Preparation and catalytic application of Ag/polydopamine composite on surface of glass substrates

Jianying Yu1, Chengyi Sun1, Shixiang Lu1,3, Wenguang Xu1, Zhehan Liu1 and Dongsheng He2

1 School of Chemistry, Beijing Institute of Technology, Beijing, 100081, P.R. China.  
2 School of Mechanics and Civil. & Architecture, Northwestern Polytechnical University, Xi’an, 710072, P.R. China.

E-mail: shixianglu@bit.edu.cn

Abstract. In this work, Ag/polydopamine composite on glass substrates (Ag/PDA@slides) were formed by using polydopamine (PDA) as both reducing and stabilizing agent to reduce silver salts to silver nanoparticles (NPs) and adhesive them to slides. The morphology and chemical composition of the composite material was characterized by scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD). The prepared Ag/PDA@slide was a highly active catalyst for the reduction of 4-nitrophenol (4-NP) in the presence of sodium borohydride (NaBH4) aqueous solution at room temperature. The reduction rate of the optimal catalyst was as fast as 10 s and it was stable up to 6 cycles without a significant loss of its catalytic activity. By measuring the UV-Vis absorption bonds of Ag/PDA@slides, it proved that condition of the strongest surface plasmon resonance of Ag/PDA@slides is the optimal condition of catalytic reduction of 4-NP.

1. Introduction  
Silver nanoparticles (Ag NPs) possess many excellent properties and are widely applied in optics, catalysis and antibacterial field [1-3]. Among these properties, catalytic activity and localized surface plasmon resonance (LSPR) have attracted considerable interests. It is a kind of effective catalyst for many practical applications, such as the reduction of 4-nitrophenol (4-NP). Nitrophenols are one of the most common organic pollutants in industrial and agricultural waste water and is highly toxic. While its reduced product 4-aminophenol (4-AP) is low toxicity as well as a chemical and pharmaceutical intermediate [4]. Therefore, reducing 4-NP to 4-AP is of significant importance. Ag NPs can catalyze the reduction of 4-NP effectively. There are many methods to synthesize Ag NPs, among which chemical reduction is a commonly used way. The reductants often used are sodium borohydride, ascorbic acid, compound with hydroxyl group or aldehyde functional group and so on [5-7]. Recently, dopamine (DA), a kind of biopolymer, was successfully used to prepare metal NPs, as which can reduce metal salts to metal NPs through successive reactions. Dopamine, a biological adhesive inspired by mussel, can form polydopamine (PDA) films by self-polymerization onto various kinds of materials in weak alkaline condition, especially pH 8.5 [8]. Dopamine has been widely studied for surface modification due to the ability to self-polymerize to form polymer films on nearly all substrates[9-11]. Using dopamine to prepare silver nanoparticles is a facile and environmentally-benign way. Ag’ salts could be easily reduced to Ag NPs and adsorbed on the support simultaneously. For example, Li et al. used dopamine to synthesize Ag@AgCl nanophotocatalyst, which showed
superior photocatalytic performance [12]. In addition, the reusability is one of important performances for catalyst. Slides, unlike common particle supports for catalysts, are easy to operate, which needn’t centrifugation and filtration. Besides, slides have no effect on the catalytic reaction and are low-cost.

In this work, we prepared Ag NPs on glass substrate by using PDA as both reducing and adhesive agent. The prepared Ag/PDA@slides showed high catalytic performance for the reduction of 4-NP.

2. Experimental section

2.1. Sample preparation

2.1.1. Preparation of PDA@slides. Slides with a size of 25mm×5mm×1mm were firstly ultrasonically cleaned for 3 min in ethanol. Then it was washed with deionized water and ethanol again in the same way to remove grease and other dirty on the surfaces. 0.5 mol/L NaOH solution was injected to 5 mL 20 mg/mL dopamine solution to tune the pH to 8.5. A clean slide was vertically immersed in the dopamine solution for 1 h, and then rinsed with deionized water. The polydopamine film (PDA@slide) was obtained.

