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Facile synthesis of Ag nanoparticles-anchored polydopamine-modified polyurethane sponge for the effective catalysis of organic pollutants from wastewater

Guangcheng Luo, Zhigang Jia*, Tao Ni, Ziyu Li, Jun Chen, Hongping Wu, Nannan Wang

School of Chemistry and Chemical Engineering, Anhui University of Technology, No. 59 Hudong Road, Ma'anshan, 243002 Anhui Province, China, emails: zjchemyue@126.com(Z. Jia), 1176800640@qq.com(G. Luo), 3013261430@qq.com(T. Ni), 496761147@qq.com(Z. Li), 43949336@qq.com(J. Chen), 1366023125@qq.com(H. Wu), 47309287@qq.com(N. Wang)

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ABSTRACT

In this study, the novel three-dimensional porous silver/polydopamine/polyurethane (Ag/PDA/PU) sponge was synthesized by a facile method. The PU sponge modified by polydopamine (PDA/PU) was employed not only as a carrier but also as a reducing agent. Ag ions can be *in situ* reduced on the fiber surface of PDA/PU sponge. The as-prepared Ag/PDA/PU sponge was characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), and energy-dispersive X-ray (EDX). The results showed that the as-formed Ag nanoparticles had been successfully loaded onto the fiber surface of the sponge. The Ag/PAD/PU sponge exhibited higher catalytic activity for the organic pollutant in wastewater with the assistance of $NaBH_4$ medium. The novel Ag/PDA/PU sponge has the potential application for the treatment of wastewater containing organic pollutant due to its high catalytic efficiency, low cost, and facile synthesis process.

Keywords: Nanoparticles; Porous materials; Catalytic performance; Wastewater treatment

1. Introduction

Noble metal nanoparticles (NPs) have attracted much attention due to their intriguing physicochemical properties, such as unique optical [1], electronic [2], magnetic [3], and catalytic [4] properties. Especially, noble metal NPs display excellent catalysis performance because of small sizes, high surface areas, and special surface chemistries compared with their bulk materials. Among the various noble metals, silver (Ag) NPs have gained considerable importance for intriguing application and environmental friendship in catalysis filed compared to other noble metals. However, the naked Ag NPs easily aggregate due to their high surface energy during the catalytic process, which leads to a greater reduction in their activity area and a distinct decrease in their catalytic activity. Moreover, Ag NPs in powdery form suffer from the difficulties of separation and recyclability due to the nanosized particles, which limited their practical applications [2,5]. To solve these problems, the immobilization of Ag NPs on various support materials or stabilization by organic ligand is widely investigated [6–8]. In fact, the covering of organic ligand on Ag NPs also causes the decrease in catalytic activity, and the immobilization of Ag NPs on the powdery carrier is equally difficult to separate the catalysts from the reaction system. Therefore, these unfavorable factors have hampered the extensive practical applications for the large-scale reaction system [9–11].

Commercial three-dimensional (3D) polymeric sponges, such as polyurethane (PU) sponge, melamine-formaldehyde (MF) sponge, and polypropylene (PP) sponge, have attracted a great deal of attention due to their excellent properties compared with other porous bulk materials, such as

* Corresponding author.

low-cost, high porous, and high surface area. These properties make sponge ideal support with high dispersion. Therefore, commercial 3D polymeric sponges as frameworks to load large quantities of noble metal nanostructures are the suitable platform for environment protection and industrial applications. 3D sponges with polymer skeletons have been widely researched in oil–water separation, adsorption, and the surface-enhanced Raman spectroscopy (SERS) substrate [12–14]. 3D framework of low-cost PU sponge with flexibility, high pore volume, and low bulk density supplies an excellent means for the catalytic application of Ag NPs in practical situation. However, to the best of our knowledge, there are few reports that 3D framework of commercial PU sponge as carrier was employed in catalytic field.

Herein, a simple, scalable, and low-cost approach is devised to develop an Ag NPs-anchored PU sponge as a 3D flexible framework. Ag NPs were *in situ* formed on the pore surface of the sponge. The novel Ag/PDA/PU sponge framework possesses outstanding catalytic performance for the degradation of wastewater containing 4-nitrophenol (4-NP), methylene blue (MB), and methyl orange (MO).

