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Preparation of poly(ε-caprolactone) grafted titanate nanotubes

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Abstract

This work reported for the first time the surface functionalization of titanate nanotubes (TNTs) with biodegradable poly(ε-caprolactone) (PCL). A ''grafting from'' approach based on *in situ* ring-opening polymerization of ε-caprolactone from TNTs with a special surface modification was adopted to prepare the PCL-*g*-TNTs. The thickness of the grafted PCL shell can be controlled by increasing reaction time. After grafted with PCL, both the dissolubility and flexibility of the tubes were greatly improved. The obtained PCL-*g*-TNTs can easily disperse in several organic solvents, and the dispersal stability depends on solvent polarity and PCL shell thickness. Furthermore, the PCL immobilized on the surface of TNTs still possessed a good biodegradable capacity and could be completely decomposed in the presence of *Pseudomonas* (PS) lipase. The PCL-*g*-TNTs reported here are promising in biotechnology applications due to good dissolubility, flexibility, biocompatibility and the tubular nano-structure.

Keywords: Titanate nanotubes; ε-Caprolactone; Surface grafting

1. Introduction

In recent years, the researches about nanomaterials, including the carbon nanotubes (CNTs) [1–3], silica nanoparticles [4,5], gold and silver nanoparticles [6,7], titania and titanate nanomaterials [8,9], have attracted much attention due to their fascinating capacity and applications in nanoengineering [10,11], catalyst supports [12], photocatalysts [13], solar-energy conversion [14], lithium-ion-battery materials [15,16], etc. However, the application of inorganic nanomaterials in biomaterial fields is greatly limited for their cyto-toxicity [17]. As a special case, titanium dioxide (rutile) nanoparticles possess a lower cyto-toxicity [17], and have displayed a great potential in biomedicine fields [18]. Nevertheless, TNTs with high aspect ratio, uniform one-dimensional nanochannel structure, electronic conductivity, larger surface area and lower toxicity [19], have hardly been used as biomaterials. In our opinion, the inherent shortcomings of TNT including the strong aggregation, poor dissolubility and high brittleness, may greatly block its applications in the field of biomaterials and others. To break this limitation, organic functionalization of TNTs may be a good alternative.

The *in situ* surface grafting strategy has been widely employed to modify the CNTs [1–3], silica particles [4,5], gold nanoparticles [6,7], etc. It is an effective way to improve their dissolubility in various solvents and their compatibility with other polymers so as to enlarge the application fields. However, to the best of our knowledge, surface functionalization of TNTs has seldom been reported yet. Herein, we provide a first example to modify the TNT with biodegradable polymers.

Similarly to functionalized CNTs, a ''grafting from'' strategy was employed to covalently introduce biodegradable poly(ε-caprolactone) (PCL) onto the surface of TNTs. Although, there are many Ti–OH groups on the surface of TNT [20,21], such inorganic hydroxyl groups have a low reactivity and can not directly initiate the graft polymerization of

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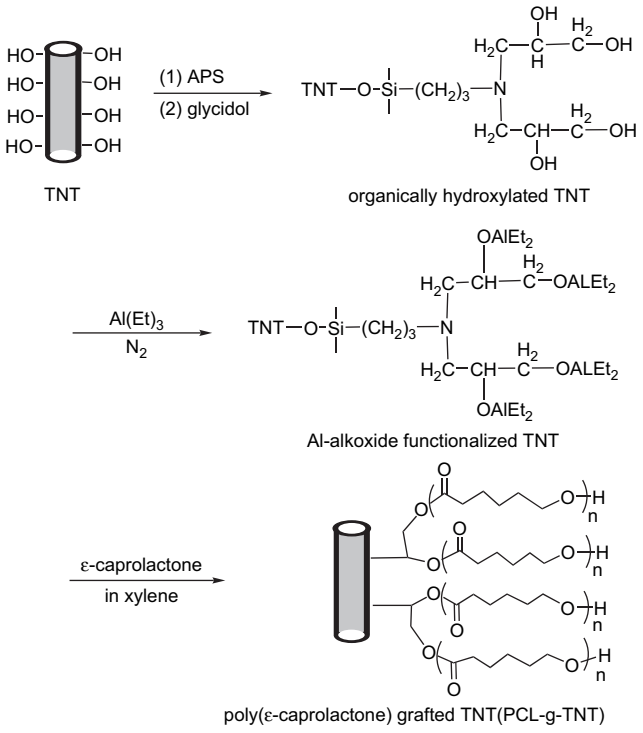

Scheme 1. Schematic illustration of preparation of PCL grafted TNT.

