Photocatalytic property and pH-response behavior of modified ZnO electrospun nanofibers grafted with poly(methyl methacrylate)

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Abstract

ZnO nanomaterials have been widely studied in medical and biological fields owing to their better biocompatibility, pH-responsibility and higher photocatalytic ability as drug carriers and disease therapy agent. However, the unstability of ZnO nanomaterials within aqueous solution restricts the applications of it to some extent. In this work, ZnO nanofibers with relative higher porosity were fabricated by electrospinning to improve the load capacity as carriers, and then were modified by hydrophobic poly(methyl methacrylate) (PMMA) through graft polymerization on the surface to improve their stability in aqueous solution. Observations on the morphologies of the nanofibers by SEM showed that the surface modification of PMMA well enhanced the water-stability of ZnO nanofibers. Moreover, the photocatalytic degradation of Rhodamine B was investigated, and pH sensitive release behaviors were studied in details under different pH values, by taking Nifedipine as drug model. The results indicated that PMMA modified ZnO nanofibers showed obvious photocatalytic performances and maintained relative excellent pH-response properties. These findings all suggested that the modified ZnO nanofibers might be one kind of excellent material as medical carrier or therapy agents.

Keywords ZnO nanofibers · Electrospinning · PMMA · pH-response · Photocatalytic property

1 Introduction

ZnO nanomaterials, due to their better biocompatibility and lower costs, have shown promising potentials in drug delivery and therapy treatment [1, 2]. With the generated reactive oxygen species (ROS) under UV illumination, ZnO nanomaterials with photocatalytic activity would show the ability of killing [3, 4], virus [5, 6] and cancer cells [7, 8] effectively. Moreover, pH response of ZnO nanomaterials to the applied medium would further make them ideally selectable for target drug delivery [9–11]. With the changing of pH values from 7.4 or higher to acidic condition (e.g., in tumor cells/microenvironment), the comparatively stable ZnO would slowly dissolve into Zn^{2+} and thus lose its morphology and following release the loaded drugs gradually into the solution. At present, better biocompatible

and non-toxic ZnO nanomaterials with relative large sizes have been regarded as safe food additives by U.S. Food and Drug Administration (FDA) [12, 13]. It implies the excellent potential applications of ZnO nanomaterials in the fields of medicine and biologicals.

Up to now, ZnO quantum dot with fluorescence property has been one kind of the most common type of ZnO nanomaterials used in biomedical applications [14–16]. However, recent researches have shown that smaller sizes of ZnO nanomaterials (such as ZnO quantum dot) have potential toxicity to normal cells when their concentrations are relative high [17–19]. Moreover, ZnO nanoparticles of small sizes are usually unstable in aqueous solution because of their higher surface energies. These disadvantages would inevitably limit the applications of ZnO nanomaterials in great extent. In contrast, larger sizes

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of ZnO nanomaterials of micro and/or nanofibers would be significant in the application of biomedical because of their lower toxic and non-toxic, and their high porosity and specific surface areas are also both beneficial to load larger quantities of drugs or therapy agents [20]. Some researches on the fabrication of ZnO nanofibers through electrospinning technology have been reported in recent years, due to their high porosity, large surface-to-volume ratio [21], and enhanced properties by modified functional polymers [22, 23]. In order to control the drug releasing process or the therapy treatment procedure, different responding conditions were often employed. And since pH values in tumors and inflammatory tissues are usually lower slightly than those in blood and normal tissues, thus pH values are of the great significance among those responding conditions [24]. And ZnO nanofibers could maintain the pH-sensitivity [25, 26] to become advantageous in target drug delivery.

In view of these researches, we are naturally inspired to explore the potential application of the photocatalytic and pH response of polymer modified ZnO nanofibers. ZnO nanofibers were fabricated by electrospinning and followed by the grafted technology to obtained PMMA modified ZnO nanofibers. The Morphologies and the structure of the composite nanofibers were characterized by SEM and FT-IR, respectively. And the composite nanofibers with better water-insolubility were obtained by changing the molar ratios of ZnO to MMA monomer. Besides, Rhodamine B (RhB) and Nifedipine (NIF, widely used drug in the treatment of hypertension and angina, and would induce detrimental effects with an excess therapeutic dose [27]) were chosen as model for the study of the photocatalytic degradation and the pH-sensitive load-delivery of the composite nanofibers, respectively. The loading efficiency of NIF, the pH response behavior and the photocatalytic performance of PMMA modified ZnO nanofibers (the composite nanofibers) were all investigated.