2. Experimental

2.1. Materials

PU sponge with density of 8 mg cm^{-3} and high porosity of >99% was purchased from Shanghai Chengda Sponge Product Co., Ltd. (China). Silver nitrate ($AgNO_3$) was supplied by Tianjin Yingda Rare Chemical Reagents Factory (Tianjin, China). Dopamine hydrochloride and Tris(hydroxymethyl) aminomethane hydrochloride were provided by Aladdin Industrial Co. (China).

2.2. Synthesis of Ag/PDA/PU sponge

The commercial PU sponge is cut into 4 × 4 × 2 cm^3 and immersed into 50 mL of Tris–HCl buffer (10 mM, pH 8.5) containing dopamine (2 mg mL^{-1}), and then let stand for 4 h. The dark gray product was taken out from the solution and washed by deionized water for several times to remove the redundant PDA onto PDA/PU sponge. Subsequently, the as-prepared PDA/PU sponge was put into 30 mL of $AgNO_3$ solution (20 mM) for 2 h at room temperature, and Ag NPs were *in situ* deposited on the fiber of sponge. Finally, the resulting materials sponge was taken out, washed with ethanol, and dried at 80°C in air to obtain Ag/PDA/PU sponge.

2.3. Characterization

Ag phase onto PU sponge was detected on an X'Pert Powder XRD instrument with Cu Kα radiation (λ = 0.154 nm) in the 2θ range of 10°–90°. Surface microstructure of the sponges was observed by JSM-6490LV scanning electron microscope (SEM) operated at an accelerating voltage of 5.0 kV. Elemental analysis was performed using an X-ray energy dispersive spectroscopy (EDS) detector (IE 300X, Oxford, UK) on the microscope. FT-IR measurements were performed using a Nicolet 5700 spectrometer (Thermo Nicolet Corporation, US) in the range of 4000–5000 cm^{-1}.

2.4. Catalytic reduction of 4-NP and organic dyes

The catalytic efficiency of the sponge was demonstrated by degrading hazardous 4-NP or organic dye (MB and MO) in aqueous solution at room temperature. In a typical assay, 30 mL of freshly prepared $NaBH_4$ (0.3 M) solution was mixed with 30 mL of 4-NP (1 mM) in a beaker. Then, the Ag/PDA/PU sponge (20 mg) was added into the above solution mixture to start the catalytic reaction. The progress of the conversion of 4-NP into 4-AP was monitored using UV-visible spectrophotometer with the maximum adsorption wavelength at certain time intervals. Similarly, the initial concentration of both MB and MO is 20 mg L^{-1}.

Dynamic flow catalytic tests for 4-NP or organic dye (methylene blue and conge red) were also conducted. The Ag/PDA/PU sponge can be easily placed into sand core funnel for dynamic flow catalytic degradation of organic pollutant. First, in the dynamic catalytic tests, the cylindrical Ag/PDA/PU sponge with height 2.0 cm and diameter 1.0 cm was filled in a sand core funnel as catalytic column. Then, 30 mL of freshly prepared NaBH4 (0.3 M) solution was previously mixed with 30 mL of 4-NP (1 mM) in a beaker. The mixture was continuously passed through the column at a flow rate of ~15.0 mL min^{-1}. The eluates were continuously collected and analyzed to determine the remaining concentration. For the recycling experiments, the mixture of $NaBH_4$ (0.3 M) solution and wastewater was continuously passed through the column at the same flow rate to test the cycling stability. Similarly, the initial concentration of both MB and MO is 10 mg L^{-1}.

3. Results and discussion

The commercial PU sponge was first modified by PDA. PDA can serve as a reducing and capping agent to reduce noble metallic salts into metallic NPs [15,16]. Ag NPs were *in situ* reduced by PDA and fixed onto the surface of the texture of sponge. The phases and purity of the Ag NPs were characterized by XRD analysis. As shown in Fig. 1(a), it is easy to observe that the three sharp diffraction peaks of Ag at 38.1°, 44.3°, and 64.5°, corresponding to (111), (200), and (220) crystal planes of Ag (JCPDS 65-2871), indicating elemental Ag was *in situ* formed and coexistence into the texture of PU sponge. Fig. 1(b) shows a typical SEM image of the Ag/PDA/PU sponge. It can be clearly seen that massive microscale fibers are connected with each other to form 3D self-supported networks, and the space sustained by elastic fibers constructed the irregular pores ranging from tens to hundreds of microns. A close-up SEM (Fig. 1c) image reveals that plenty of Ag NPs were deposited onto the surface of the fiber of PDA/PU sponge. It is believed that PDA plays a significant role in preventing the metal NPs from agglomeration by quinones and unoxidized catechol groups [17]. The as-deposited metal Ag bounds at the N-site and O-site of PDA and serves as the seed for the formation of Ag NPs with the constant reduction of Ag^+. Furthermore, successful deposition of the Ag NPs on the sponge surface was further confirmed by the EDS measurement (Fig. 1d). The peak at about 3 keV further confirmed the existence of Ag NPs. Nitrogen adsorption–desorption isotherms were obtained to examine the surface areas of the as-synthesized Ag/PAD/PU

