

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



ARTICLE

Study of Catalytic Ability of *in situ* Prepared AgNPs-PMAA-PVP Electrospun Nanofibers

Lin Zhong,^a Tong Yang,^b Jian Wang,^{*a} Cheng Zhi Huang^{*a,b}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The catalysis of nanomaterials are interesting and attractive. Here, electrospinning was employed to afford poly (methyl acrylate) (PMAA)-poly (vinyl pyrrolidone) (PVP) electrospun nanofibers. Next, *in situ* photosynthesis resulted in the formation of a uniform assembly of silver nanoparticles (AgNPs) over the electrospun fibers, generating AgNPs-PMAA-PVP electrospun nanofibers, the as-formed AgNPs-PMAA-PVP electrospun nanofibers were utilized for investigating the catalytic reduction of 4-nitrophenol (4-NP) in the presence of NaBH₄. For the *in situ* synthesis, the available light sources were used including sunlight, table lamps, and 365 nm UV lamps, and the results showed that the AgNPs-PMAA-PVP electrospun nanofibers could catalyze 4-NP in the presence of NaBH₄, generating 4-aminophenol (4-AP) and reducing the toxicity of 4-NP. After the use of AgNPs-PMAA-PVP electrospun nanofibers for up to 4 cycles, the catalytic efficiency remained as high as 90%, suggesting that the noble metal/polymeric electrospun nanofibrous catalyst is highly effective and reusable.

INTRODUCTION

Nanoparticles have attracted significant attention, particularly in fields that environmental problems arise,¹⁻³ caused by their small size effect, surface effect and catalytic performance. Recently, silver nanoparticles (AgNPs) and their composite materials have been widely used in the field of catalysis, such as for the reduction of methyl orange,⁴ methylene blue,^{5, 6} janus green,⁷ trypan blue,⁸ and 4-nitrophenol (4-NP).⁹

On one hand, nitrophenol (NP) is an important chemical intermediate, which has been widely used for the manufacturing of chemicals, biochemicals and medicine. Unfortunately, all of its three isomers, ortho-isomer (1-NP), meta-isomer (2-NP) and para-isomer (4-NP) are toxic. Especially, the para isomer exhibits the highest toxicity.¹⁰ 4-NP exhibits good water solubility; however, it does not undergo general electrophilic reactions, caused by the electron-withdrawing nitro group, as a result, it is resistant to decomposition by oxidase in common microorganisms, thereby leading to long-term persistence in the soil and water.¹¹⁻¹³ Moreover, 4-NP can enter the human body through the respiratory tract and skin, thereby damaging the hematopoietic and nervous systems, and resulting in tumors

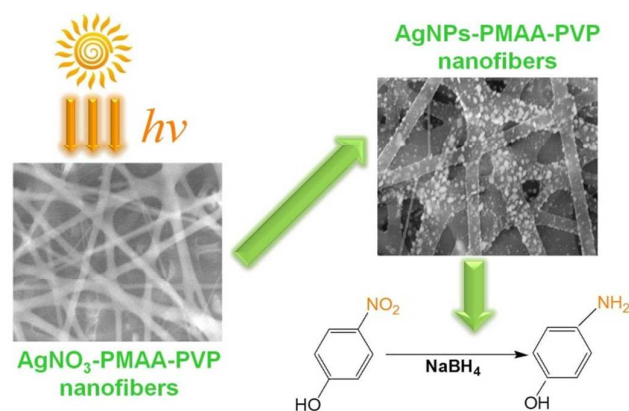
as well as producing mutation, finally causing tremendous damage to human health.¹⁴ For these reasons, it is vital to effectively treat such compounds.

On the other hand, electrospinning, in which a high-speed spray is generated by a conducting flow under a high-voltage static field, is a technique for the large-scale production of fibers on the order of magnitude of sub-micrometers, or even nanometers. As a result, nanofibers are obtained in a dash receiver by solvent evaporation or melt cooling.^{15, 16} As the equipment employed for electrospinning is simple and easy to operate, it is easy to control the chemical composition and physical properties of the electrospun nanofibers. In addition, the obtained non-woven fabrics exhibit advantages of large specific surface areas, high porosity, and uniformity,¹⁷ and the applications of electrospun nanofibers in the fields of biomedicine and electricity as well as optics have attracted significant attention.^{18, 19} Up to now, there are numerous studies about the preparation of the AgNPs-loaded micro- and nanofibrous materials by electrospinning, such as direct doping,²⁰ chemical reductions,²¹ photoreductions²² and decompositions,²³ *ect.* Wherein, *in situ* photoreduction is considered to be simple and easy, thus we choose this method to prepare the composite nanofibers.