ε-caprolactone. So it is necessary to transform the inorganic hydroxyl groups into organic hydroxyl groups for the functionalization. We presented here a new method to functionalize the TNT as shown in Scheme 1. Firstly, TNT was modified with 3-aminopropyl-triethoxysilane (APS) and glycidol, and as a result the organic hydroxyl groups were introduced onto the surface of the TNT. Secondly, the organic hydroxyl groups were used to initiate the ring-opening polymerization of ε-caprolactone in the presence of triethylaluminum as catalyst to generate the PCL-*g*-TNT. The advantage of our method is that every inorganic Ti–OH group can be enlarged into four organic hydroxyl groups, which provides more chance to initiate the living ring-opening polymerization of monomers from the TNT surface and facilitate the complete functionalization.

In addition, the properties of the PCL modified TNTs were also evaluated in the work. Compared with the pristine TNTs, the PCL-*g*-TNTs display a greatly improved dispersibility and flexibility as well as a good biodegradability, which will extend the application potentials of TNTs in biomaterials and biotechnology.

2. Experimental section

2.1. Materials

Triethylaluminum (25% w/w in hexane) was purchased from Alfa Aesar Company. Titanate nanotubes were obtained from Institute of New Energy Material Chemistry Department of Material Chemistry, Nankai University. All the other chemical reagents were purchased from the Aldrich Chemical Co. and dried with calcium hydride (CaH_2) before using.

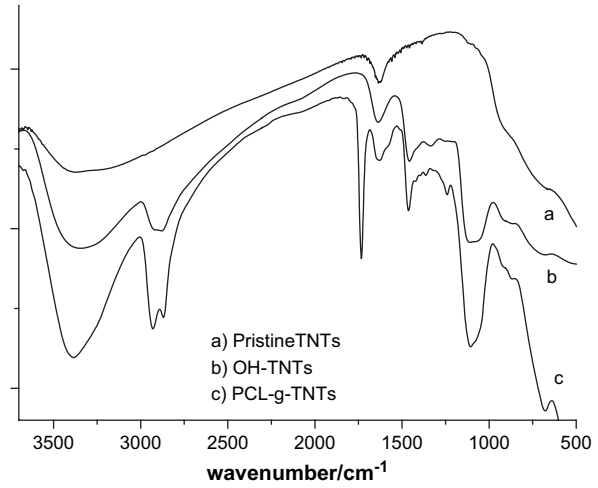

Fig. 1. The FT-IR spectra of (a) pristine TNTs; (b) OH–TNTs; (c) PCL-*g*-TNTs.

2.2. Organic hydroxylation of TNT

The preparation of TNTs was described in literature [22]. The average diameter of the TNTs is about 10 nm, and the length ranges from 300 nm to 800 nm. The obtained TNTs were modified with 3-aminopropyl-triethoxysilane (APS) according to literature [23,24]. Then, the APS-modified TNTs (0.50 g) and 0.5 mL glycidol were put into 30 mL dried xylene. The reaction was performed at 60 °C for 5 h under the nitrogen atmosphere. The resulting product was washed with tetrahydrofuran for five times till all of the unreacted glycidol molecules were removed, and then it was dried at 40 °C under vacuum for 48 h. FT-IR (Fig. 1) and ^{1}H NMR (Fig. 2) spectra were used to characterize the organically hydroxylated TNTs (OH–TNTs).

2.3. Grafting PCL from the surface of OH–TNTs

OH–TNTs (0.05 g) were put into 15.0 mL dried xylene, and then 0.2 mL triethylaluminum (25%, w/w) was injected

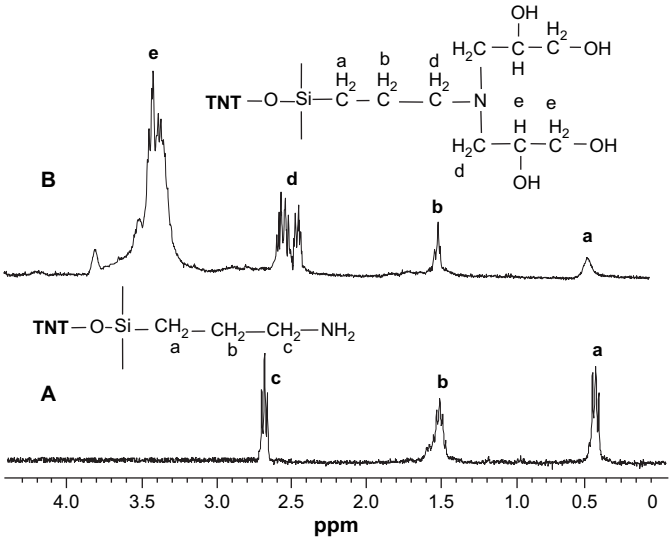

Fig. 2. ^{1}H NMR spectra of (A) APS–TNTs and (B) OH–TNTs in D_2O.