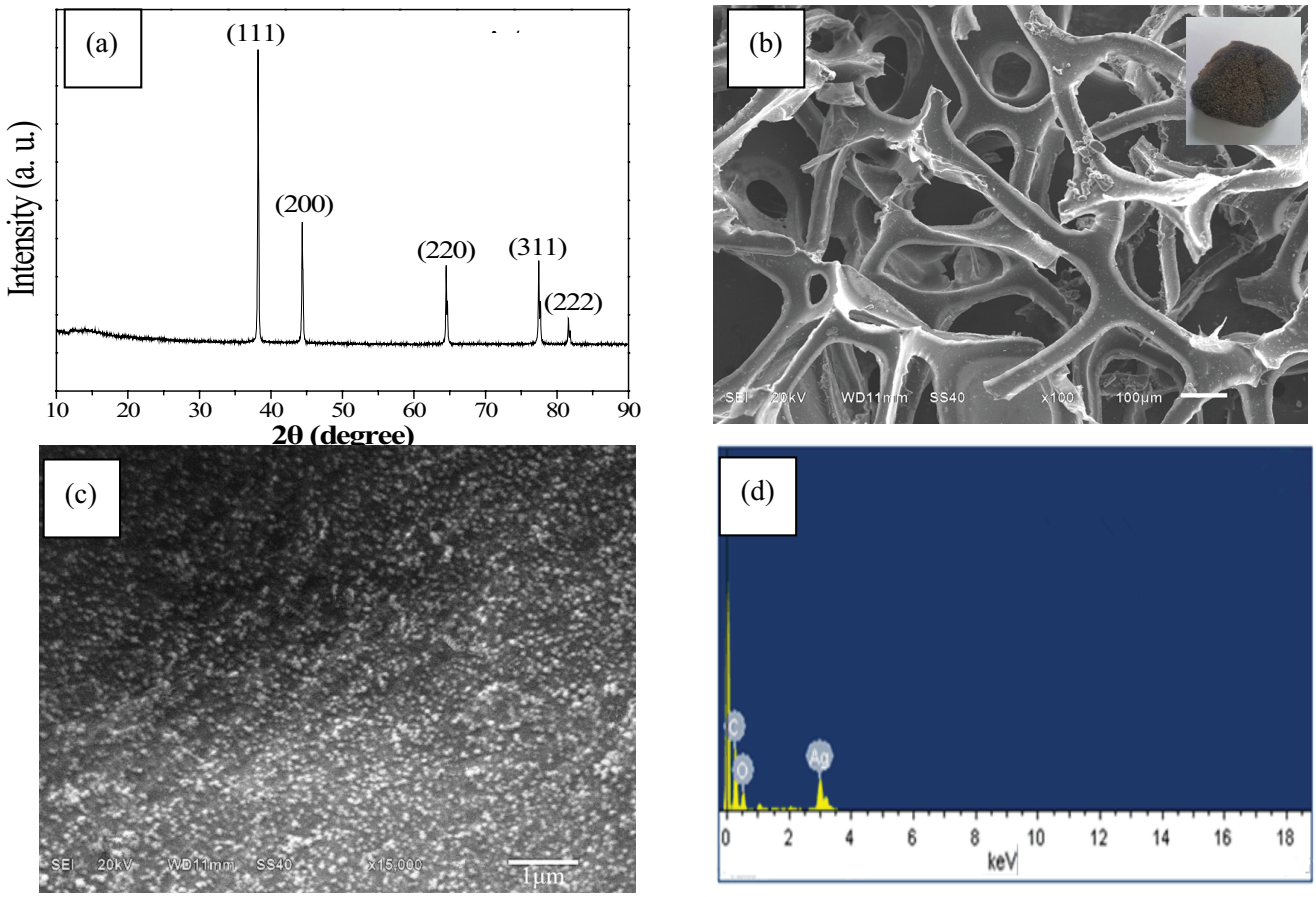


Fig. 1. XRD of Ag/PDA/PU sponge (a), SEM of Ag/PDA/PU sponge (b), an enlarged view of (figure b) (c), and EDS spectrum of Ag/PDA/PU sponge (d).

sponge (Supplemental Fig. S1). The samples with the surface area of 29.5 m^3 g^{-1} showed a typical type-II behavior with a steep increase at low relative pressure, suggesting a macroporous nature of this kind of material.

