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Supporting Information

Structure and Properties of nanoparticle: DES-lignin-g-PNVCL coated Aspirin by self-assembly

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2. Experimental section

2.1 Preparation of DES-lignin

The deep eutectic solvent was prepared by stirring choline chloride and lactic acid (molar ratio 1:10) in a water bath at 60 °C. After the reaction completed, the solvent was transparent. Then, the poplar wood powder was extracted by the National Renewable Energy Laboratory (NREL) Analytical Procedure. The mass ratio of extracted poplar wood powder and DES was 1:10, and reacted at 130 °C for 12 h. Then the reaction mixture was separated by filter under vacuum with ethanol washed. Tenfold water (based on filtrate) was added to precipitate lignin. DES-lignin was obtained after centrifugation, washing with 10% ethanol to improve the purity and drying in vacuum at 50 °C. Ethanol was removed by rotary evaporation and DES was recovered.

2.2 Preparation of degraded DES-lignin

Filled into a round bottom flask with 4 g DES-lignin and 80 mL 2 mol/L NaOH, then heated to 90 °C under stirring. Slowly added 10 mL of 30% H_2O_2, reacted at 90 °C for 3 h, cooled to room temperature, dialyzed to neutrality and freeze-dried to obtain degraded DES-lignin.

2.3 The preparation of Aspirin@LTNP by self-assembly

Fig.S1 showed the LCST of the DES-lignin-g-PNVCL.

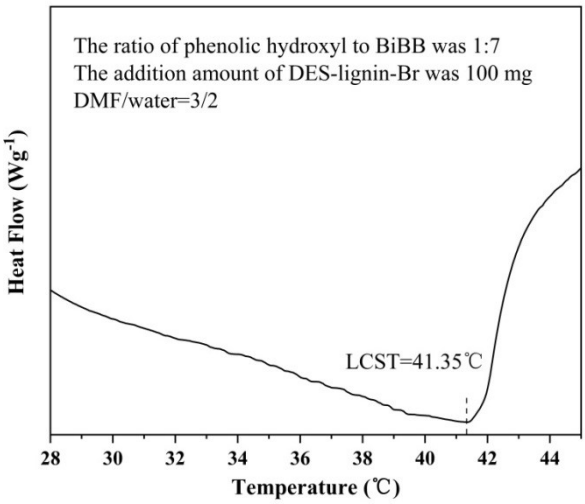

Fig.S1. The LCST of DES-lignin-g-PNVCL

3. Results and discussion

3.1 The synthetic characterization of DES-lignin-g-PNVCL

3.1.1 FT-IR analysis

Fig.S2 showed the infrared spectra of degraded DES-lignin, DES-lignin-Br, PNVCL and DES-lignin-g-PNVCL. In addition to the characteristic absorption peak in degraded DES-lignin, several new peaks appeared in DES-lignin-Br. The absorption peak at 1716 cm^{-1} correspond to the C=O stretching vibration of esters. The absorption peak at 1269 cm^{-1} was the C-O-C stretching vibration of esters. The absorption peak at 632 cm^{-1} was the stretching vibration of C-Br. The appearance of these new peaks indicated that BiBB was successfully grafted onto degraded DES-lignin. The characteristic absorption peak of PNVCL at 3225 cm^{-1} was the stretching vibration of CH= and CH_2=. The absorption peak at 2931 cm^{-1} was the C-H stretching vibration of aliphatic. The absorption peak at 1621 cm^{-1} and 1395 cm^{-1} were the stretching vibration of the amide bond -CONH. The absorption peak at 1470 cm^{-1} was the stretching vibration of C-N. The absorption peak at 1432 cm^{-1} was the stretching vibration of CH_2-C=O. By comparing the FT-IR of DES-lignin-Br and DES-lignin-g-PNVCL, it could be seen that the absorption peak of DES-lignin-g-PNVCL at 1597 cm^{-1}, 1513 cm^{-1}, and 1459 cm^{-1} was the characteristic absorption peak of the benzene ring skeleton. The absorption peak at 1716 cm^{-1} and 1269 cm^{-1} were the C=O and C-O-C stretching vibration of esters, respectively. In addition, the absorption peak at 1640 cm^{-1} was the C=O stretching vibration of amide, 1621 cm^{-1} and 1395 cm^{-1} were the stretching vibration of the amide bond -CONH, and 1470 cm^{-1} was the stretching vibration of C-N, which indicated that DES-lignin-g-PNVCL was successfully prepared.

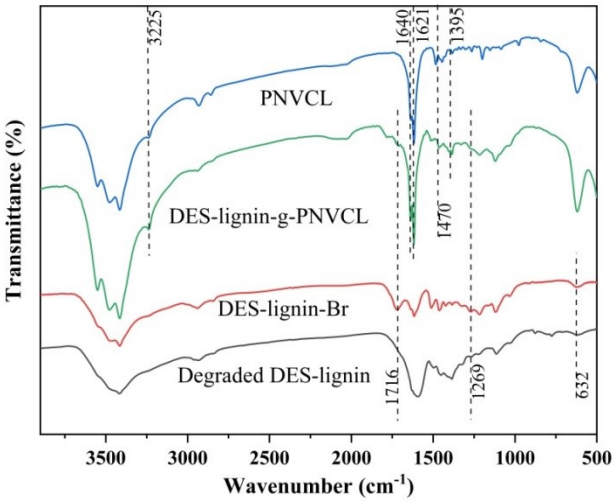

Fig.S2. FT-IR of degraded DES-lignin, DES-lignin-Br, PNVCL and DES-lignin-g-PNVCL