2 Materials and methods

2.1 Materials

Zinc acetate dehydrate (99.0%) and *N,N*-Dimethylformamide (DMF) (99.5%) were purchased from Xilong Chemical Co. Ltd. of China. Polyvinylpyrrolidone (PVP) K90 (AR) was purchased from Aladdin. Triethoxyvinylsilane (VTEO) (AR) was courtesy of Harbin Research Institute of Chemical Industry of China. Tris (2-Hydroxyethyl) Amine (TEA) (99.5%) was purchased from Tianjin Guangfu Fine Chemical Research Institute of China. Methyl methacrylate (MMA) (AR) was purchased from Tianjin Fudi Chemical Co. Ltd. of China. The purity of Nifedipine (NIF) was 99.8%, provided by Jianyuan Chemical

Co. Ltd. of China. 2, 2'-Azobis (2-methylpropionitrile) (AIBN) (AR), ethanol (AR) and other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. of China. They were all in analytical grades and used directly without further purification.

2.2 Synthesis of ZnO and fabrication of ZnO nanofibers

Zinc acetate was dissolved in DMF by ultrasonic treatment for 10 min at room temperature. Then PVP was added into the above mixture to form uniform solutions by stirring and ultrasonic treatment for 2 h. The component ratio of $\text{Zn}(\text{Ac})_2$ to PVP was 5:3 (w/w). The solution was transferred into a 5 mL syringe with a metal needle of 0.55 mm in inner diameter. The flow rate of the solution and the applied voltage were set as 0.10 mL h^{-1} and 11 kV, respectively. A grounded aluminum sheet was used as a collector and the distance between the tip of the needle and the collector was 22 cm. After dried in air oven at 50°C for 2 h to totally remove the residual DMF, the electrospun $\text{Zn}(\text{Ac})_2/\text{PVP}$ nanofibers were put into Muffle furnace and calcined at 690°C for 3 h to obtain ZnO nanofibers.

2.3 Preparation of poly(methyl methacrylate) (PMMA) modified ZnO nanofibers

0.1628 g ZnO nanofibers were dispersed into a round-bottom flask with 8 mL ethanol. The mixture was heated in a water bath at 60°C . Then 42 μL TEA, 10 μL ammonium hydroxide and 244 μL deionized water were injected into the flask. Subsequently, 42 μL VTEO was added in dropwise. The reaction temperature was kept at 60°C for 6 h to get the white product. Then the product was separated by distillation and then washed with ethanol to remove the unreacted reagents. The obtained product was dried in air oven at 50°C for 2 h for further grafting.

The above obtained product was dispersed into a three-necked flask with 10 mL ethanol. The mixture was heated in a water bath at 75°C under reflux condensation. Then 0.63 mL MMA and 89.5 μL AIBN were added into the flask successively. The reaction temperature was kept at 75°C for 12 h to get the product. The product was separated and washed to remove the unreacted reagents, then dried in air oven at 50°C for 2 h. The procedures were shown in Scheme 1. Furthermore, the PMMA modified ZnO nanofibers with different molar ratios of ZnO to MMA (1:10, 1:50 and 1:100) were fabricated by the same method.