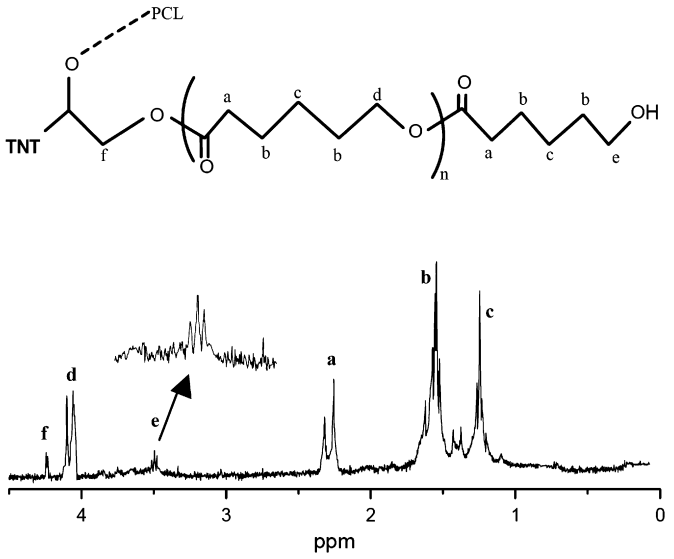

Fig. 3. ^{1}H NMR spectrum of PCL-*g*-TNTs in $CDCl_3$ (note: the signals of the space groups of APS and glycidol between TNT and PCL shell were totally covered by the PCL signals).

into the mixture. The reaction was carried out at room temperature for 2 h under nitrogen atmosphere to obtain Al-alkoxide functionalized TNTs, and the product was centrifuged under the protection of nitrogen atmosphere to remove the residual free triethylaluminum. Then, 15.0 mL dried xylene, 0.5 mL (5.8×10^{-3} mol) ε-caprolactone and the purified Al-alkoxide functionalized TNTs were mixed together under the nitrogen atmosphere. The mixture was reacted at 80 °C for a certain time. The products were dispersed under ultrasonication and then centrifugated for five times in acetone to remove the homopolymers completely. The final products were dried at 40 °C under vacuum for 24 h to obtain the white powders. Evidences for the successful graft come from the FT-IR spectrum (Fig. 1), ^{1}H NMR measurements (Fig. 3), TEM images (Fig. 4) and TGA data (Fig. 5).

2.4. Biodegradation

The degradation test was carried out in a swing bed (37 ± 3 °C, 170 r/m). A PCL-*g*-TNT sample collected after grafted for 48 h were divided into several parts, and every part was immersed in phosphate buffer solution (PBS) (0.025 M) containing *Pseudomonas* (PS) lipase (4.0 mg) [2]. After a certain time interval, one share of sample solution was centrifuged, washed three times with methanol and dried at 40 °C under vacuum for 24 h. The resulting white powders were analyzed by TEM and TGA. The degradation rate curve of PCL-*g*-TNTs is shown in Fig. 6, and Fig. 7 displays the typical TEM images of PCL-*g*-TNTs degraded for 12 h and 36 h, respectively.

2.5. Dispersibility evaluations

The PCL-*g*-TNTs with about 21 nm in diameters were dispersed in different polarity solvents with a constant TNT concentration of 1.0 mg/mL by ultrasonic. Then, the solution was transferred to a quartz cell and the light transmittance was measured at 510 nm with a UV–vis spectrophotometer (sp-1901UV, Shanghai Spectrum Instruments Co., Ltd) continuously. Only the transmittance of the upper solution was recorded for the measurements. The results are shown in Fig. 8.

To clarify the effect of PCL shell thickness on dispersibility, three PCL-*g*-TNT samples with PCL shell thickness of about 5.5 nm, 3.5 nm and 2 nm were dispersed in chloroform by ultrasonic. Then the deposition process was recorded by a digital camera (Sony, DSC-S70). The resultant pictures are shown in Fig. 9.

