 4, upper) shows only one broad peak at $2\theta = 22.5^\circ$, which is a characteristic for amorphous silica [28]. This amorphous character of silica ensured its high adsorbing capacity toward AgNP. Besides the characteristic broad peak at 22.5° , the XRD pattern of Ag/SiO₂ shows two small peaks at 2θ at 38.18° and 44.25° , which are characteristic for (111) and (200) planes of silver (JCPDS file, No. 4-783). These peaks were not sharp and clear due to the small content of Ag in the nanocomposite. The XRD method provides information about the arrangement of atoms/ions in bulk crystals (size > 10 nm). Therefore, the small sizes of Ag nanocrystals in this study (<10 nm from TEM images) are another reason for the apparently low crystallinity. The XRD result agrees with the TEM images analysis that the AgNP were small in size and highly dispersed on the SiO₂ surface, which are suitable properties for catalytic applications.

Since the XRD is not quantitative in assessing the presence of AgNP, the AAS (detection limit of 11 ppb) was carried out to quantify silver in the centrifuged Ag/SiO₂ and the supernatant. The AAS showed that the concentration of Ag in the supernatant was 11.37 ppm, compared to the initial 25 ppm concentration. This result means that, about 50% of the initial Ag was adsorbed on the surface of SiO₂.

3.1.2. Influence of AgNO₃ Concentration. Figure 5 shows the UV-vis absorption spectra after 2 h of the reaction mixtures containing a fixed amount of 0.5 g of SiO₂ and different concentrations of AgNO₃ (0–5 mM).

The spectrum of the solution with 0.1 mM AgNO₃ has no clear peak but is different from the solution of 0 mM AgNO₃. This means that the reaction took place with that lowest studied concentration of AgNO₃. When the AgNO₃ concentration increased to 1, 2, and 5 mM, the absorbance peak became higher and shifted from 405 to 414 and 424 nm, respectively. The increase in peak height indicates more AgNP produced, while the shift of the peak to longer wavelengths indicates that the AgNP became larger in size.

3.1.3. Influence of SiO₂ Content. In this series of experiments, the amount of AgNO₃ used was fixed at 100 μ L of 0.1 M, while SiO₂ amounts were varied (0, 0.1, 0.5, 2.0, and 5.0 g). The solution without SiO₂ did not change its colour

during the reaction, while the other solutions turned yellow and became darker over time. After 24 h, the solutions turned from yellow to orange and did not show any precipitates. These colour changes of the solutions are expressed in their UV-vis spectra (Figure 6).

Figure 6 shows that when there is no SiO₂, the reduction of Ag⁺ ions occurs at a very slow speed. Although it was reported that silver ions are reduced by solely glycerol at RT [25], our result indicates that the presence of SiO₂ facilitates the formation of AgNP. This means there are interactions between SiO₂ and glycerol that contributed to the reduction of silver ions and stabilization of the produced AgNP/SiO₂ nanocomposite. This hypothesis is supported by our observation that the produced Ag/SiO₂ dispersion was very stable against settling (no deposit after one month of preparation), despite the high difference in densities of silica and glycerol. Because no report was found on the stability of the popular silica-glycerol dispersion, we speculate that the ultrasonic treatment during the dispersion of silica caused the interactions between glycerol and silica surfaces. If this hypothesis was correct, we can further speculate that if other methods of dispersing SiO₂ were used instead of sonication, such as ball-milling, which also imparts mechanical energy to SiO₂, the similar effects would also be observed. Compared to sonicating probes, advanced ball mills equipped with internal temperature sensors can help to control the interactions between SiO₂ and glycerol.

When the amount of SiO₂ increased to 2 g and 5 g, the peak of AgNP gradually disappeared (Figure 6). This may be due to the strong adsorption of AgNP on the SiO₂ surface in the presence of excess SiO₂. This resulted in a low concentration of free AgNP in the solution that can show surface plasmon resonance. The majority of AgNP was in the adsorbed state, which demonstrated a weak surface plasmon resonance due to the intermolecular interactions between AgNP and the SiO₂ surface.