Fig. 2 shows the Fourier transform infrared (FTIR) spectra of the PU sponge, PDA/PU sponge, and Ag/PAD/PU sponge. The peak centered at 3440 cm^{-1} is attributed to the asymmetry stretching vibration of -NH_2 groups [18]. After the coating of PDA for PU sponge, the band at 3440 cm^{-1} becomes wider due to the asymmetry stretching vibration of aromatic -OH and -NH_2 groups. The C–H vibration at 2927 cm^{-1} became stronger. The peak centered at 1610 cm^{-1} belongs to the vibration of benzene ring skeleton and "–C=C–" of PDA [19]. The strong peak centered at 1380 cm^{-1} ascribes to the stretching vibration of C–O formed due to the oxidation–reduction reaction of PDA and Ag^+ [20].

PU sponges with a unique 3D structure have been applied as absorbents and oil–water separating materials for their large surface area and surface roughness. However, there are few reports about the application of PU with 3D framework in catalytic field [21–24]. In this study, the as-prepared Ag/PDA/PU sponge was employed as catalyst for the degradation of organic pollutant in wastewater. The catalytic degradation of wastewater containing 4-NP using Ag/PU sponge as catalysts was investigated. Fig. 3(a) represented that the absorption band of 4-NP was known to appear at 400 nm

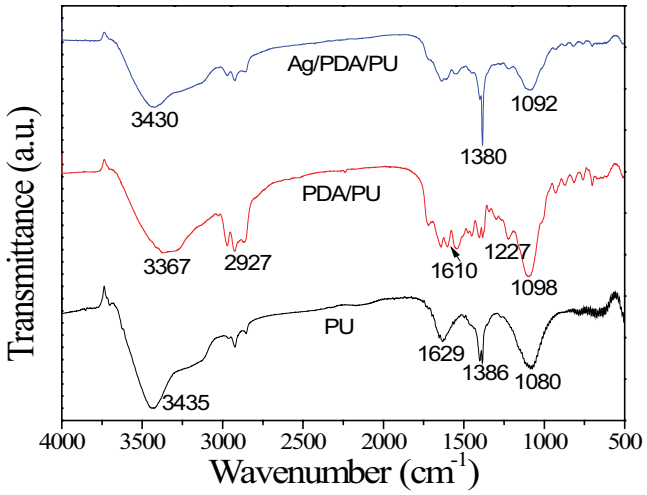


Fig. 2. FTIR spectra of PU sponge, PDA/PU sponge, and Ag/PDA/PU sponge.

in the presence of $NaBH_4$. As the reaction proceeded, the absorption peak at 400 nm rapidly decreased along with the increase of a new absorption peak at about 300 nm, suggesting the formation of 4-AP. Fig. 3(b) and (c) shows the plots of C/C_0 and ln C_t/C_0 versus reaction time for the reduction of