2.1.2. Preparation of Ag/PDA@slides. Determination of optimal concentration of AgNO$_3$ aqueous solution: In order to determine the optimal concentration of AgNO$_3$ aqueous solution, PDA@slides were immersed in 3 mL AgNO$_3$ aqueous solution of different concentrations for 2 h at ambient temperature. 0.01 mol/L, 0.05 mol/L, 0.1 mol/L, 0.2 mol/L and 0.4 mol/L AgNO$_3$ aqueous solutions were used to prepare Ag/PDA@slides.

Determination of optimal reaction time: PDA@slides were immersed in 3 mL 0.05 mol·L$^{-1}$ AgNO$_3$ aqueous solution for 15 min, 30 min, 45 min, 60 min at ambient temperature respectively.

2.2. Characterization

The surface morphology was observed using a NovaNano 430 scanning electron microscope (SEM). The crystalline structure was investigated by X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Germany) with Cu $K_a$ radiation (40 kV, 40 mA, and $\lambda = 0.15418$ nm) at X’Celerator’s scanning rate of 3ºmin$^{-1}$. The UV-Vis spectra were recorded with a HITACHI U-3310 UV-Vis spectrophotometer.

2.3. LSPR and catalytic study

Prepare Ag/PDA@slides obtained at different AgNO$_3$ immersion time. After drying, UV-Vis spectrophotometer was used to detect the absorption peaks to investigate the LSPR of the Ag NPs.

The catalytic reduction of 4-NP was carried out at room temperature in a quartz cuvette. Ag/PDA@slide was added in the cuvette containing 4-NP (2.5 mL, 0.1 mmol·L$^{-1}$) and freshly prepared aqueous solution of NaBH$_4$ (250 $\mu$L, 0.1 mol·L$^{-1}$). UV-Vis absorption spectra were recorded to monitor the change of the reaction mixture.

3. Results and discussion

3.1. Morphology and chemical compositions

Figure 1 shows the morphology of samples. The slide has a smooth surface as shown in figure 1(a). PDA@slide is lightly crumpled on the surface as shown in figure 1(b). Figure 1(c) shows images of Ag NPs which produced on the surface of PDA@slides that were immersed in 0.05 mol·L$^{-1}$ AgNO$_3$ aqueous solution for 30 min. Figure 1(d) is an enlarged image of figure 1(c). There are countless nanoparticles on the surface of Ag/PDA@slides as shown in figure 1(c) and (d). The nanoparticles are spherical, and the size of the particles is from 20 to 50 nm.
Figure 1. SEM images of slide (a), PDA@slide (b), Ag/PDA@slides immersed in 0.05 mol·L⁻¹ AgNO₃ solution for 30 min (c,d), respectively.

Figure 2 shows XRD pattern in the 2θ region of 30-70° of Ag/PDA@slides. XRD patterns of slides, PDA@slides and Ag/PDA@slides obtained in 0.05 mol·L⁻¹ AgNO₃ solution for 30 min are shown in figure 2(A), (B) and (C). The symbols of *, # and  represent the peaks of slides, Ag and Ag₂O respectively. The diffraction peaks of slides are shown in figure 2(A). Six peaks at 36.5°, 43.1°, 48.8°, 54.5°, 56.7°, 59.4° correspond to planes of slides. The first peak at 36.5° corresponds to hexagonal SiO₂ (110) (JCPDS 04-0836). When formed PDA film, no new diffraction peaks appear on the surface of PDA@slides compared with slides as shown in figure 2(B). For Ag/PDA@slides, new diffraction peak appeared at about 2θ = 44.2° is assigned to cubic Ag (200) (JCPDS 04-0783). The diffraction peaks at 36.5° and 38.6° correspond to hexagonal Ag₂O (JCPDS 04-0836) to (002) and (101) planes, respectively. The presence of Ag₂O is most likely due to the oxidation of Ag when it exposed to air. The peaks of Ag₂O (002) and SiO₂ (110) coincide, so the diffraction peak at 36.5° is strong.
3.2. LSPR of Ag/PDA@slides