Scheme 1 Procedures to synthesize PMMA modified ZnO nanofibers

2.4 Fabrication of NIF loaded ZnO nanofibers and PMMA modified ZnO nanofibers

10 mg the PMMA modified ZnO nanofibers were dispersed into a flask with 50 mL phosphate buffer solution (pH value of 7.4). Then a certain amount of Nifedipine was added into the PMMA modified ZnO nanocarrier mixture with the ratio of NIF to modified ZnO of 1:4 (w/w). A few drops of ethanol were added to enhance the solubility of NIF. Then the flask was placed in a shaker bath with 150 rpm at room temperatures for 12 h. After centrifuging for 5 min and removing the solution, the NIF loaded the PMMA modified ZnO nanofibers were obtained. And NIF loaded the ZnO nanofibers would be obtained through the same procedures. The encapsulation efficiency (EE) and the loading efficiency (LE) were calculated as the following equations of $EE = (W_t/W_d \times 100\%)$ and $LE = (W_t/W_f \times 100\%)$, where W_t (mg) referred to the weight of NIF in NIF-loaded nanofibers; W_d (mg) referred to the initial weight of NIF; W_f (mg) referred to the weight of NIF-loaded nanofibers.

2.5 Characterizations

XRD spectra for the samples were characterized by D/max-rB high-power rotating anode X ray diffractometer (D8 ADVANCE, Bruker, Germany). $^1\text{H-NMR}$ spectrum was got from a 400 MHz spectrometer (Avance III, Bruker, Switzerland). FT-IR spectra were obtained by FT-IR spectrometer (AVATAR 360, Nicolet, USA). The surface morphologies of the electrospun nanofibers were observed through field emission scanning electron microscope (SEM) (Helios Nanolab 600i, FEI, USA) after coating the samples with gold. After getting the SEM images of the nanofibers, the average diameter and the water-insolubility of the nanofibers were obtained by the software of ImageJ. TGA curves were acquired to investigate the thermo-stability and the grafting behavior of PMMA on the surface of ZnO nanofibers by thermogravimetric analyzer and differential thermal analyzer (SDTQ600, Universal V4.5A TA

Instruments, USA). The concentrations of NIF in the solution during the release process were monitored using a double beam UV-vis spectrometer (760CRT, Lengguang, China) at certain wavelength.

2.6 Photocatalytic properties of ZnO and PMMA modified ZnO nanofibers

15 mg ZnO nanofibers and PMMA modified ZnO nanofibers were dispersed into a beaker with 50 mL Rhodamine B solution (6 mg/L in concentration) respectively. The mixture was stirred for 12 h in dark to reach the adsorption–stripping balance. After that, the solution was placed under high pressure mercury lamp to start the photocatalytic reaction. At each specified time point, 2 mL of solution was removed to quantify the absorbance and the concentration of Rhodamine B. And the temperature of the Rhodamine B solution remained unchanged during the photocatalytic process. The percentages of the degradations of Rhodamine B were referred to that of $A_t/A_0 \times 100\%$ (where A_0 and A_t equal to the absorbance of solution before and after the photocatalytic experiment, respectively). The degradation and the concentrations of Rhodamine B in the solution were monitored by a double beam UV-vis spectrometer (760CRT, Lengguang, China) at certain wavelength.

2.7 In vitro release test of NIF from PMMA modified ZnO nanofibers

In vitro release tests of NIF-loaded PMMA modified ZnO nanofibers were studied at the physiological temperature of 37 °C and at different pH values of 5.0, 6.0, and 7.4, respectively. In each experiment, 10 mg of the drug carrier was dispersed into 50 mL of the buffer solution in a conical flask. The flask was incubated in a shaker bath under 37 °C and at 150 rpm. 2 mL of solutions were removed every 1 h to quantify the absorbance of NIF.

3 Result and discussion

3.1 SEM observations and water-insolubility analysis of ZnO nanofibers and PMMA modified ZnO nanofibers

Figure 1a showed SEM image of the prepared ZnO nanofibers that obtained from the calcinations of Zn(Ac)₂/PVP electrospun nanofibers at 690 °C. After

calcination process, the ZnO nanofibers with rough surface were obtained. It could be seen that the fibers aligned in random orientations and the average diameters of the fibers were about 350 nm. Obviously, nanofibers changed into nanoparticles mostly after the contacting with aqueous solution for a certain period of times (as shown in Fig. 1b). Comparably, Fig. 1c showed SEM images of PMMA modified ZnO nanofibers, of which the average diameter changed to approximate 380 nm. And as shown in Fig. 1d, after immersed in aqueous solution