In our previous study, electrospun nanofibers containing AgNPs were successfully prepared by the combination of electrospinning and *in situ* photosynthesis that can be used for enhancing Raman scattering signals.²⁴ Further investigation found that the AgNPs-PMAA-PVP electrospun nanofibers exhibited good catalytic activity, which was almost difficult for AgNPs to detach from the composite nanofibers, thereby retaining the catalytic activity of AgNPs after several recycling and reusability steps. Furthermore, this catalytic activity of

^a Key Laboratory of Luminescence and Real-Time Analytical Chemistry, Ministry of Education, College of Pharmaceutical Sciences, Southwest University, Chongqing 400715, China. E-mail: wj123456@swu.edu.cn; Phone: (+86) 23-68254059; E-mail: chengzhi@swu.edu.cn; Phone: (+86)23-68254659.

^b College of Chemistry and Chemistry Engineering, Southwest University, Chongqing 400715, China.



Scheme 1 Schematic of *in situ* photosynthesis of electrospun nanofibers and the catalysis activity towards 4-NP.

AgNPs-PMAA-PVP electrospun nanofibers was evaluated toward the reduction of 4-NP in the presence of NaBH₄ by the redox reaction (scheme 1). Results from the investigations indicated that the electrospun nanofibers doped with AgNPs photosynthesized *in situ* can be repeatedly used, and the high catalytic activity is retained even after four cycles. To our surprise, by the redox reaction, the toxicity of 4-NP decreased simultaneously. 4-aminophenol (4-AP) resulting from the reduction of 4-NP is an important chemical and a pharmaceutical intermediate, which is applicable to antipyretic, analgesic drugs, paracetamol, and dyestuff.^{25, 26}

EXPERIMENTAL SECTION

Instruments and reagents

To prepare the electrospun nanofibers, the DFS-01 electrospinning apparatus (Beijing Kai-weixin Technology Co., Ltd, China) was utilized. A desk lamp (11 W), a UV lamp of 365 nm with a power of 11 W, and sunlight were employed as the irradiation sources for preparing AgNPs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded using an S-4800 SEM system (Hitachi, Tokyo, Japan) and a TEM system (Hitachi, Tokyo, Japan), respectively. A TSX-6-12 muffle furnace (Beijing Xinite electric furnace company) was used for the calcination of the electrospun nanofibers to improve their stability. UV-vis absorption spectra were recorded with a U-3010 spectrophotometer (Shimadzu, Japan) at room temperature. SDT-Q600 (TA Instrument Company, American) was used to record thermogravimetric analysis data at a heating rate of 20 °C min⁻¹. A digital camera (Olympus E-510) was used to capture photographs.

Poly (vinyl pyrrolidone) (PVP, Mw = 1300000) was supplied by Aladdin, Ltd. Poly (methyl acrylate) (PMAA, Mw = 9500) and silver nitrate were purchased from Sigma-Aldrich. Dehydrated alcohol (>99%) was obtained from Chongqing Chuandong Ltd. All chemicals were used without further purification. Water purified by a MilliQ system (Millipore) was used throughout.

Preparation of AgNPs-PMAA-PVP electrospun nanofibers

Firstly, 5 mL of 8% PVP and 0.74 mL of a freshly prepared 0.6 mol/L silver nitrate solution was thoroughly mixed and then placed in a dark area with continuous magnetically stirring for 3 h. Secondly, 0.26 mL of a 10 % PMAA solution was added into the mixture, which was then magnetically stirred in a dark area until PMAA was totally dispersed. Thirdly, the mixture was transferred to a 10 mL tip plastic syringe for electrospinning. The commercial DFS-01 electrospinning apparatus was operated at an applied voltage of 20 kV, a collection distance of 20 cm, with an electrospinning solution feed rate controlled at 0.03 mm/min under a humidity of 50%-60% and a temperature of 25 °C - 30 °C. Next the as-prepared nanofibers were collected as overlaid membranes on an electrically grounded aluminum foil that covered the plate, and they were dried under vacuum at 30 °C overnight for removing the residual solvent and moisture. Finally, the electrospun nanofibers were illuminated under different light sources mentioned above, which could obtain different colors electrospun nanofibers. At last, the electrospun nanofibers were calcined at 200 °C for 4 h to get the stable AgNPs-PMAA-PVP electrospun nanofibers.

Catalytic properties of AgNPs-PMAA-PVP electrospun nanofibers

First, 0.036 g of the as-prepared electrospun nanofibers at room temperature were added into a mixture containing 0.25 mL of 1.0 × 10⁻² mol/L 4-NP, 0.25 mL of 5 mol/L NaBH₄, and 19.5 mL water. Under magnet stirring, UV-vis absorption was measured. The solution was filtered with a 0.45 μm filter film for removing the impurities before measurement, followed by capturing photographs of the mixture.