The optical properties of Ag NPs were monitored by UV-Vis spectra as presented in figure 3. Ag NPs, a kind of noble metal nanoparticles, possess compelling localized surface plasmon resonance (LSPR) properties due to the collective oscillation of conduction band electrons. LSPR of plasmonic nanostructure is strongly dependent on its size, shape, inter-particle distance, and particularly the refractive index (RI) of the surrounding environment [13]. After 15 min of AgNO₃ immersion time, a peak at about 400 nm appeared, corresponding to the SPR band of Ag NPs. When the reaction time prolonged to 30 min, a strong band appeared. The full width at half-maximum (FWHM) broadened when AgNO₃ immersion time prolonged to 60 min. As the AgNO₃ immersion time increased from 15 min to 60 min, the SPR band first gradually intensified and then gradually broadened. The SPR peak was strongest when the AgNO₃ immersion time was 30 min. It is speculated that the sharper and more intensified resonance peaks in the Ag NPs are better if applied to sensors [14]. Thus, immersing for 30 min is the best time for SPR.

Figure 3. UV-Vis spectra of Ag/PDA@slides obtained at different AgNO₃ immersion time.
3.3. Catalytic reduction of 4-NP

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was chosen as a model reaction to evaluate the catalytic performance of the prepared Ag NPs. NaBH₄ was chosen as a reducing agent, and the concentration of it largely exceeded the concentration of 4-NP. Without Ag/PDA@slides, the reaction was not performed. The mixture of 4-NP and NaBH₄ showed a yellow color. After Ag/PDA@slide was put in, the reaction began. As the reaction proceeded, the color of the solution became fading. As monitored by UV-Vis spectra, the absorption peak of 4-NP at 400 nm gradually disappeared, and a new peak at 300 nm progressively increased, which means the reduction of 4-NP and the formation of 4-AP. The reduction of 4-NP is illustrated in figure 4.

![Figure 4](image)

**Figure 4.** Illustration of the reduction of 4-NP by Ag/PDA@slides.

In order to determine the optimal concentration of AgNO₃, 0.01 mol/L, 0.05 mol/L and 0.1 mol/L, 0.2 mol/L and 0.4 mol/L AgNO₃ aqueous solutions were used to prepare Ag/PDA@slides which were next used to catalyze the reduction of 4-NP respectively. Experiments demonstrated that the fastest rate of the reduction was added in the Ag/PDA@slides which obtained in 0.05 mol/L AgNO₃ aqueous solution, so the optimal concentration of AgNO₃ aqueous solution is 0.05 mol/L.

Next different AgNO₃ immersion time was investigated. Figure 5 shows the UV-Vis spectra of 4-NP after the addition of the as-prepared Ag/PDA@slides. According to experiments, the conversion time of 4-NP was 50 s, 10 s, 30 s and 30 s respectively when added the catalysts obtained by AgNO₃ immersion of 15 min, 30 min, 45 min and 60 min. According to experiments, the reduction could be completed in only 10 s when added in the Ag/PDA@slide obtained by 30 min immersion. Obviously, the immersing time in AgNO₃ aqueous solution plays an important role in the catalytic process, as which may impact the amount and the dispersion of Ag NPs.

