OPEN ACCESS

ACTA METALLURGICA SLOVACA

2020, VOL. 26, NO. 3, 100-103

RESEARCH PAPER

FACILE DECORATION OF SILVER NANOWIRES MICROSTRUCTURE WITH CARBON NITRIDE NANOPARTICLES AS A MEMBRANE FOR WATER TREATMENT

Thuyet Minh Nguyen[1*], Hung Thai Le[1], Khanh Quoc Dang[1]

[1] School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

*Corresponding author: thuyet.nguyenminh@hust.edu.vn, tel.:+84 24 3868 0409, School of Materials Science and Engineering, Hanoi University of Science and Technology, No.1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam

Received: 09.06.2020
Accepted: 27.07.2020

ABSTRACT

Silver nanowires (AgNWs) decorated by carbon nitride nanoparticles (CNPs) have been successfully synthesized using glucose as a carbon source, melamine as a nitrogen source and $AgNO_3$ as a silver source via the hydrothermal process and applying in the preparation of fouling membranes. Together, the freshly synthesized AgNWs and CNPs produced through redox reaction of glucose and melamine, processes the in-situ assembly of the coaxial 1D nanostructure of Ag covered by CNPs. The obtained CNPs with the uniform size of around 20 nm were aggregated on the surface of AgNWs which has average diameter of 50 nm. The fabricated AgNWs/CNPs membrane performances an enhanced photocatalytic activity under visible-range irradiation and shows excellent dye degradation catalyst.

Keywords: Silver nanowire, carbon nitride nanoparticle, membrane, hydrothermal method, photocatalytic

INTRODUCTION

Recently, membrane filtration technology has been widely applied due to its reliability and facile operation [1]. Up to different pollutants, the membrane fouling can be categorized into organic fouling, inorganic fouling, and biofouling [2]. Whatever kind of fouling happens, it will lead to a critical decrease in filtration activity, thus increasing maintenance price and shortened life-time of the membrane. Therefore, huge efforts have been invested to comprehend this problem as an urgent need.

Up to now, various nanomaterials have been demonstrated and decorated into membrane matrixes to form nanocomposite membranes in order to achieve specific desired properties. Among them, Silver nanowire (AgNWs) have attracted a lot of attention in modifying membrane materials due to their superior antibacterial characteristics. The AgNWs based nanocomposites membranes show crucial antibacterial and anti-biofouling behavior, which is assigned to the release of ion Ag+ [3].

Graphitic carbon nitride (CNPs) having the similar 2D layered structure of graphene possesses excellent visible photocatalysis as well as low cost and simple synthetic process that makes it the most attractive materials in the field of photocatalytically environmental purification [4-7]. However, the CNPs still has a limit due to the recombination of photo-induced charge carriers. Therefore, many approaches have been developed to improve electron-hole separation in pure CNPs [8-11]. Compared to other strategies, noble metal decoration has been regarded as a facile method for remedying the issue. According to several reports, CNPs combined with silver nanostructures can effectively improve charge separation performance, thus leading to boost the photocatalytic activity of the composite.To the best of our knowledge, the synthesis of AgNWs decorated by CNPs nanoparticles and its photocatalytic effect has not been reported yet.

Herein, the AgNWs/g-CNPs nanocomposite was synthesized via the simple mixing process from two fresh nanomaterials AgNWs and CNPs which were fabricated through the hydrothermal method. The as-synthesized composites were characterized by different analyses, then it could be used to introduce to the membrane for real applications.

MATERIAL AND METHODS

Materials and processing

In this study, Silver nitrate (AgNO3**)** was used as the precursor in the preparation of AgNWs. Firstly, the oven was turned on within 15 minutes to heat the glass bottle contained 20ml ethylene glycol (EG). During heating time, 17mg NaCl was supplemented and waited until the temperature reached to 100ºC then 20 mg $AgNO_3$ was added to the solution. Continuously, the temperature was increased slowly in 10 minutes to reach 135 – 140ºC, and 300 mg PVP was poured into. In next 8 minutes, the temperature was heated up to 155-160ºC and finally 250 mg $AgNO_3$ was added to the solution. This amount of $AgNO_3$ played the role of providing the Ag atoms toward the formation of Ag nanowires. To complete the reaction, the solution was heated at 160ºC for 6 hours and then cooled to the room temperature. In addition, centrifugal technique was used to dislodge the liquid and remove EG and excess PVP. Finally, the AgNWs was stored in ethanol to from the Ag nanowire suspension.