3. Characterization

^{1}H NMR measurements were performed on a Varian Mercury plus-400 spectrometer. TGA was carried out on a Perkin–Elmer TGA-7 instrument with a heating rate of 20 °C/min under a nitrogen flow (20 mL/min). FT-IR was conducted on a Perkin–Elmer Paragon 1000 instrument. All samples were prepared as pellets using spectroscopic grade KBr. TEM studies were performed on a JEOL JEM-2100F instrument operating at a voltage of 200 kV. Samples were prepared by dropping the sample solutions onto carbon-coated copper grids, and then air-dried before measurement.

4. Results and discussion

4.1. Organic hydroxylation of TNTs

The FT-IR and ^{1}H NMR spectra were used to characterize the products. In the FT-IR spectrum of OH–TNTs (Fig. 1b), 2900 cm^{-1} (the stretching vibration of C–H groups), 1442 cm^{-1} (the bending vibration of C–H groups) and 1095 cm^{-1} (the Si–O groups) could be clearly detected. It indicates the successful anchoring of organic groups onto the surface of TNTs. ^{1}H NMR (Fig. 2) spectra provide more detailed evidences to prove that APS and glycidol have been grafted onto the surface of TNTs successfully. In the ^{1}H NMR spectrum (Fig. 2A) of APS–TNTs, three proton peaks around $\delta = 0.45$ ppm (peak a), 1.5 ppm (peak b) and 2.8 ppm (peak c) assigned to the various methylenes of the grafted APS units were clearly shown. After further reacted with glycidol, the proton peak c (Fig. 2B) disappeared, and two new peaks around $\delta = 2.55$ ppm assigned to the tertiary amine-linked methylene groups (peak d) and around $\delta = 3.5$ ppm assigned to the hydroxyl-linked methylenes of glycidol units (peak e) appeared. Evidently, all $-NH_2$ groups in APS–TNTs have reacted with glycidol. Thus, every inert inorganic hydroxyl group in TNTs (TNT–OH) was transformed into four active organic hydroxyl groups by sequential reactions with APS and glycidol.

4.2. Grafting PCL from the surface of TNT

The PCL-*g*-TNTs were prepared via the *in situ* initiating polymerization of ε-caprolactone monomers from the surface of OH–TNTs. Compared with OH–TNTs, the FT-IR