Fig. 1 SEM images of **a** ZnO nanofibers (inset: the enlarged SEM image and the diameter distribution histogram of ZnO nanofibers), **b** ZnO nanofibers under the aqueous solution treatment for 24 h,

c PMMA modified ZnO nanofibers (inset: the diameter distribution histograms of PMMA modified ZnO nanofibers), **d** modified ZnO nanofibers under the aqueous solution treatment for 24 h

Fig. 2 SEM images of PMMA modified ZnO nanofibers with different molar ratios of ZnO to MMA (**a**, 1:10; **b**, 1:50; **c**, 1:100—the same image with that of Fig. 1(d)) under the aqueous solution treatment

for 24 h, PMMA modified ZnO nanofibers showed the enhanced water-insolubility, and could maintain the linear fiber morphology after the treatment with aqueous solution. The presence of the hydrophobic polymer of PMMA grafted on the surface of ZnO nanofibers would improve the hydrophobicity of the system, thus protect the nanofibers from the changing of the morphology in the aqueous solution.

To compare the water-insolubility of PMMA modified ZnO nanofibers with different molar ratios of ZnO to MMA, the morphologies of the samples that being treated with water were observed by SEM. As shown in Fig. 2, with the amount of PMMA increased, the stability of PMMA modified ZnO nanofibers after the treatment by aqueous solution increased correspondingly. For that with the molar ratio of 1:100 of ZnO to MMA, the nanofibers would almost unchange the morphology and exhibit excellent water-insolubility. These results indicating the fabricated nanofibers could be used to photocatalytic in aqueous solution.

3.2 X-ray powder diffraction studies of ZnO nanofibers and PMMA modified ZnO nanofibers

To investigate the influences of the grafting reaction and the copolymerization process on the crystalline structures of ZnO nanofibers, X-ray diffraction patterns of ZnO nanofibers, VTEO grafted ZnO nanofibers and PMMA modified ZnO nanofibers were recorded in Fig. 3. XRD spectra of the PMMA modified nanofibers were nearly the same as those of pure nanofibers, indicating that the series of reactions did not altered the crystalline structures of ZnO nanofibers. This also meant that the chemical properties of ZnO nanofibers wouldn't change obviously after the grafting and the copolymerization. In addition, the presences of silane coupling agent and copolymer resulted

Fig. 3 X-ray diffraction patterns of, a ZnO nanofibers, b VTEO grafted ZnO nanofibers and c PMMA modified ZnO nanofibers

in the unobvious change in the intensities of the sharp diffraction peaks. The result inferred the maintained photocatalytic performance after the modification of ZnO nanofibers.

3.3 FT-IR spectrum and analysis of the grafted and PMMA modified ZnO nanofibers

Figure 4 showed FT-IR spectra of ZnO nanofibers, VTEO grafted ZnO nanofibers and PMMA modified ZnO nanofibers, respectively. As shown in Fig. 4a, the peak at 1613 cm^{-1} corresponded to the stretching vibration of $\text{C}=\text{C}$, indicating the reaction of VTEO with ZnO and the formation of VTEO grafted ZnO. As shown in Fig. 4b, the peak at 3420 cm^{-1} implied the presence of $-\text{OH}$ group within ZnO nanofibers. The absorption peaks in the region of $2900\text{--}3000\text{ cm}^{-1}$ corresponded to the stretching vibration

Fig. 4 FT-IR spectra of ZnO and ZnO/VTEO (a), and ZnO nanofibers and PMMA modified ZnO nanofibers (b) (inset: the correspond spectrum at the wavelength ranges of 1950–1500 cm⁻¹)

of the groups of $-\text{CH}_2$ and $-\text{CH}_3$ of PMMA in the copolymer of modified ZnO nanofibers. The absorption bands near 1720 cm⁻¹ that corresponded the characteristic peaks of PMMA (as reported in reference [28]) became unobvious and weak. Thus the conclusion could be drawn that the strong absorption bands at 1567 cm⁻¹ and 1400 cm⁻¹ corresponded to COO- group of PMMA. When it accepted electron from other atoms, the characteristic absorption bands of PMMA would shift from higher wave numbers to the lower ones [29]. Thus it inferred that the copolymerization process provide electron from other atoms to the group of $-\text{C}=\text{O}$ in PMMA, indicating the existence of a strong interaction between ZnO nanofibers and the copolymer of PMMA [30].