To synthesis of CNPs, 400 mg Melamine was dissolved in 80 ml DI water. This solution was ultrasonic vibrated for 1 hour then transferred into a 100ml Teflo-line stainless steel autoclave and reacted under the solvothermal condition at 180ºC in 24 hours. Finally, the yellow product which is known as CNPs was collected after 5 times of centrifugal operation at 10000 rpm in 15 minutes. The obtained CNPs then was dried overnight in the oven under vacuum at 60ºC.

The CNPs/AgNWs cellulose ester membranes was fabricated by a process as follows. Firstly, CNPs/AgNWs was prepared by adding 20 mg CNPs into 30 ml AgNWs 0.1 mg/mL, stirring in 2 hours, filtrating by 200nm filter paper then washing and drying in vacuum for 6 hours. Secondly, 100 mg dried CNPs/AgNWs powder were added into DMF and well dispersed by ultrasonic. Then the cellulose ester was dissolved, heated up and kept at 60ºC until the dissolution was completely. Finally, the solution was degassed at 60ºC and then scattered on class petri-dish. The nascent membrane was dipped in pure water at room temperature to induce phase inversion.

Characterization

Morphological structures of samples were characterized by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystal structure was examined by X-ray diffraction (XRD)at a scanning rate of 10 min^{-1} in the range of 10–80. To investigate the optical properties the UV-Vis absorption spectra were collected at room temperature. Methylene Blue photodegradation of the synthesized samples under visible light was investigated as well.

RESULTS AND DISCUSSION

Figure 1 shows the synthesized Ag nanowire suspension, the XRD pattern and SEM images of dried AgNWs confirmed that the AgNWs have been synthesized successfully. Thus, from the XRD parttern (Fig. 1b), there are two obvious peaks with the positions in coherence with a standard spectrum of silver metal (JCPDS file No. 04-0783) at $2\theta \sim 38^0$ and $2\theta \sim 44^0$. These peaks correspond to the 111 and

200 reflections, respectively, of the silver cubic lattice indicating that the AgNWs were obtained in a crystalline form [12-14]. The morphology of the synthesized nanowires was observed by the scanning electron microscope, the results are presented in Figs 1c and d. These SEM images indicate that the prepared AgNWs sample consisted of uniform wires of solid form with smooth surface and have an average diameter and an average length of 50 nm and 30 µm, respectively that could be estimated from the insert images in Fig 1.

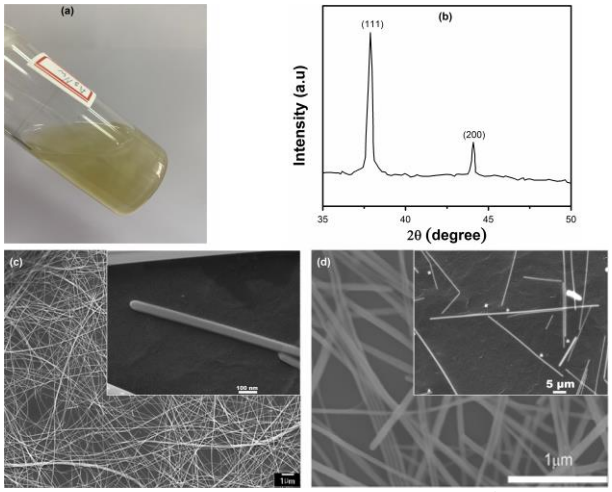

Fig. 1 (a) Ag nanowire in ethanol solvent. (b) XRD pattern of Ag nanowire. (c), (d), SEM images of Ag nanowires

In this work, melamine was used as the initial material for the synthesis of CNPs via the hydrothermal process which was mentioned in the early part of this paper. The prepared powder has yellow color as being seen in Fig. 2a and Fig. 2b. The morphology of the powders was probed by SEM and shown in Fig. 2c and Fig. 2d. The results indicate that the fabricated CNPs are uniform with the near-spherical shape and an average particle size of about 20 nm.

The CNPs/AgNWs nanocomposites was synthesized in the decoration procedure, CNPs powder was added into the AgNWs solution and stirred for 2h. Finally, the CNPs/AgNWs composite was achieved by filtration, washing, and drying. The morphology of the obtained CNPs/AgNWs sample was observed by SEM and presented in figure 3a. The result indicates that the nanocomposites were successfully synthesized with a large amount of the CNPs decorated firmly on the surface of the AgNWs. This would be beneficial for the transfer of the electrons to the surface, improving the electron-hole separation and boost the photocatalytic activity of the composite [7, 8].