Reusability of AgNPs-PMAA-PVP electrospun nanofibers

The as-prepared electrospun nanofibers (0.08 g), which had been illuminated with different light sources at room temperature, were placed in mixture of solutions containing 0.25 mL of 1.0 × 10⁻² mol/L 4-NP, 0.25 mL of 5 mol/L NaBH₄, and 19.5 mL water, followed by magnetic stirring at room temperature. the solution was filtered using a 0.45 μm film for removing the impurities before measurements. And then, UV-vis absorbance was measured at 250 nm-550 nm every other 15 min. When the catalysis finished, the used electrospun nanofibers were collected, washed with water, and dried, then added to another cycle of 4-NP treatment. A treatment of 4 cycles was conducted for the catalysis of 4-NP.

Estimation of cytotoxicity

To estimate the cytotoxicity, 0.036 g of the as-prepared electrospun nanofibers illuminated using a UV lamp of 365 nm at room temperature was placed in a mixture of solutions containing 0.05 mL of 4-NP at different concentrations, 0.05 mL of 5 mol/L NaBH₄, and 3.9 mL water. After finishing the reaction, the solution was filtered with a 0.45 μm film for removing the impurities, which resulted in a colorless solution. Next, human laryngeal epithelial cells at a concentration of 1.0 × 10⁻⁴ were planted to each grid, which were incubated for 24 h to investigate the cytotoxicity of the filtrate.

RESULTS AND DISCUSSION

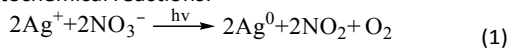
Preparation of electrospun AgNPs-PMAA-PVP electrospun nanofibers

Sunlight is an important ubiquitous source of light in the nature, hence, we checked whether the electrospun nanofibers could exploit natural sunlight. As shown in Fig. 1 A, with increasing the illumination time, the color of the membrane gradually deepened from brown till finally changing to pink after 24 h, suggesting that AgNPs were generated on the electrospun nanofibers after illumination with natural sunlight. In other words, natural sunlight can be used for the *in situ* photo synthesis.

Fig. 1B also shows the properties of the electrospun nanofibers under illumination by different light sources. Without light irradiation, the electrospun nanofibers did not exhibit any absorption band, while under illumination by a UV lamp of 365 nm, table lamp and sunlight, the nanofibers exhibited the maximum absorption band at 424 nm, 430 nm, and 432 nm, respectively. The absorption spectra, colourful images and solution suggested the generation of AgNPs after light irradiation.²⁷

As shown in Fig. 2, the amount of the AgNPs photosynthesized in the electrospun nanofibers illuminated by a 365 nm UV lamp (B), table lamp (C), and sunlight (D) increased as compared with that of nanofibers without illumination (A). The AgNPs-PMAA-PVP electrospun nanofibers illuminated by a UV lamp of 365 nm were taken as a representative example to explore the fine structure of the nanofibers. After the size statistics of AgNPs on the nanofibers, it is found that the AgNPs with diameters ranging from 15 to 25 nm are distributed on the surface of the PMAA-PVP electrospun nanofibers (inset from Fig. 2B). It is also demonstrated that the illuminations will further promote the formation of AgNPs.

The elemental analysis profiles in Fig.3 also show that the electrospun nanofibers under illumination with different light sources contained Ag, C and O. Particularly, the atom percentage of Ag were more than 3.80%, suggesting the formation of AgNPs on nanofibers. Hence, the corresponding reactive processes of generating AgNPs are presumed as follows: (1) the partial Ag^+ ions were dispersed homogeneous in solution by chelating effect and reduced to tiny Ag atoms as seeds with the carbonyl oxygen of PVP; (2) the rest of Ag^+ might be adsorbed around the surface of nuclei, which were potential foreshadowing for the following photoreduction; (3) photochemical reactions:^{24, 28}



In order to evaluate the mass content of AgNPs on the AgNPs-PMAA-PVP electrospun nanofibers, thermogravimetric analysis was examined. As shown in Fig. 4, all samples displayed two loss distinct weight loss regions in 50-500 °C range. The first weight loss region could be attributed to the desorption of the water at about 100 °C, and the second weight loss was due to degradation of the polymer molecules at about 300 °C. This different maximum decomposition was

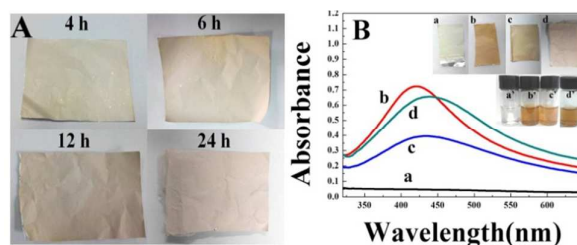


Fig. 1 Optical properties of the as-prepared electrospun nanofibers without calcination. (A) Photographs of the electrospun nanofibers from the AgNO_3 -PMAA-PVP solution illumination by sunlight at different times. (B) UV-vis absorption spectra of aqueous suspensions of the as-prepared products. Insets in (B) show the photographs of electrospun nanofibers illuminated with different light sources (top), and the optical images of the as-prepared products in the reaction solution are shown at the bottom. a, before illumination; b, illumination under a UV lamp of 365 nm; c, illumination under desk lamp; d, illumination under sunlight.