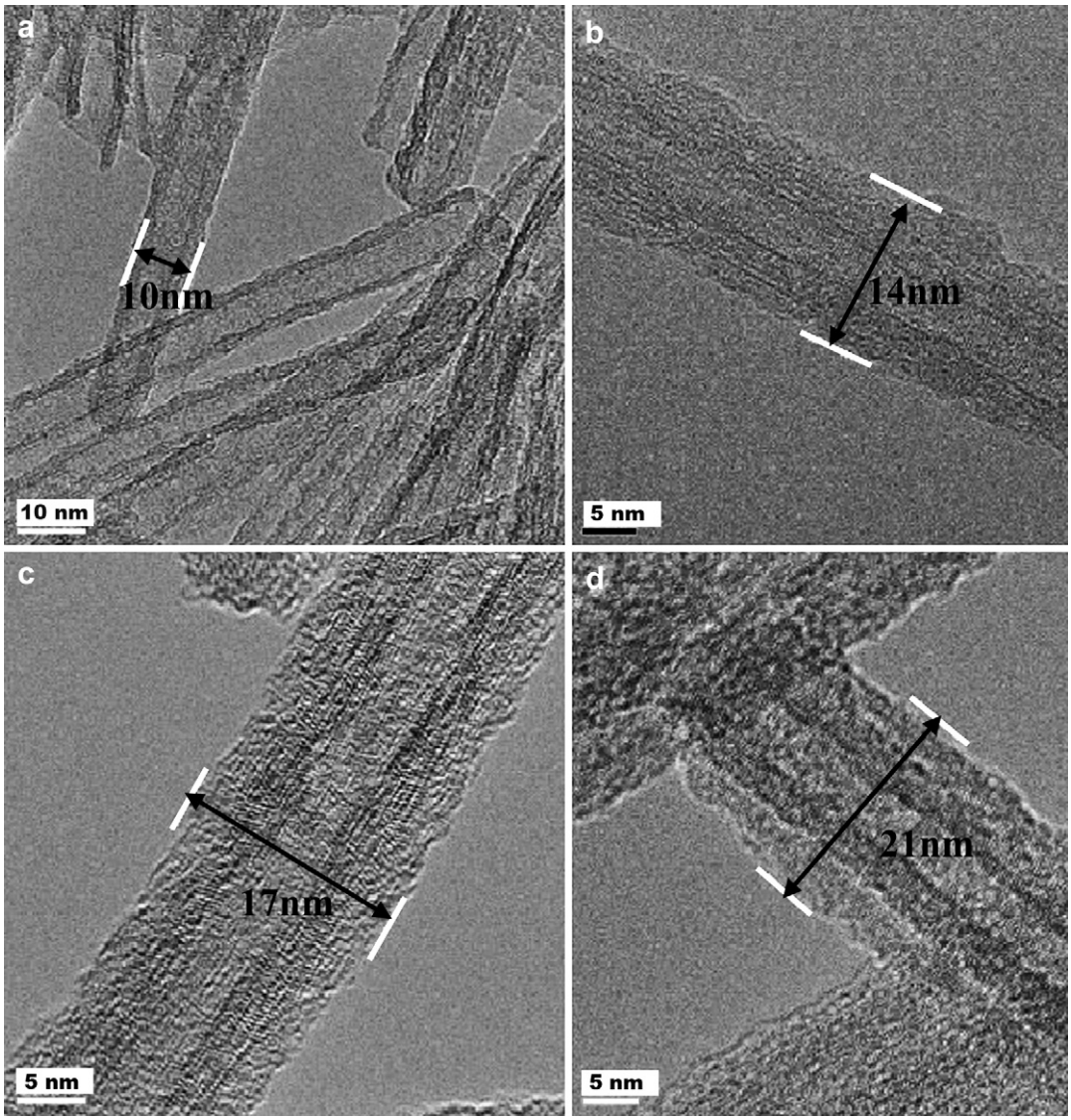

Fig. 4. TEM images of (a) pristine TNTs and PCL-*g*-TNTs after reacted (b) 12 h; (c) 24 h; (d) 48 h.

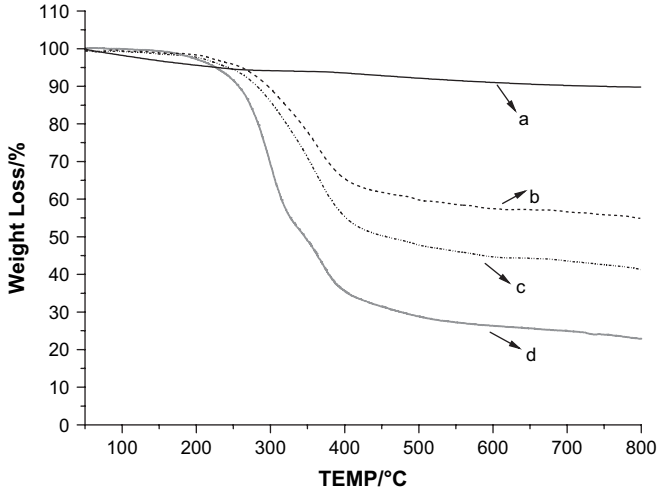

Fig. 5. The TGA data of (a) pristine TNTs and PCL-*g*-TNTs after reacted (b) 12 h; (c) 24 h; (d) 48 h.

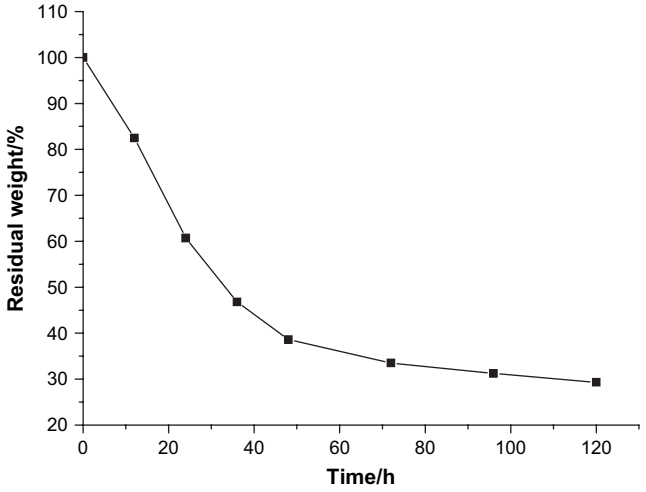

Fig. 6. The degradation rate curve of PCL-*g*-TNTs.