3.4 ¹H-NMR spectra of PMMA modified ZnO/nanofibers

Figure 5 showed ¹H-NMR spectra of PMMA modified ZnO nanofibers. Peak a ($\delta=7.35$ ppm) was proton resonances of the solvent CDCl_3 . For peak b, methyl ($-\text{CH}_3$) proton resonances of $-\text{OCH}_3$ appeared at $\delta=3.65$ ppm. Methylene protons ($-\text{CH}_2-$) appeared at $\delta=1.56$ ppm (peak c), and the presence of peak d ($\delta=1.21$ ppm) referred to $-\text{CH}_3$ proton resonances from $-\text{C}-\text{CH}_3$ of polymer unit. These good matches between proton resonances and PMMA structure indicated the graft copolymerization reaction between ZnO nanofibers and PMMA.

3.5 TGA analysis of PMMA modified ZnO nanofibers

The amount of grafted polymers onto the nano-ZnO surfaces were determined by the percentage of grafting,

Fig. 5 ¹H-NMR spectra of PMMA modified ZnO nanofibers

which could be obtained from the weight loss at 500 °C in air by the using of thermogravimetric analysis (TGA). The weight loss curves of PMMA modified ZnO nanofibers with different molar ratios of ZnO to MMA were shown in Fig. 6. As shown in Fig. 6a (the molar ratio of ZnO to MMA was 1:10), the first decrease of weight (0.25%) at above 100 °C could be attributed to the loss of water. And the second weight loss (2.261%) corresponded to the decomposition of PMMA. Thus it could be calculated that there were approximately 97.49% ZnO within the modified nanofibers. So the percent of grafting could be concluded as 2.32% ($2.261/97.49 \times 100\%$). This value was much smaller than that of PMMA grafting onto ZnO nanoparticles (~50 nm) [30]. The main reason might result from the fact that the total surface area of small ZnO nanoparticles was much larger than the average diameter (350 nm) of electrospun

Fig. 6 TGA curves of PMMA modified ZnO nanofibers with different molar ratios of ZnO to MMA (**a**, 1:10; **b**, 1:50; **c**, 1:100)

Fig. 7 Absorbance of Rhodamine B solution for modified ZnO nanofibers (**a**) and ZnO nanofibers (**b**) with the changing of time (the inset ones were the optical photos of the relative solutions)

ZnO nanofibers (as shown in Fig. 1a). Moreover, with the molar ratio of MMA units increased, the weight loss (%) of the products, as shown in Fig. 6, would increase gradually from 2.26 to 78.22%. Therefore, the amount of MMA units played a significant role in determining the grafting percentage on the surface.

3.6 Photocatalytic properties of PMMA modified ZnO nanofibers

For studying the photocatalytic properties of PMMA modified ZnO nanofibers, Rhodamine B was chosen as model agent in photocatalytic experiments. The absorbance of Rhodamine B solution at 554 nm in UV-vis spectra under different conditions were shown in Fig. 7. The degradation percent of Rhodamine B was 89.7% (for ZnO nanofibers) and 82.5% (for PMMA modified ZnO nanofibers), respectively. It was found that the values of characteristic absorption peak declined gradually under ultraviolet light

Fig. 8 Chemical structure of NIF

in the presence of ZnO nanofibers or PMMA modified ZnO nanofibers, which indicated that modified nanofibers still maintained the photocatalytic activity of ZnO nanomaterials. However, it's obvious that the degradation rate of Rhodamine B for PMMA modified ZnO nanofibers were less than that for ZnO nanofibers (as shown in Fig. 7a). According to the mechanism of photocatalytic degradation [31], ultraviolet light could excite the nano-sized ZnO materials and a great deal of reactive oxygen species radicals with high oxidative activity could be formed on the surface of ZnO nanomaterials. Thus an assumption could be made that the presence of PMMA on the surface of ZnO nanofibers might prevent the formation of oxidative radicals to some degree. Also the isolation of ZnO partly with Rhodamine B by PMMA might be another reason. However, the better remained photocatalytic activity for the modified nanofibers inferred that it might be useful in photodynamic therapy (PDT), where photo induced reactive oxygen species would play important roles [32].