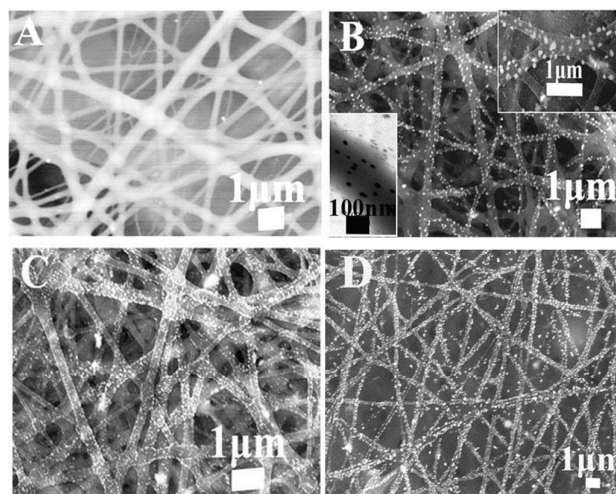


Fig. 2 SEM images of the AgNPs-PMAA-PVP electrospun nanofibers prepared under different light sources. All nanofibers were calcined at 200 °C for 4 h. A, Before illumination; B, illumination under a UV lamp of 365 nm, with insets showing the high-resolution SEM image (top right) and TEM image (bottom left); C, illumination under desk lamp; D, illumination under sunlight.

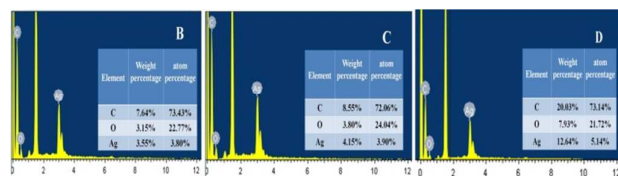


Fig. 3 Elemental analysis profiles of the AgNPs-PMAA-PVP electrospun nanofibers under illumination by different light sources. All nanofibers were calcined at 200 °C for 4 h. B, illumination under a 365 nm UV lamp; C, illumination under desk lamp; D, illumination under sunlight.

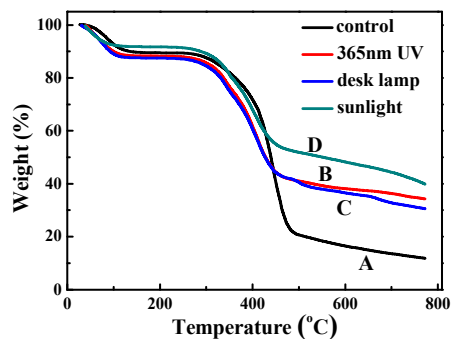


Fig. 4 Thermogravimetric analysis curves of AgNPs-PMAA-PVP electrospun nanofibers prepared under different light sources. A, pure PMAA-PVP electrospun nanofibers; B, illumination under a UV 365 nm lamp; C, illumination under desk lamp; D, illumination under sunlight.

affected by AgNPs residue. Herein, the AgNPs weight of with a 365 nm UV lamp, a table lamp, and sunlight were 20.58%, 19.70%, 30.76%, respectively. That is to say, the real content of AgNPs depends on the light source used, which is similar to the result in Fig. 3. We take AgNPs-PMAA-PVP electrospun nanofibers under illumination of a 365 nm UV lamp as a representative example to study the properties of AgNPs-PMAA-PVP electrospun nanofibers considering the following issues: (1) sunlight will vary with the changes of season and weather; (2) the humidity in the air is high and AgNPs-PMAA-PVP electrospun nanofibers hard to keep the normal morphology.

Notably, the AgNPs-PMAA-PVP electrospun nanofibers exhibit strong hygroscopicity, which is a characteristic not beneficial for storage. In this case, we prepared the electrospun nanofibers by calcination at 200 °C for 4 h, rendering them stable. By subjecting the electrospun nanofibers to a thermal treatment at 200 °C, inter- and intra-molecular anhydridization reaction involving the carboxylic acid groups of PMAA,^{29,30} and the shrinking of the nanofibers with evaporation of remanent solvent³¹ could solidify the composite nanofibers to form a water-stable material. As shown in Fig. 5 the morphology of the AgNPs-PMAA-PVP electrospun nanofibers was almost unchanged after calcinations and contacting with aqueous solution. What's more, it has been reported that PMAA and PVP present good thermal stabilities, which will be degraded until 420 °C and 380 °C, respectively.³⁰ In our work, AgNPs-PMAA-PVP electrospun nanofibers were calcinated at 200 oC, which could degrade neither PMAA nor PVP. That is, the electrospun nanofibers remain unchained in structure after calcination at 200 °C.