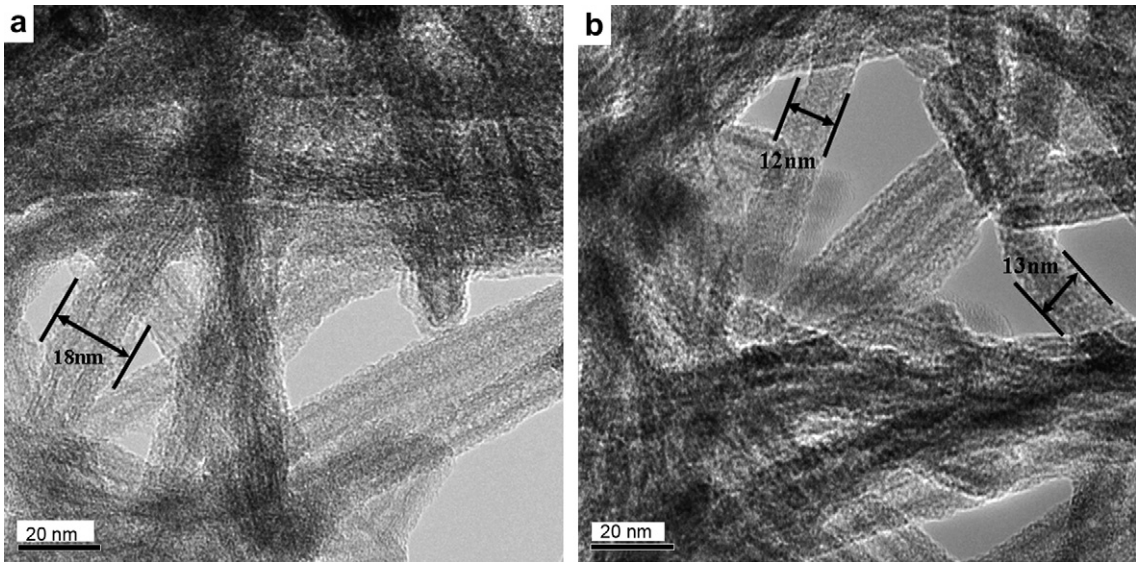

Fig. 7. TEM images of PCL-*g*-TNTs in PBS in the presence of PS lipase after (a) 12 h; (b) 36 h.

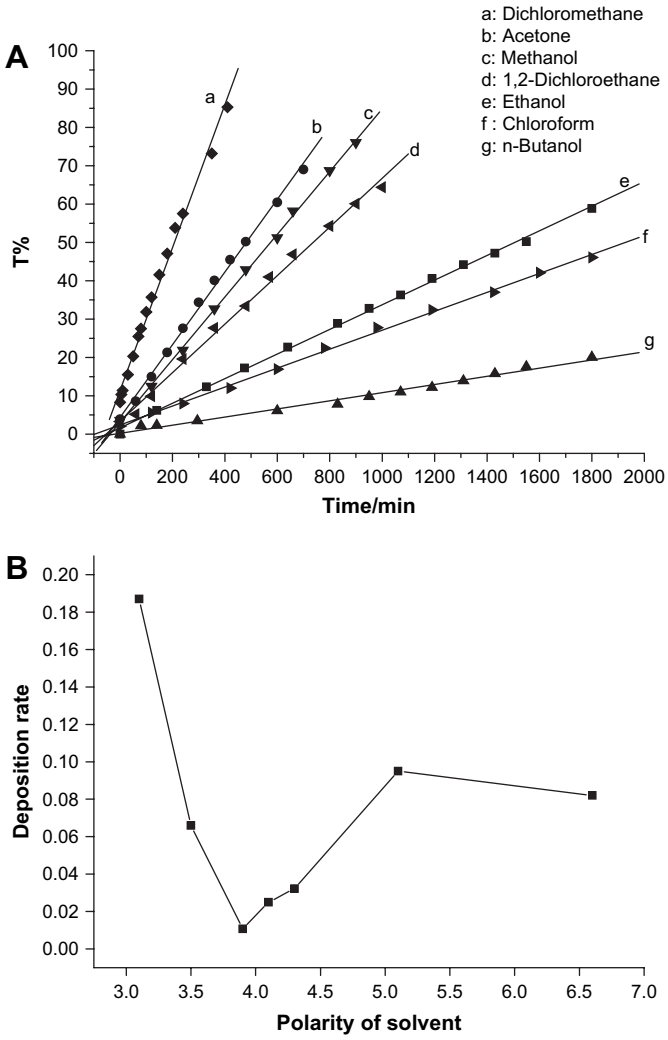

Fig. 8. The dispersibility of PCL-*g*-TNTs with about 21 nm diameter in different solvents at the same concentration (1.0 mg/mL). (A) Variation plots of the solution light transmittance with the deposition time. (B) Relationship of deposition rate *vs* solvent polarities.

spectrum (Fig. 1c) of the PCL-*g*-TNTs demonstrates a new strong peak occurred at 1735 cm^{-1}, which is ascribed to the C═O groups of the grafted PCL polymers. The ^1H NMR spectra together with the detailed attributions of PCL-*g*-TNTs are shown in Fig. 3, which provides the further evidences to prove the graft reaction. More attention should be paid to the proton peak around $\delta_H = 4.25$ ppm (peak f). It indicated that the organic hydroxyl groups in the glycidol units of hydroxylated TNTs had initiated the ring-opening polymerization of ε-caprolactone monomers to form the ester bonds [25], which provides a direct evidence for the covalent graft of PCL from hydroxylated TNTs.