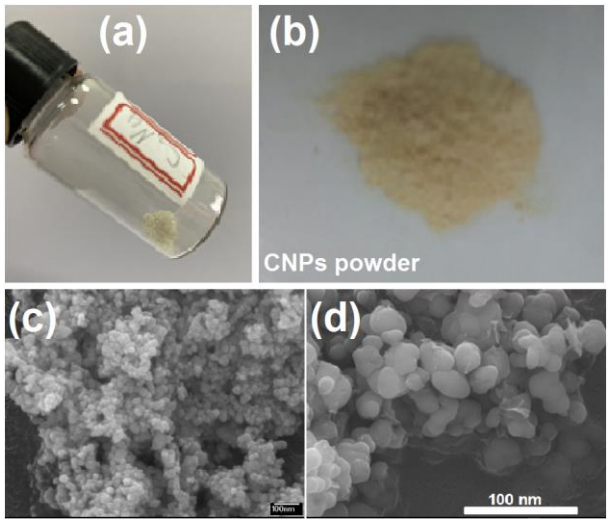

Fig. 2 (a), (b) The as-synthesized CNPs powder, and (c), (d) their SEM images

The as-fabricated CNPs/AgNWs nanocomposites then was used to prepare CNPs/AgNWs cellulose ester membranes by using the wet phase inversion process [15]. In that process, CNPs/AgNWs composite was dispersed in polymer matrix. Fig. 3b shows that the dispersion is uniformly. Fig. 3c shows the real image of the prepared CNPs/AgNWs cellulose ester membrane scattered on a class petri-dish.

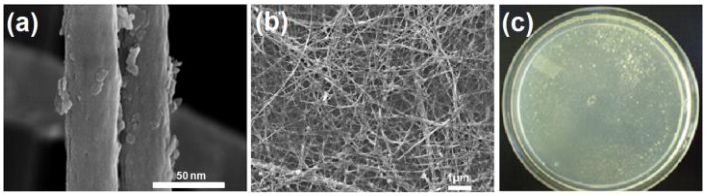

Fig. 3 SEM images of (a) the AgNWs decorated by CNPs and (b) The distribution of CNPs/AgNWs in polymer matrix and (c) the CNPs/AgNWs cellulose ester membrane

To study the optical properties, the UV-Vis absorption spectra of the samples were collected at room temperature and the results are presented in the figure 4. In case of the synthesized AgNWs sample, we have to note that the UV-Vis absorption goes along with the length direction (known as longitudinal plasma band) and along with the width direction to be called transverse plasma band [16, 17]. Figure 4 shows the UV-Vis spectra of the prepared AgNWs with a standard ultraviolet-visible absorption of pure silver nanowires, indicating the typical characteristic of AgNWs related to the localized surface plasmon resonances [18, 19]. Indeed, the presence of a small absorption peak at 350 nm which is similar to the bulk silver could be attributed to the plasmon response of long silver nanowires, whereas the maximum peak at about 380 nm maybe attributed to the transverse plasmon mode of silver nanowires. However, a peak at 410 nm corresponding to silver nanoparticles did not show up in the spectrum. In case of the CNPs the absorbance curve exposes an absorption edge at around 460 nm, corresponding to a bandgap of 2.270 eV that has been confirmed from other previous studies [4, 8, 20]. The result also shows that the absorption edge of the as-synthesized CNPs/AgNWs exposes a slight shift to 480 nm. Moreover, the light absorption ability of the CNPs/AgNWs is much higher in comparison with the CNPs. In addition, the composite also exhibits a wider range absorption to visible range compared with CNPs, indicating that the open of band gap of the composite which may result from charges transfer from the AgNWs to the CNPs. It is the fact that the wider light absorption range and stronger absorption ability can benefit the photoactivity significantly.