Catalysis of AgNPs-PMAA-PVP electrospun nanofibers on the reduction of 4-NP

Nano-silvers, similar to other nanoparticles,³²⁻³⁴ exhibit surface effects, catalytic performance, and other special properties, which significantly depend on the particle size, specific surface area, as well as state and shape. In such cases, the composite nanofibers produced by nanoparticles obtained by electrospinning are thought to exhibit high catalytic activity as the resulting fibers exhibit a large specific surface area and

high porosity.¹⁰⁻¹⁴ Hence, the catalytic performance of AgNPs attached to the electrospun nanofibers was investigated. First,

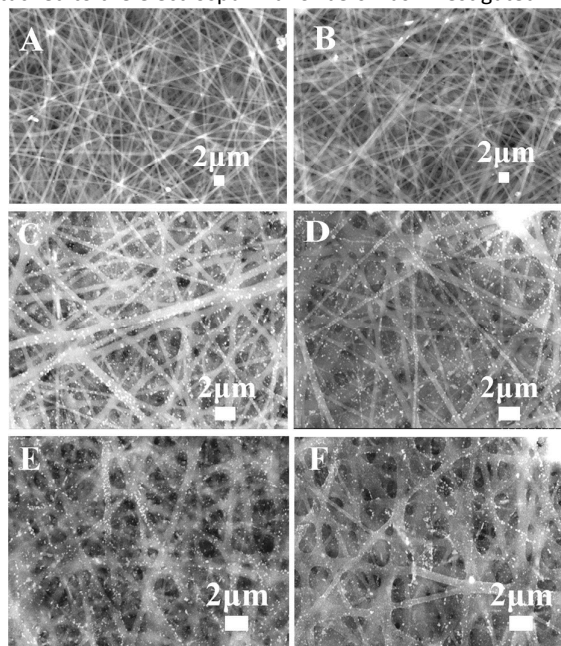
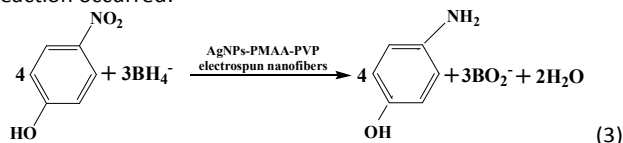


Fig. 5 (A-B) SEM images of AgNPs-PMAA-PVP electrospun nanofibers without illumination. A, before calcination; B, after calcination. (C-F) SEM images of calcinated AgNPs-PMAA-PVP electrospun nanofibers under illumination by a UV lamp of 365 nm after contacting for different time with aqueous solution. C, 0 min; D, 10 min; E, 20 min; F, 35 min.

we examined the reaction of a mixture of solution containing 4-NP and NaBH₄ without the AgNPs-PMAA-PVP electrospun nanofibers and observed that absorbance at 400 nm, which is attributed to the characteristic absorption band of 4-NP. The inset of Fig. 6 A exhibited no changes for the 4-NP and NaBH₄ mixture that without the AgNPs-PMAA-PVP electrospun nanofibers, suggesting that the redox reaction related to 4-NP does not occur, and the decrease of absorbance is solely attributed to the physical adsorption of 4-NP on the surface of the composite nanofibers.^{21, 35} However, in the presence of AgNPs-PMAA-PVP electrospun nanofibers, the absorbance of the mixture containing 4-NP and NaBH₄ at 400 nm gradually decreased with prolonging the reaction time. Simultaneously, a new small absorption band was observed at 290 nm, which is attributed to the characteristic absorption of 4-AP (Fig.6 B, C, and D).³⁶⁻³⁹ As a consequence of the catalysis reaction, 4-NP gradually converted to 4-AP, and the solution color faded from yellow (the insets in Fig. 6 B, C, and D), wherein the following reaction occurred:³¹



In such cases, the change in the concentration of 4-NP at different times can be expressed as follows:

$$A = \epsilon cL \quad (4)$$

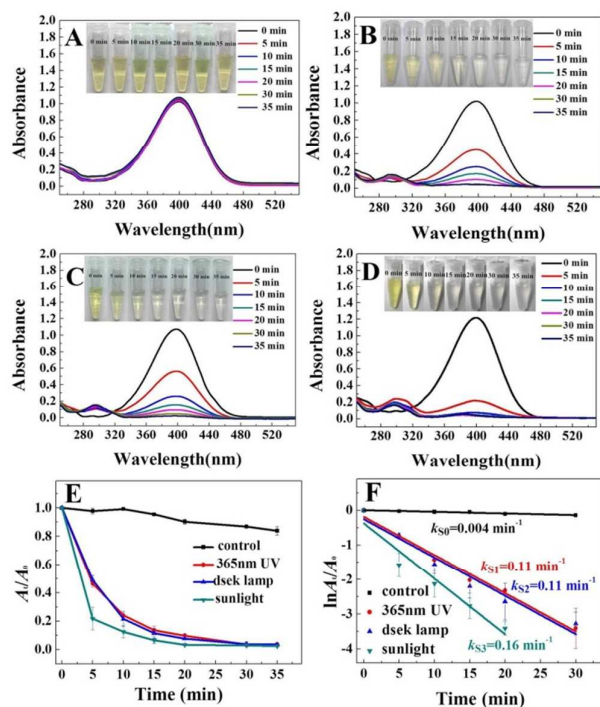


Fig. 6 (A-D) UV-vis absorption spectra and photographs (insets) of 4-NP solutions at different reaction times. A, before illumination; B, under illumination of a 365 nm UV lamp; C, under illumination of a desk lamp; D, under illumination of sunlight. E, A_t/A_0 versus reaction time for the reduction of 4-NP; F, Degradation kinetics of 4-NP. All nanofibers were calcined at 200 °C for 4 h. The weight of the electrospun nanofibers was 0.036 g. C_{4-NP} , 1.25×10^{-4} mol/L; C_{NaBH_4} , 6.25×10^{-2} mol/L.

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (5)$$

From these equations, we have,

$$\ln\left(\frac{A_t}{A_0}\right) = -kt \quad (6)$$

Here, A is absorbance, A_0 is the initial absorbance, A_t is the absorbance at corresponding time t , ε is the absorptivity, c is the concentration (mol/L), L is the thickness of the absorption cell (cm), and t is the reaction time (min), k is rate constant for the reductive reaction. According to Eq (6) as well as the plot of A_t/A_0 versus reaction time for the reduction of 4-NP shown in Fig. 6 E, and the kinetics of the degradation of 4-NP shown in Fig. 6 F, the catalytic performance of the AgNPs-PMAA-PVP electrospun nanofibers was almost the same as that exhibited by AgNP-containing PAA-PVA nanofibrous mats.²¹ At the same time points, the catalytic reductive efficiency of 4-NP follows the order from the rate constants: sunlight > UV lamp of 365 nm \approx table lamp, this result might be because of the amount of AgNPs are different, which also corresponded with the elemental analysis profiles (Fig.3) and thermogravimetric analysis curves (Fig.4).

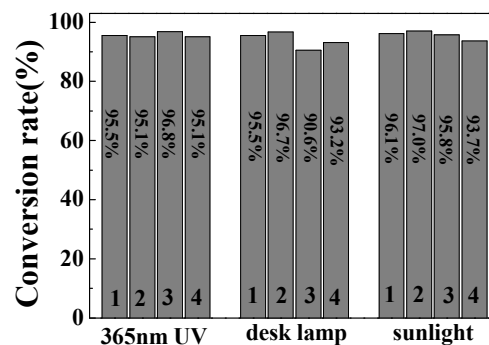


Fig. 7 Conversion rates of AgNPs-PMAA-PVP electrospun nanofibers catalytic ability (4 cycles) prepared under illumination with different light sources. All nanofibers were calcined at 200 °C for 4 h. The weight of electrospun nanofibers was 0.08 g. C_{4-NP} , 1.25×10^{-4} mol/L; C_{NaBH_4} , 6.25×10^{-2} mol/L.

Reusability

For testing the recyclability of the AgNPs-PMAA-PVP electrospun nanofibers, the electrospun nanofibers were repeatedly used. In such cases, we measured the conversion rate of 4-NP, which could be defined as follows:

$$r_w = \frac{A_0 - A}{A_0} \times 100\% \quad (7)$$

Here, r_w represents the conversion rate of 4-NP into 4-AP, A_0 is the initial absorbance; A is the absorbance of which reaction time is 15 min. The reusability of the electrospun nanofibers illuminated by 365nm UV lamp, desk lamp and sunlight were conducted, as shown in Fig. 7. The conversion rates of 4-NP catalyzed with AgNPs-PMAA-PVP electrospun nanofibers were more than 90%, suggesting that the catalytic ability of the AgNPs-PMAA-PVP electrospun nanofibers kept very well after reuse. In other words, the catalytic properties of the fibrous materials performed in aqueous solution of 4-NP were very stable.

Stability and recovery are the two key factors determining whether the AgNPs-PMAA-PVP electrospun nanofibers can be recycled.⁴⁰ Generally, because of the van der Waals force and high surface energy, the nanoscale metal particles in solution can mutually combine, resulting in the increase of particle size and the decrease of number as well as the decrease of the potential difference between metal particles and 4-NP, which decrease or lower the catalytic rate.⁴¹ However, in this work, the introduction of PMAA in PVP polymeric nanofibers can significantly improve the stability of catalysts. The side chain of PMAA, which has been proven to be a versatile template for preparing Ag nanoclusters, has sufficient carboxylic acid groups, which not only exhibits strong adsorption for silver ions but also prevent nanoclusters from further growing to large nanoparticles; in other words, the carboxyl acid groups of PMAA do not coordinate with Ag ions.¹⁸ Simultaneously, PMAA can eliminate free radical hydroxyl ions for preventing the oxidation of silver nanoclusters into silver oxide.⁴² What's