TEM images of resultant PCL-*g*-TNT samples with different reaction times are presented in Fig. 4. The clear polymer shells around the TNTs strongly supported the successful graft of PCL from the surface of TNT. It is interesting to note that the thickness of the grafted polymer shells increases with increasing reaction time. The diameter of PCL-*g*-TNTs measured from the TEM images is approximately 14 nm in average (Fig. 4b) when reacted for 12 h, and it increases to 17 nm (Fig. 4c) and 21 nm (Fig. 4d) after reacted for 24 h and 48 h, respectively. TGA data provided a further evidence to support the controllable PCL shells determined by the reaction time (Fig. 5). In the TGA curves, the weight loss before 400 °C was attributed to the thermal degradation of PCL polymers coated on the TNTs, from which the PCL content in PCL-*g*-TNTs can be calculated. For example, the PCL content in PCL-*g*-TNT with a diameter of 14 nm is 32.5%, while it becomes 63.3% when the diameter is 21 nm.

4.3. Biodegradation

Biodegradation tests were performed in PBS in the presence of PS lipase. The degradation rate curve presented in Fig. 6 shows the residual weight of PCL-*g*-TNTs as a function of degradation time. According to the degradation rate curve,

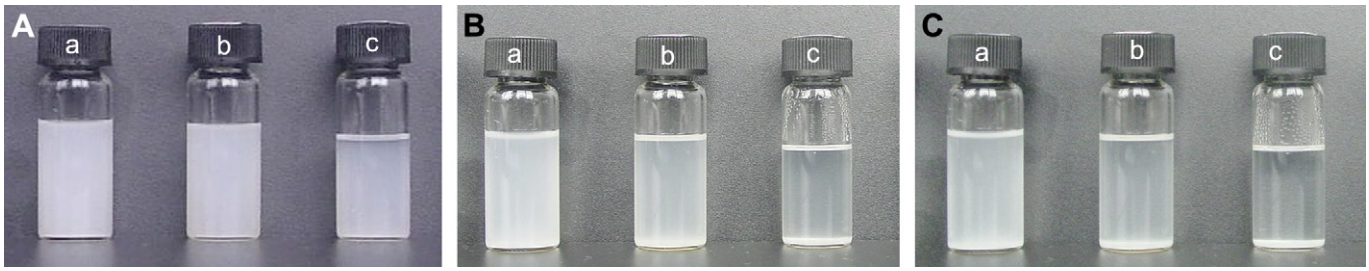

Fig. 9. The dispersal photographs of PCL-*g*-TNTs with different PCL shell thicknesses of about 5.5 nm (a), 3.5 nm (b) and 2 nm (c) in chloroform after standing for (A) 5 min; (B) 120 min; (C) 240 min.

the PCL decomposed quickly within the first 24 h, and then slowed down. The complete degradation time of PCL is about 96 h, which agrees well with the literatures [2]. Fig. 7 displays the typical TEM images of PCL-*g*-TNTs when degraded by PS lipase for 12 h and 36 h. The decreased diameters of PCL-*g*-TNTs with increasing degradation time provide a vivid evidence to prove the proceeding of biodegradation. Evidently, the PCL remains the biodegradability even if it is immobilized onto the surface of TNT.

4.4. Dispersibility and brittleness

The pristine TNT has a poor dissolubility, and will precipitate quickly when added into organic solvents. After grafted with PCL, the dispersibility of PCL-*g*-TNT was improved greatly. In addition, we also find a strong dependence of the PCL-*g*-TNT dispersibility on solvent polarity and PCL shell thickness. Firstly, we should explain our method to characterize the dispersibility. When the modified TNTs were put into organic solvent, it first evenly dispersed into the solvent for a certain time and then gradually deposited at the bottom of the vial, which led to a gradually decreasing opacity at the upper solution layer. Thus, we can evaluate the deposition rate of PCL-*g*-TNTs by measuring the transmittance of the upper solution. Fig. 8A shows the variation of the solution transmittance with the deposition time, and a linear relationship is found between them. The slop of every transmittance curve indicates the deposition rate of the modified TNTs in the solvent, and the smaller is the slop, the smaller is the rate. Evidently, PCL-*g*-TNTs have a relatively good dispersibility in *n*-butanol, chloroform and ethanol, but the dispersibility decreases a lot when in dichloromethane. Fig. 8B displays the deposition rate as a function of solvent polarity. With the increase of solvent polarity, the deposition rate of PCL-*g*-TNTs first decreased and then increased. *n*-Butanol, with a solvent polarity of 3.9, has the best capability to disperse the PCL-*g*-TNTs. We think that such dissolubility dependence is related with polarity of the grafted PCL on TNTs.