3.7 NIF loaded modified ZnO nanofibers and in vitro release with the changing of pH values

In present work, NIF (Nifedipine, its structure was shown in Fig. 8) was chosen as the drug model owing to its rich hydrophobic groups to carry out the loaded experiments

Fig. 9 In vitro release behaviors of NIF at different pH values for NIF-loaded ZnO nanofibers (a); NIF-loaded the PMMA modified ZnO nanofibers (b)

and the in vitro release experiments from nanofibers. The pH response of in vitro release behaviors of NIF from NIF-loaded ZnO nanofibers and NIF-loaded the PMMA modified ZnO nanofibers were studied, respectively. The encapsulation efficiency and the loading efficiency of NIF loaded the modified nanofibers were assessed and were calculated as $60.02 \pm 1.30\%$ and $6.02 \pm 0.36\%$, respectively, contrasting to the values of $28.29 \pm 0.36\%$ and $3.02 \pm 0.03\%$ for ZnO nanofibers. The results showed that the grafted PMMA did improve the NIF loading efficiency of ZnO nanofibers, making them act more efficiently as drug delivery's carrier of NIF. After grafting with PMMA, the presence of the organic chains improved the interaction between the nanofibers and NIF owing to the hydrophobic characters of both PMMA and NIF. Thus the loading efficiency of NIF into the system was improved.

As shown in Fig. 9, the release amounts of NIF from ZnO and PMMA modified ZnO nanofibers were both dependent on the pH values of the solution, as well as the releasing time. The release of NIF from the modified nanofibers at pH of 7.4 was relative slower with a releasing ratio of about 26% within 24 h, than that of ZnO nanofibers with the value of about 36%. Nevertheless, the release rate of NIF from the modified nanofibers became much faster with the decreased pH values. Thus, the released NIF was approximately 60% (at pH of 6.0) and 84% (at pH of 5.0) within 24 h, respectively. And the values were 64% (at pH of 6.0) and 91% (at pH of 5.0) for that of ZnO nanofibers. These results showed that ZnO nanofibers and modified ZnO nanofibers both had pH-sensitive characteristics. However, the modification of the hydrophobicity of PMMA would induce the decrease of hydroxyl ion on

ZnO nanofibers, and then would result in the difference of the pH response between ZnO nanofibers and PMMA modified ZnO nanofibers, therefore, at pH value of 7.4, the NIF release from the modified nanofibers was much less than that from ZnO nanofibers. As a result, the modified nanofibers seemed to be a better choice than that of pure nanofibers for NIF's delivery. A hypothesis could be made here that most drug would remain in the modified nanofibers (carrier) during the in vitro release experiment at normal physiological conditions (at pH of about 7.4), indicating the potential value for the prolonged drug retention time within the blood circulation and thereby greatly reducing the side effects of drug. In contrast, once the drug loaded nanofibers reached the target organs where the local pH value was lower than that of the normal system, a faster release might occur, leading to a significant improvement in treatment efficiency.

4 Conclusion

PMMA modified (by grafting) ZnO electrospun nanofibers were successfully fabricated and the potential value of the modified nanofibers in controlled drug delivery and photocatalytic degradation were explored in details, by taking NIF as drug model and Rhodamine B as degraded model, respectively. PMMA modified ZnO nanofibers could maintain better morphologies than that of ZnO nanofibers with the treatment by aqueous solution, leading to an increase of availability of ZnO nanofibers to apply in aqueous medium. Moreover, the modified nanofibers obtained higher encapsulation efficiency than ZnO nanofibers and

maintained relative excellent pH-response in the NIF loaded delivery system. The photocatalytic degradation results indicated that, the modified nanofibers could remain the photoactivity of ZnO nanomaterials mostly. These results indicated the potential applications of such modified nanofibers in photodynamic therapy (PDT).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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