3.2. Reduction of 4-NP Using NaBH₄ and Ag/SiO₂ Catalyst

3.2.1. Reaction Kinetics. The reduction of 4-NP by NaBH₄ in aqueous alkaline solution is a popular model reaction to evaluate catalytic activity of nanomaterials [1]. In the alkaline solution, 4-NP molecules are converted to 4-nitrophenolate ions with negative charges, such as borohydride ions. Having the same signs of charges, these phenolate and borohydride ions are hard to get in contact and react with each other, which results in a very slow reaction, even though it is thermodynamically favoured [1]. In our study, the presence of Ag/SiO₂ nanocomposite catalyzes the reduction of yellow 4-NP into the colourless product 4-AP (Figure 7 inset). The UV-vis spectra of the reaction solution after adding Ag/SiO₂ (Figure 7) demonstrate the decrease of the absorbance peak at 401 nm and the appearance of the 4-AP peak at 298 nm. Isobestic points at 280 and 314 nm indicate that the reaction produced 4-AP as the only product [29].

To evaluate the effect of SiO₂ on the catalytic activity, we compare the time-dependent absorbance at 400 nm of the

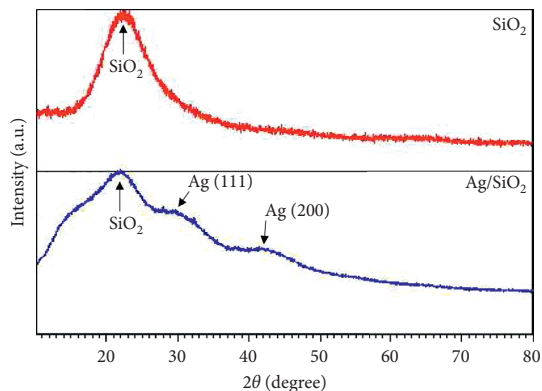


FIGURE 4: XRD patterns of pure SiO₂ and the synthesized Ag/SiO₂ nanocomposite.

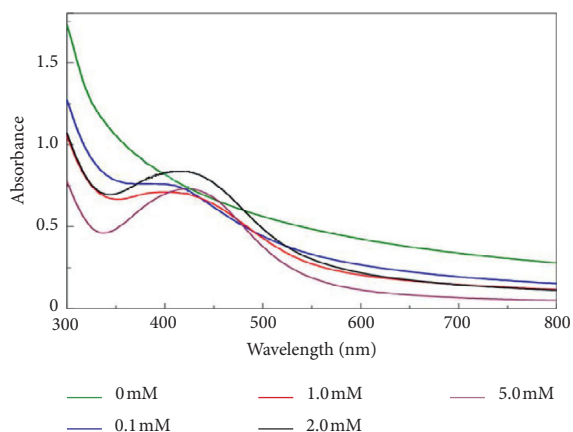


FIGURE 5: UV-vis spectra of glycerol solutions containing 2 g SiO₂ and different AgNO₃ concentrations after 2 h.

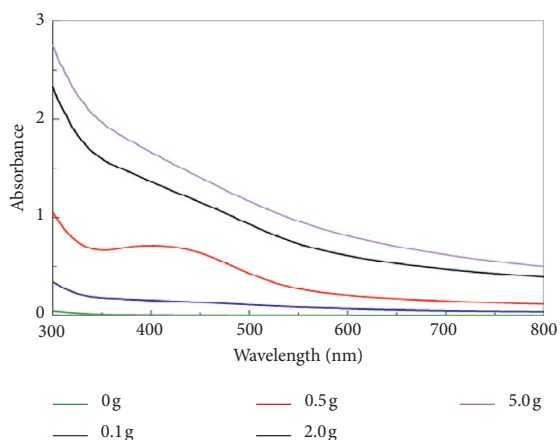


FIGURE 6: UV-vis spectra of reaction solutions with different amounts of SiO₂ after 2 h.

reaction mixture when using Ag/SiO₂, SiO₂, or AgNP (synthesized by heating AgNO₃-glycerol solution at 100°C in the absence of SiO₂). AgNP and Ag/SiO₂ catalysts used in the experiment were equivalent in silver content.

Figure 8 shows that SiO₂ does not adsorb 4-NP and catalyze the reduction of 4-NP. At the same equivalent silver content, Ag/SiO₂ shows higher catalytic activity than AgNP.

This can be explained as follows. Before being reduced to Ag, silver ions were uniformly absorbed on the surface of SiO₂. Therefore, when the reduction by glycerol occurred, AgNP had less chance to collide to grow in size, thus ensuring small sizes and high surface area [29].