![Figure 5](image)

**Figure 5.** UV-Vis spectra of 4-NP after the addition of Ag/PDA@slides obtained by the AgNO₃ immersion time of 15 min (a), 30 min (b), 45 min (c) and 60 min (d).
In the experiment, A, B, C, D represent the Ag/PDA@slides which reacted with 0.05 mol/L AgNO$_3$ aqueous solution for 15 min, 30 min, 45 min, 60 min respectively. The kinetic constant $k$ of the reduction of 4-NP were $6.7 \times 10^{-2}$ s$^{-1}$, $3.9 \times 10^{-1}$ s$^{-1}$, $9.7 \times 10^{-2}$ s$^{-1}$, $9.3 \times 10^{-2}$ s$^{-1}$ when A, B, C, D were used as catalysts respectively. Figure 6(a) shows the plot of ln ($c_t/c_0$) versus time. The kinetic equation of the reaction is as follow:

$$\ln(C_t/C_0) = -kt$$

The reusability of Ag/PDA@slides was investigated by repeating the catalytic reaction with the same catalyst as shown in figure 6(b). After each reaction, the catalyst was taken out of the cuvette by a tweezer and it was used directly in the next reaction after washing with deionized water. As shown in figure 6(b), the catalyst possesses high reusability, which could be used for 6 times without obvious loss. Moreover, the prepared Ag/PDA@slides exhibited significant advancement over common particulate catalyst in the catalytic reduction of 4-NP because Ag/PDA@slides could be directly reused without filtered and centrifuged. The reuse process was much simpler.

The prepared Ag/PDA@slide has higher catalytic rate for the reduction of 4-NP and simpler preparation process than other nano-Ag catalysts. To the knowledge of authors, the reduction of 4-NP used as-prepared Ag/PDA@slide immersed in 0.05 mol/L AgNO$_3$ aqueous solution for 30 min is the fastest among other nano-Ag catalysts.

4. Conclusion
In summary, an Ag/polydopamine composite has been prepared on the glass surface by self-polymerization and reduction properties of polydopamine. Ag/PDA@slide is a highly efficient catalyst which could catalyze the reduction of 4-NP in 10 s when at optimal condition. The UV-Vis absorption peak of Ag/PDA@slides proved that the condition of the strongest SPR of Ag/PDA@slides is the optimal condition of catalytic reaction. In addition, the catalyst is prepared on the surface of glass, so it is easy to be recycled.

Acknowledgements
We gratefully thank the National Natural Science Foundation of China (no. 21271027) for this work.

References
[1] Xiong S Q, Wang Y, Zhu J, Yu J R and Hu Z M 2015 Langmuir 31 5504-5512
[2] Rostami-Vartooni A, Nasrollahzadeh M and Alizadeh M 2016 Journal of Alloys and Compounds 680, 309-314
[3] Wan X, Zhuang L, She B, Deng Y, Chen D and Tang J 2016 Materials science & engineering. C, Materials for biological applications 65 323-330
[4] Zelekew O A and Kuo D H 2016 Phys. Chem. Chem. Phys. 18 4405-4414
[5] Arthur E E, Li F, Momade F W Y and Kim H 2014 Energy 76 822-829
[6] Ye W C, Chen Y, Zhou Y X, Fu J J, Wu W C, Gao D Q, Zhou F, Wang C M and Xue D S 2014 Electrochim. Acta 142 18-24
[7] Chou K S and Lai Y S 2004 Mater. Chem. Phys. 83 82-88
[8] Lee H, Dellatore S M, Miller W M and Messersmith P B 2007 Science 318 426-430
[9] Wang C, Zhu W, Lan Y, Zhang M, Tian T, Wang H and Li G T 2014 J. Phys. Chem. C 118 10754-10763
[10] Yu X Q, Wang H, Guo L P and Wang L 2014 Chem.-Asian J. 9 3221-3227
[11] Postma A, Yan Y, Wang Y J, Zelikin A N, Tjipto E and Caruso F 2009 Chem. Mat. 21 3042-3044
[12] Li W, Ma Z Y, Bai G Q, Hu J M, Guo X H, Dai B and Jia X 2015 Applied Catalysis B-Environmental 174 43-48
[13] Beeram S R and Zamborini F P 2009 J. Am. Chem. Soc. 131 11689-+
[14] Lee K S and El-Sayed M A 2006 J. Phys. Chem. B 110 19220-19225