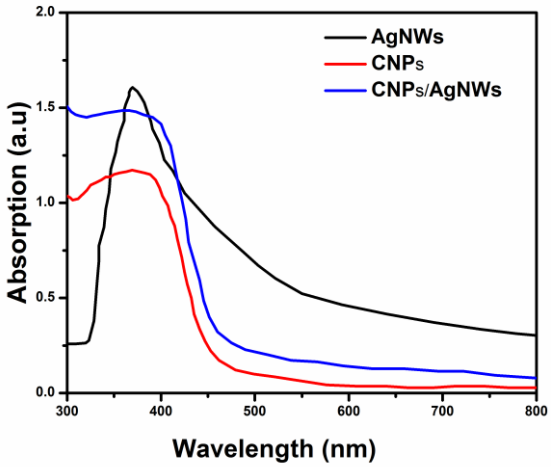

Fig. 4 UV-Vis absorption spectra of the synthesized AgNWs, CNPs and CNPs/AgNWs samples

In order to examine the photocatalytic activity of the synthesized materials and the performance of the membrane, the photodecomposition rate of methylene blue (MB) under visible light irradiation was conducted (Fig. 5). In experiment procedure, the feed stream of MB (100 ppm) is pumped to the coated side of the photocatalytic membrane and flows in parallel with the surface of the membrane. The permeate flow moves through the membrane in a direction perpendicular to the membrane surface while the solar-simulator was placed on top as the light source (Xenon lamp with 400 nm cut-off filter, 500W). The permeate flow was recycled back to the feed tank during the operation. The nanofiltration performance was evaluated after employing the membranes into photocatalytic filtration for different times.

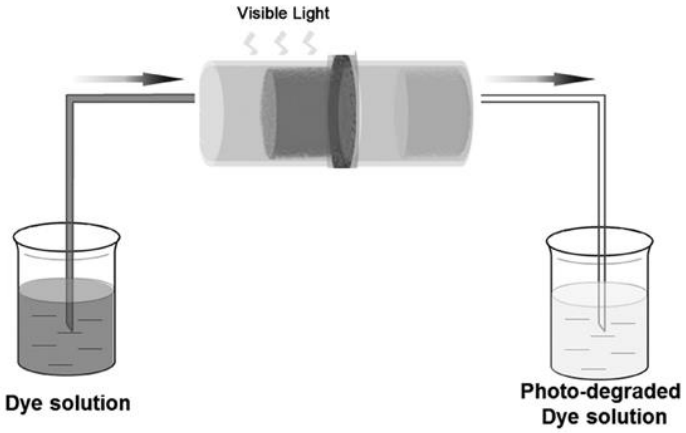

Fig. 5 The photodecomposition rate of methylene blue (MB) under visible light irradiation analysis

Figure 6 illustrates the relation between MB normalized concentration (C/C0) and reaction time of AgNWs, CNPs, and CNPs/AgNWs composite, respectively. The AgNW exhibits a very low catalytic activity with 7% of MB decomposed after 100 mins. In contrast, CNPs shows a higher photocatalytic efficiency with approximately 65 % of degraded dye. Interestingly, by combing CNPs and AgNWs, only 10 % of MB remains in the solution, indicating that visible-light MB degradation is significantly enhanced due to the decoration of CNPs on the surface of AgNWs that reduces the penetration of light into the photocatalyst and generates larger amount of photon adsorbed on the catalyst surface [8]. In addition, it could be attributed that the plasmon effect of AgNWs [21] can enhance electron ejection to CNPs, thus leading to improve photocatalyst efficiency. However, due to the lack of active sites AgNW shows a very poor activity. These results demonstrate that the hybrid materials CNPs/AgNWs is an appropriate material for the best performance with the dye degraded time of 100 min. It also indicates the high performance of membrane in water treatment.

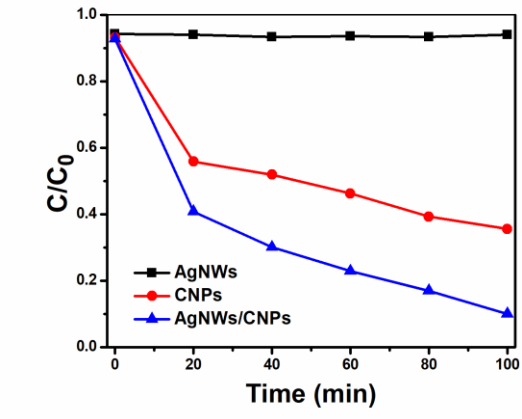

Fig. 6 Methylene blue dyes decomposition of various samples under visible light (> 400 nm)

CONCLUSION

Slive nanowires (AgNWs), carbon nitride nanoparticles (CNPs), a hybrid AgNWs/CNPs composite, and the CNPs/AgNWs membrane were successfully fabricated via a simple route. The characteristics of the as-synthesized materials were systematically studied.