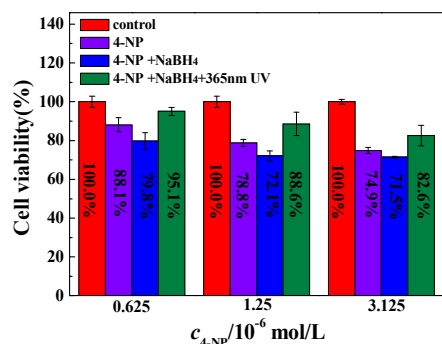


Fig.8 Cytotoxicity test of 4-NP solutions before and after treatment with AgNPs-PMAA-PVP electrospun nanofibers under illumination with a 365 nm UV lamp. All nanofibers were calcined at 200 °C for 4 h. The weight of electrospun nanofibers was 0.036 g. c_{NaBH_4} , $6.25 \times 10^{-2} \text{ mol/L}$.

more, the strong coordination between carbonyl oxygen of PVP and Ag enable PVP as a protective agent for preventing AgNPs from aggregating.²⁴

In addition, the combination of high-voltage static electrospinning and *in situ* photo synthesis produce AgNPs exhibiting catalytic activity fix on the microscopic base of the electrospun nanofibers, in other words, the stability of the AgNPs-PMAA-PVP electrospun nanofibers further increases. Thus, upon recycling, AgNPs nearly do not detach from the AgNPs-PMAA-PVP electrospun nanofibers, which is attributed to the calcination at 200 °C, enable these electrospun nanofibers with high water-stability to separate from the water for recycling.

Cytotoxicity test

To evaluate the effect of reduction of toxic 4-NP by the AgNPs-PMAA-PVP electrospun nanofibers, the *in vitro* cytotoxicity of all solutions was tested. As shown in Fig. 8, the higher concentration of 4-NP led to the greater cytotoxicity. The presence of AgNPs-PMAA-PVP electrospun nanofibers promotes to increase cell viability, suggesting that the catalysis of the AgNPs-PMAA-PVP electrospun nanofibers reduces the cell cytotoxicity of 4-NP solutions. This reduction in cell toxicity is possibly attributed to the conversion of 4-NP to 4-AP after catalysis with AgNPs-PMAA-PVP electrospun nanofibers, and the cytotoxicity of 4-AP is less than that on 4-NP.⁴³

CONCLUSIONS

AgNPs-PMAA-PVP electrospun nanofibers, prepared from high-voltage static electrospinning and *in situ* photo synthesis, exhibit good catalytic performance for the conversion of 4-NP to 4-AP with high stability and recycling ability. As the introduced PMAA can adsorb significant amount of Ag⁺ on polymers, the AgNPs were tightly held by the electrospun nanofibers mats. Undoubtedly, the photosynthesis of AgNPs-PMAA-PVP electrospun nanofibers makes this a facile technique with high energy saving.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (NSFC, 21375109), the National Innovation and Entrepreneurship Training Program of Southwest University (201410635061), and undergraduate innovative experimental projects of Southwest University College of Pharmaceutical Sciences.