The kinetics of this reaction can be treated using the Langmuir-Hinshelwood model: both borohydride and

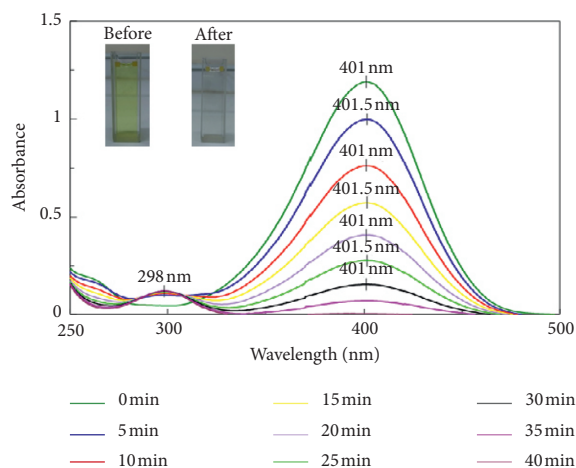


FIGURE 7: Time-dependent UV-vis spectra of the reduction of 4-nitrophenolate reduction by NaBH_4 in the presence of the Ag/SiO_2 catalyst.

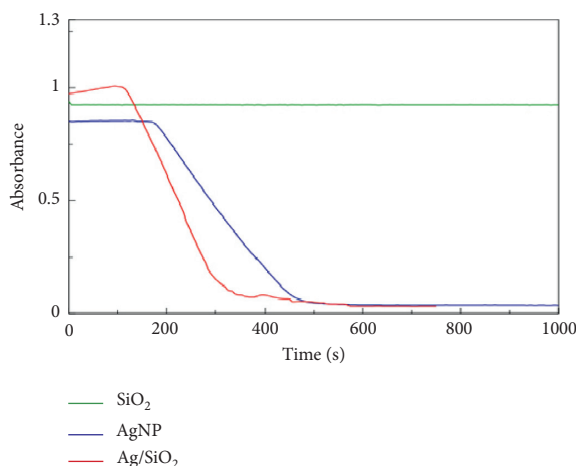


FIGURE 8: Reaction kinetics with different catalysts monitored by the absorbance at 400 nm of the solution.

4-nitrophenolate ions quickly adsorb on the surface of the catalyst before the reaction. Because the adsorption of both substrates is fast, it can be modelled as an equilibrium process described by a Langmuir isotherm. The adsorbed ions then react, and finally the products BO_2^- and 4-AP dissociate from the catalyst surface [30]. Because the chemical reaction takes place between the adsorbed ions, the presence of SiO_2 template could facilitate the adsorption, thus increase the overall reduction reaction of 4-NP, as observed by UV-vis spectroscopy.

To assess the influence of Ag content on catalytic reduction of 4-NP, we carried out an additional experiment, varying the amount of Ag in the catalyst. Figure 9 shows the reaction kinetics of 4-NP reduction with the Ag/SiO_2 catalyst prepared from different initial AgNO_3 concentrations (0.2, 2.0, 4.0, and $10 \mu\text{M}$) with a fixed 0.5 g of SiO_2 .

The decrease of the absorbance over time indicates the reduction of 4-NP to the colourless 4-NA. Compared to the control (no catalyst, the green line), the presence of the

Ag/SiO_2 catalyst triggered the reduction of 4-NP after an induction period of 50–150 s. This induction period is due to the presence of dissolved oxygen, which competes with 4-NP to react with NaBH_4 in the presence of catalysts [31]. Increasing Ag content in the catalyst decreased the induction time (Figure 9), indicating the increase in the catalytic activity of Ag/SiO_2 reduction of dissolved oxygen by NaBH_4 . This increase in the catalytic activity can also be seen in the decrease of the reaction time between 4-NP and NaBH_4 (from the moment the absorbance decreases to the moment it went flat) when increasing the Ag content in the catalyst.

Figure 10 shows the apparent rate constants k of the reaction between 4-NP and NaBH_4 in the presence of Ag/SiO_2 catalysts with different amounts of Ag. These constants were determined by fitting the pseudo-first-order law to the experimental data during the reaction time when the absorbance decreased. Increasing Ag content in the catalyst generally increased the values of apparent rate constant k , i.e., enhanced the catalytic activity (blue line in Figure 10).