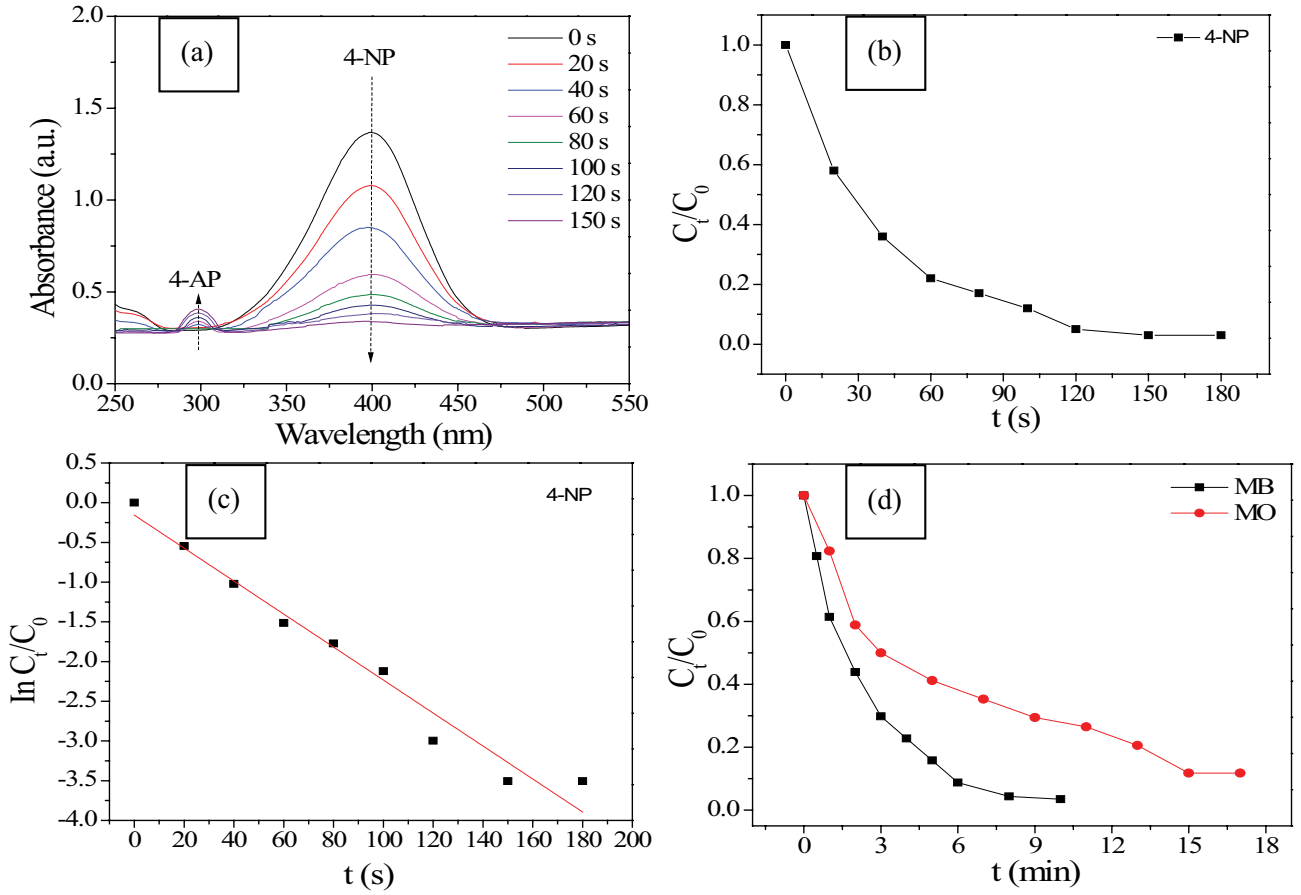
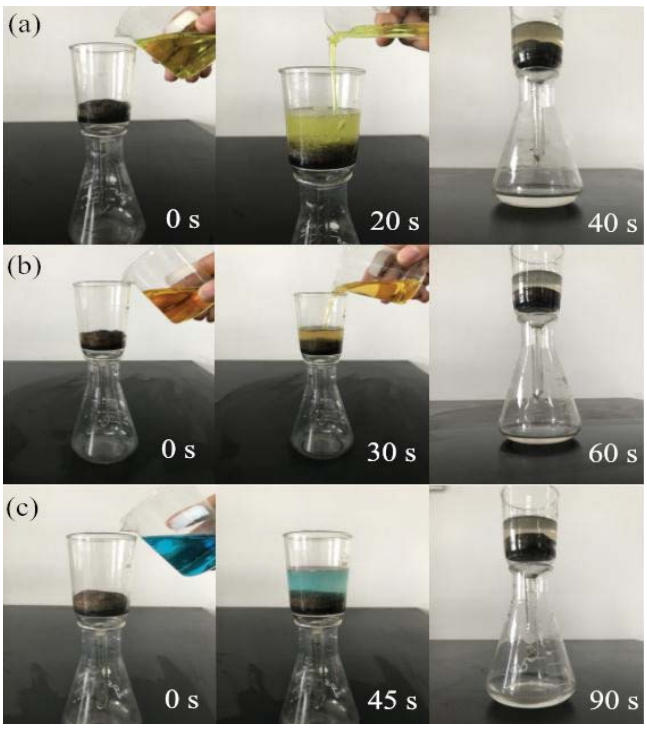


Fig. 3. UV-visible spectra of 4-NP reduction in the presence of synthesized Ag/PDA/PU sponge (a), plot of C_t/C_0 versus time (min) for catalytic degradation of 4-NP (b), the plot of ln (C_t/C_0) on reaction time (c), and the degradation curve of MB and MO onto Ag/PDA/PU sponge (d). * C_0 is the initial 4-NP concentration, and C is the 4-NP concentration at time t.