Notes and references

- A. K. Roy, S. Y. Park and I. In, *Nanotechnology*, 2015, 26, 105601.
- D. P. Kumar, *RSC Adv.*, 2014, 4, 45449-45457
- V. V. Kumar and S. P. Anthony, *RSC Adv.*, 2014, 4, 18467-18472.
- A. Bhanekar, M. Giri, K. Yadav and N. Jaggi, *Indian J. Phys.*, 2014, 88, 1191-1196.
- Y. C. Tang, T. Wu, B. T. Hu, Q. Yang, L. Liu, B. Yu, Y. Ding and S. Y. Ye, *Mater. Chem. Phys.*, 2015, 149-150, 460-466.
- S. Ashokkumar, S. Ravi, V. Kathiravan and S. Velmurugan, *Environ. Sci. Pollut. Res.*, 2014, 21, 11439-11446.
- S. S. Mortazavi and A. Farmany, *J. Ind. Eng. Chem.*, 2014, 20, 4224-4226.
- T. N. Ravishankar, T. Ramakrishnappa, H. Naqabshana, V. S. Souza, J. Dupont and G. Naqaraju, *New J. Chem.*, 2015, 39, 1421-1429.
- G. Abilash, P. Ramakrishna, M. Ramakrishna, K. Lohith, J. Chelli and M. R. Apparao, *Langmuir*, 2011, 27, 15268-15274.
- F. H. Lin and R. A. Doong, *Appl. Catal. A-Gen.*, 2014, 486, 32-41.
- I. B. Zafar, H. Toda and T. Haruko, *Water Res.*, 2002, 36, 1135-1142.
- J. X. Liu, H. Chen, Z. Lin and J. M. Lin, *Anal. Chem.*, 2010, 82, 7380-7386.
- N. E. Alireza and K. Setareh, *J. Ind. Eng. Chem.*, 2014, 20, 937-946.
- T. P. Chen, F. Q. Liu, C. Ling, J. Gao, C. Xu, L. J. Li and A. M. Li, *Environ. Sci. Technol.*, 2013, 47, 13652-13660.
- Q. Dong, G. Wang, T. T. Wu, S. P. Peng and J. S. Qiu, *J. Colloid Interface Sci.*, 2015, 446, 373-378.
- L. Chen, S. Y. Wang, C. M. Zhao and Q. Wang, *Spectrochim. Acta A*, 2015, 142, 43-49.
- A. F. Che, V. Germain, M. Cretin, D. Cornu, C. Innocent and S. Tingry, *New J. Chem.*, 2011, 35, 2848-2853.
- H. Yang, P. F. Gao, W. B. Wu, X. X. Yang, Q. L. Zeng, C. Li and C. Z. Huang, *Polym. Chem.*, 2014, 5, 1965-1975.
- W. Y. Liu, J. C. Wei and Y. W. Chen, *New J. Chem.*, 2014, 38, 6223-6229.
- Z. F. Ouyang, J. F. Li, J. H. Wang, Q. Li, T. Y. Ni, X. Y. Zhang, H. X. Wang, Q. Li, Z. Q. Su and G. Wei, *J. Mater. Chem. B*, 2013, 1, 2415-2424.
- S. Xiao, W. Xu, H. Ma and X. Fang, *RSC Adv.*, 2012, 2, 319-327.
- Z. Y. Li, H. M. Huang, T. C. Shang, F. Yang, W. Zheng, C. Wang and S. K. Manohar, *Nanotechnology*, 2006, 17, 917-920.
- H. He, W. P. Cai, Y. X. Lin and Z. F. Dai, *Langmuir*, 2011, 27, 1551-1555.
- H. Yang and C. Z. Huang, *RSC Adv.*, 2014, 4, 38783-38790.
- P. Deka, R. C. Deka and P. Bharali, *New J. Chem.*, 2014, 38, 1789-1793.
- H. Li, J. Y. Liao and T. Zeng, *Catal. Sci. Technol.*, 2014, 4, 681-687.
- B. Chen, X. L. Jiao and D. Chen, *Cryst. Growth Des.*, 2012, 10, 3378-3386.
- T. Yang, H. Yang, S. J. Zhen and C. Z. Huang, *ACS Appl. Mater. Interfaces*, 2015, 7, 1586-1594.

- 29 J. Y. Park, J. J. Yun, C. H. Hwang and I. H. Lee, *Mater. Lett.*, 2010, 64, 2692-2695.
- 30 G. Polacco, M. G. Cascone, L. Petarca and A. Peretti, *Eur. Polym. J.*, 2000, 36, 2541-2544.
- 31 T. Yang, H. Y. Zou and C. Z. Huang, *ACS Appl. Mater. Interfaces*, 2015, 7, 15447-15457.
- 32 B. D. Briggs, Y. Li, M. T. Swihart and M. R. Knecht, *ACS Appl. Mater. Interfaces*, 2015, 7, 8843-8851.
- 33 H. M. Wang, D. Z. Wang, Z. Peng, W. Tang, N. Li and F. Liu, *Chem. Commun.*, 2013, 49, 5568-5570.
- 34 J. Y. Jin, X. Y. Ouryang, J. S. Li, J. S. Li, J. H. Jiang, H. Wang, Y. X. Wang, and R. H. Yang, *Sci. China Chem.*, 2011, 54, 1266-1272.
- 35 D. M. Hu, Y. P. Huang, H. Liu, H. Wang, S. G. Wang, M. W. Shen, M. F. Zhu and X. Y. Shi, *J. Mater. Chem. A*, 2014, 2, 2323-2332.
- 36 X. M. Chen, Z. X. Cai, X. Chen and M. Oyama, *J. Mater. Chem. A*, 2014, 2, 5668-5674.
- 37 P. Zhang, C. L. Shao, Z. Y. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo and Y. C. Liu, *Nanoscale*, 2011, 3, 3357-3358.
- 38 X. Fang, H. Ma, S. L. Xiao, M. W. Shen, R. Guo, X. Y. Cao and X. Y. Shi, *J. Mater. Chem.*, 2011, 21, 4493-4501.
- 39 W. N. Sun, X. F. Lu, Y. P. Xue, Y. Tong and C. E. Wang, *Macromol. Mater. Eng.*, 2014, 299, 361-367.
- 40 P. Zhang, C. L. Shao, X. H. Li, M. Y. Zhang, X. Zhang, C. Y. Su, N. Lu, K. X. Wang and Y. C. Liu, *Phys. Chem. Chem. Phys.*, 2013, 15, 10453-10458.
- 41 Q. Zhou, G. Z. Qian, Y. Li, G. Zhao, Y. W. Chao and J. W. Zheng, *Thin solid Films*, 2008, 516, 953-956.
- 42 H. Xu and K. S. Suslick, *ACS Nano*, 2010, 4, 3209-3214.
- 43 T. T. Fang, *Master's thesis of Wuhan University of Technology. Wuhan*, 2013, 13-28.