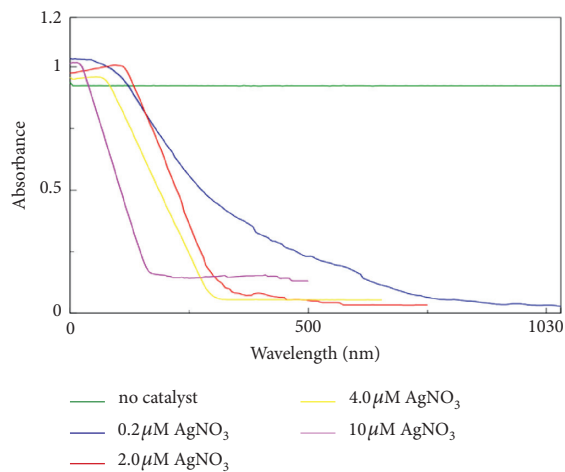


FIGURE 9: Time-dependent 400 nm absorbance of 4-NP reduction with different silver content in the Ag/SiO₂ catalyst.

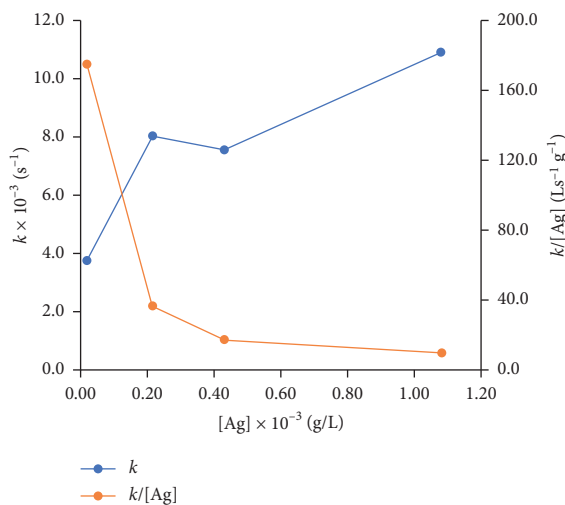


FIGURE 10: Changes of apparent rate constants k and $k/[Ag]$ with the concentration of AgNO₃.

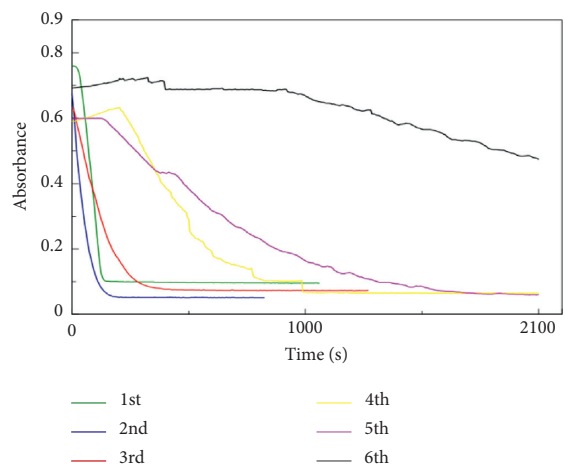


FIGURE 11: Kinetics of the catalytic reduction of 4-NP in the presence of Ag/SiO₂ after repeated uses.

The apparent rate constants in our study ranged from 4.0 to 10.7 s⁻¹, which is comparable with other studies on Ag/SiO₂ catalysts prepared by different methods [28, 32–34].

The orange curve in Figure 10 shows a decreasing trend in $k/[Ag]$ versus $[Ag]$, indicating that the extent of catalytic activity enhancement was lower than the extent of increase in Ag content in the catalyst. This may be due to the high degree of aggregation of AgNP at high concentration, which resulted in a decrease of the active surface area of AgNP on SiO₂.

3.2.2. Catalyst Stability after Repeated Uses. One important characteristic of catalysts is that their activity remained after repeated uses. Figure 11 shows that the catalytic activity of Ag/SiO₂ reduced after every cycle. The catalytic activity significantly decreased from the 4th cycle and lost almost the whole activity after 6 cycles. This result is similar to those of other studies on supported AgNP catalysts, where they lost significant activities after about 4 cycles. The possible reason for this lost activity was that AgNP were partially peeled off the SiO₂ surface after every cycle and agglomerated, which resulted in a decrease in their active surface [30].

4. Conclusion

In this study, we used a novel and green polyol approach to synthesize AgNP embedded in SiO₂: the whole synthesis was performed at RT and neutral pH. Glycerol played the multiple roles of polyol solvent, reducing agent, and capping agent for AgNP. The ultrasonic-probe dispersion of SiO₂ in glycerol may cause chemical interactions between them, which result in an enhancement in the AgNP formation and the settling stability of the Ag/SiO₂ nanocomposite. The prepared Ag/SiO₂ nanocomposites demonstrated high catalytic activities toward the reduction of 4-NP by NaBH₄, which were comparable with Ag/SiO₂ catalysts synthesized by conventional methods.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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