The synthesized AgNWs show the high quality of crystalline structure with an average diameter of 50 nm and an average length of 30 µm. The obtained CNPs powder has a yellow color and are uniform with the near-spherical shape and the average diameter of about 20 nm. The SEM pictures illustrated that the CNPs/AgNWs nanocomposites consisted of a large amount of the CNP nanoparticles decorated firmly on the surface of the AgNWs. This hybrid material not only exposed the wider light absorption range and stronger absorption ability but also exhibited the best performance with the dye degraded time of 100 mins in compare to the individual components. The results indicate that the CNPs/AgNWs composite could be a promising material for the excellent membrane fouling application.

Acknowledgments: This research is funded by the Hanoi University of Science and Technology (HUST) under project number **T2018-TĐ-007**

REFERENCES

1. W. Guo, H.-H. Ngo, J. Li: Bioresource Technology, 122, 2012, 27-34. https://doi.org/10.1016/j.biortech.2012.04.089
2. T. Nguyen, F.A. Roddick, L. Fan: Membranes, 2(4), 2012, 804-840. https://doi.org/10.3390/membranes2040804
3. X. Zhao, Y. Chen, H. Xuan, C. He: New Journal of Chemistry, 40(1), 2016, 441-446. https://doi.org/10.1039/C5NJ02030A
4. G. Mamba, A.K. Mishra: Applied Catalysis B: Environmental, 198, 2016, 347-377. https://doi.org/10.1016/j.apcatb.2016.05.052
5. C. Zhang et al.: Chemosphere, 214, 2019, 462-479. https://doi.org/10.1016/j.chemosphere.2018.09.137
6. J. Zhu, P. Xiao, H. Li, S.A.C. Carabineiro: ACS Applied Materials & Interfaces, 6(19), 2014, 16449-16465. https://doi.org/10.1021/am502925j
7. L. Wang, C. Wang, X. Hu, H. Xue, H. Pang: Chem Asian J, 11(23), 2016, 3305-3328. https://doi.org/10.1002/asia.201601178
8. C. Li, Z. Sun, L. Liu, W. Huang, S. Zheng: RSC Advances, 6(93), 2016, 91002-91011. https://doi.org/10.1039/C6RA17906A
9. B. Lin; et al.: Applied Surface Science, 357, 2015, 346-355. https://doi.org/10.1016/j.apsusc.2015.09.041
10. Y. Liao, S. Zhu, Z. Chen, X. Lou, D. Zhang: Physical Chemistry Chemical Physics, 17(41), 2015, 27826-27832. https://doi.org/10.1039/C5CP05186J
11. S. Bellamkonda, R. Shanmugam, R.R. Gangavarapu: Journal of Materials Chemistry A, 7(8), 2019, 3757-3771. https://doi.org/10.1039/C8TA10580D
12. Z. Cheng, L. Liu, S. Xu, M. Lu, X. Wang: Scientific Reports, 5(1), 2015, 10718. https://doi.org/10.1038/srep10718
13. B. Bari; et al.: Journal of Materials Chemistry A, 4(29), 2016, 11365-11371. https://doi.org/10.1039/C6TA03308C
14. G. Malandrino, S.T. Finocchiaro, I.L. Fragalà: Journal of Materials Chemistry, 14(18), 2004, 2726-2728. https://doi.org/10.1039/B408981B
15. J.M. Gohil, R.R. Choudhury: Chapter 2 - Introduction to Nanostructured and Nano-enhanced Polymeric Membranes: Preparation, Function, and Application for Water Purification. In.: *Nanoscale Materials in Water Purification*, edited by S. Thomas, D. Pasquini, S.-Y. Leu, D. A. Gopakmar, Elsevier, p. 25-57, https://doi.org/10.1016/B978-0-12-813926-4.00038-0
16. B. Liu; et al.: Nanoscale Research Letters, 12(1), 2017, 212. https://doi.org/10.1186/s11671-017-1963-6
17. D. Rossouw, G.A. Botton: Physical Review Letters, 110(6), 2013, 066801. https://doi.org/10.1103/PhysRevLett.110.066801
18. M. Rothe; et al.: Scientific Reports, 9(1), 2019, 3859. https://doi.org/10.1038/s41598-019-40380-5
19. K. Guo; et al.: Journal of Materials Chemistry A, 1(24), 2013, 7229-7234. https://doi.org/10.1039/C3TA10495H

20. J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen: Journal of Materials Chemistry, 21(38), 2011, 14398-14401. https://doi.org/10.1039/C1JM12620B

21. J. Niedziółka-Jönsson, S. Mackowski: Materials, 12(9), 2019, 1418. https://doi.org/10.3390/ma12091418