Fig. 9 shows the contrastive dispersal photographs of PCL-*g*-TNTs with different PCL shell thicknesses in chloroform. As shown, the PCL-*g*-TNTs with thickest PCL shells (Fig. 9C) would suspend in chloroform for 4 h with only a little precipitate, but PCL-*g*-TNTs with the thinnest PCL shells (Fig. 9B) precipitated seriously within 2 h. Evidently, increasing the grafted PCL contents would greatly improve the dispersibility of TNTs.

The brittleness of TNTs was also improved after grafted with PCL. When both pristine TNTs and PCL-*g*-TNTs were

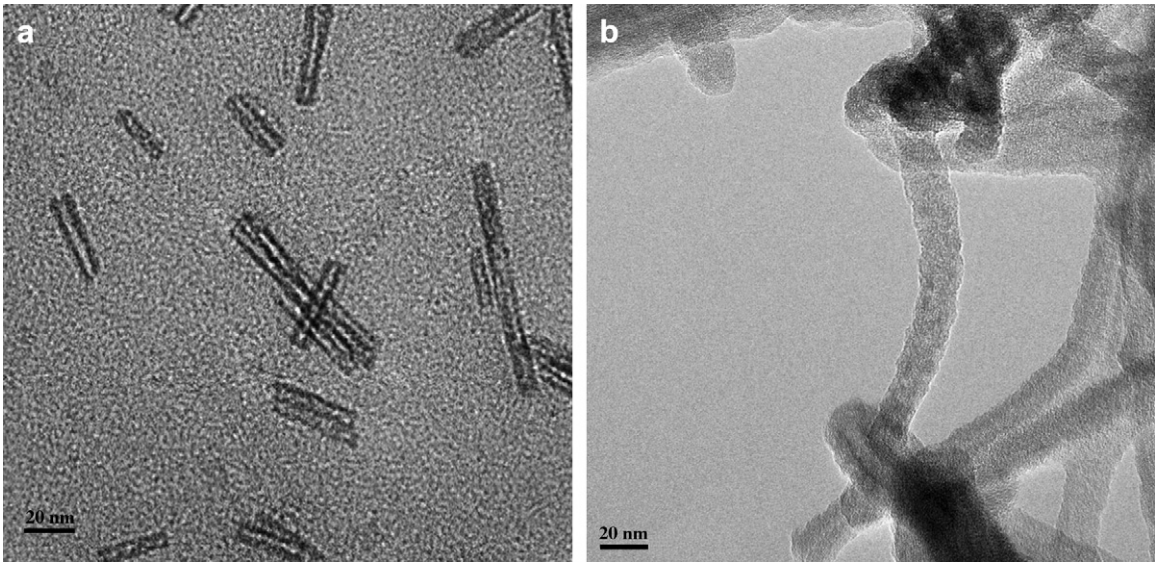

Fig. 10. TEM images of pristine TNTs (a) and PCL-*g*-TNTs (b) after treated with ultrasonic for 2 h.

treated with ultrasonic for 2 h, most of pristine TNTs were broken into fragments as shown in Fig. 10a, however, the PCL-*g*-TNTs were flexible enough to keep the intact tube morphology. In addition, the pristine TNTs are rigid and straight, while the PCL-*g*-TNTs are flexible and can be bended when disposed by ultrasonic (Fig. 10b).

5. Conclusions

In conclusion, the biodegradable PCL has been covalently grafted onto the surface of TNTs by a "grafting from" approach based on the *in situ* ring-opening polymerization. The content of grafted PCL can be easily controlled by adjusting the reaction time. The longer is the reaction time, the thicker is the PCL shell. The obtained PCL-*g*-TNTs have demonstrated great improvements on the dispersibility and flexibility. In addition, the PCL immobilized on the TNTs still possesses the biodegradability and can be completely degraded by PS lipase. All the advantages make the PCL-*g*-TNT be potentially used in biomaterials.

Acknowledgments

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