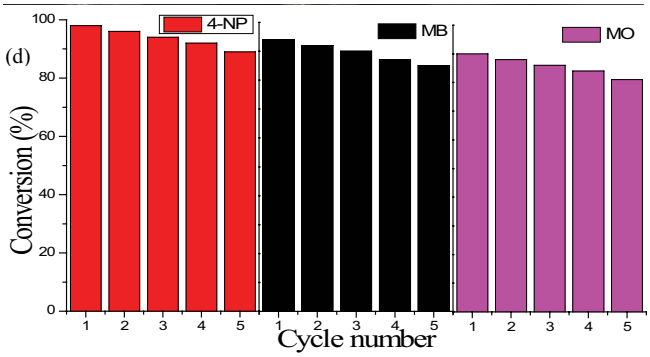


Fig. 4. Dynamic flow catalytic tests for 4-NP (a), MO (b), and MB (c), and cycling catalytic test of Ag/PDA/PU sponge monolith (d).

4-NP in the presence of an Ag/PU sponge, respectively. It was clear that the Ag/PU sponge held a great degradation rate for the reduction of 4-NP, as the reduction was achieved in 3 min. According to Fig. 3(c), the rate constant (k) was estimated to be 0.02076 s^{-1} by slope. The as-prepared Ag/PDA/PU sponge was also employed to catalyze the azo dye, such as MO and MB. As shown in Fig. 3(d), the catalytic degradation of MO and MB can be completed within 18 min and 10 min with the Ag/PAD/PU sponge and NaBH4 system, respectively.

In order to test the possibility of 3D sponge catalyst in practical application, dynamic flow catalytic tests for 4-NP, MO, and MB were also designed. Fig. 4(a–c) is the photograph of the dynamic flow catalysis of 4-NP, MO, and MB by Ag/PDA/PU sponge bulk, respectively. The organic pollutants gradually flowed through the funnel filled with Ag/PDA/PU sponge bulk, and the elute liquid is collected at the bottom of the conical flask. Clearly, the elute liquids are completely colorless with the continual through Ag/PDA/PU sponge bulk. In order to test the catalytic stability, dynamic flow catalytic tests for 4-NP were conducted five times. As shown in Fig. 4(d), there is a slight decrease in the degradation rate with the increasing cycle times. After the five recycling, the degradation rate still can reach 95.4%, 89.5%, and 86.7% for 4-NP, MO, and MB, respectively.

4. Conclusion

In conclusion, the 3D Ag/PDA/PU sponge has been fabricated by the *in situ* reduction of Ag^+ onto the surface of PU sponge modified by PDA. The as-formed Ag NPs are evenly deposited onto the surface of the fiber of PDA/PU sponge without agglomeration, which displayed eminent catalytic activity for the organic pollutant, such as 4-NP, MO, and MB. Dynamic flow catalytic tests indicated that the as-prepared Ag/PDA/PU sponge bulk possesses the potential prospect for the treatment of organic wastewater in the practical application filed.

Acknowledgments

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Supplementary Information

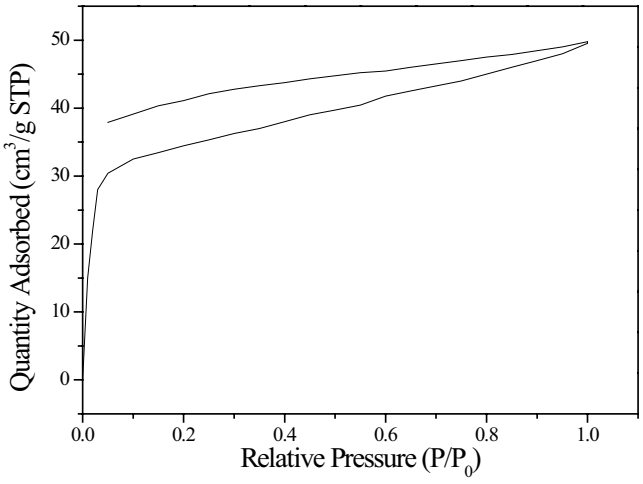

Fig. S1. N_2 adsorption–desorption isotherm of Ag/PDA/PU sponge.