3.1.2 ^{1}H-NMR analysis

Fig.S3 showed ^{1}H-NMR spectra of degraded DES-lignin, DES-lignin-Br, and DES-lignin-g-PNVCL. Aromatic H appeared at 6.75 ppm in Fig.S3 indicated that the degraded DES-lignin, DES-lignin-Br, and DES-lignin-g-PNVCL contained benzene ring. A methyl peak at 2.0 ppm corresponded to position 1 of the structure formula of the DES-lignin-Br, which indicated that BiBB was successfully grafted to degraded DES-lignin. As shown in Fig.S3c, the CH peak, CH_2 peak connected to N in PNVCL, and the CH_2 connected to C=O in PNVCL appeared at 3.82 ppm, 2.90 ppm and 2.71 ppm correspond to positions 5, 12 and 8 of the DES-lignin-g-PNVCL structural formula, respectively. CH_2 on the main chain and side chain of PNVCL appeared at 1.36-2.05 ppm correspond to positions 4, 9, 10 and 11 of the DES-lignin-g-PNVCL structural formula. The terminal methyl peak appeared at 1.25 ppm correspond to position 1 of the DES-lignin-g-PNVCL structural formula. The ^{1}H-NMR spectrum of DES-lignin-g-PNVCL not only possessed the characteristic peak at 3.8-4.3 ppm (1H, -NCH-), 2.9-3.2 ppm (2H, -NCH_2), 2.2-2.8 ppm (2H, -$COCH_2$), and 1.1-2.1 ppm (4H, -CH_2 of the caprolactam ring and main chain) of the PNVCL, but also possessed the characteristic peak of aromatic H of lignin benzene ring, indicated that DES-lignin-g-PNVCL had been successfully prepared.

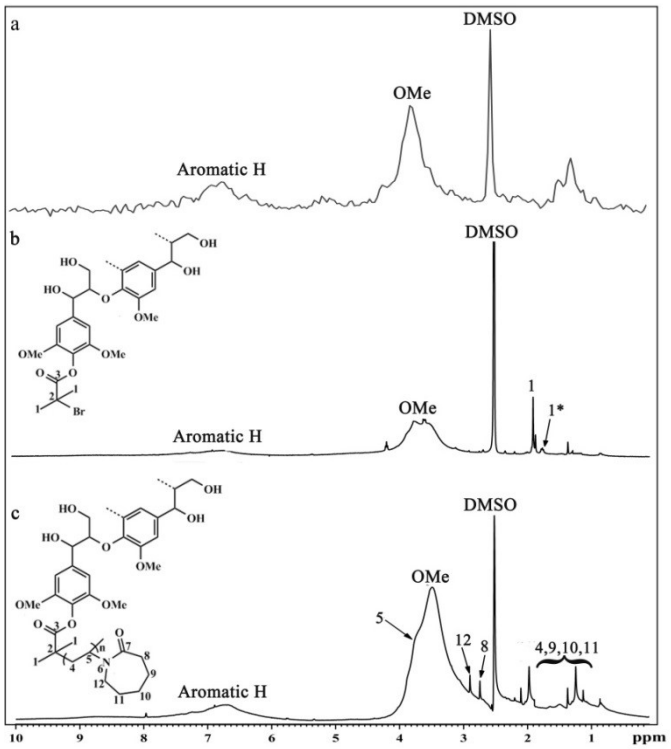

Fig.S3. ^{1}H NMR of degraded DES-lignin, DES-lignin-Br, PNVCL and DES-lignin-g-PNVCL

3.2 Effect of dripping rate on Aspirin@LTNP

Fig.S4 showed the coating rate of Aspirin@LTNP with dripping rate. It can be seen that the coating rate increased along with dripping rate when the dripping rate of ethanol was less than 2.0 mL/min. When the dripping rate was greater than 2.0 mL/min, the coating rate decreased with the increase of dripping rate. Which was consistent to the decrease of particle size of colloidal ball with the increase of dripping rate, when the dripping rate of ethanol was faster, the lignin molecules would "freeze", so that the particle size of the colloidal ball could not be increased, resulting in the reduction of the coating rate of aspirin.[1, 2] When the dripping rate was 2.0 mL/min, the coating rate of Aspirin@LTNP reached the maximum of 72.44%.

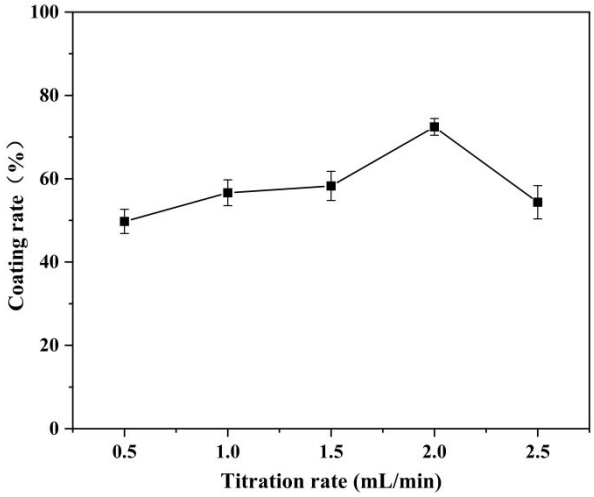

Fig.S4. Effect of dripping rate on coating rate

3.3 Effect of stirring rate on Aspirin@LTNP

Fig.S5 showed of coating rate of Aspirin@LTNP with stirring rate. It can be seen that the coating rate increased along with stirring rate when the stirring rate was less than 500 rpm. When the stirring rate was greater than 500 rpm, the coating rate decreased with the increase of stirring rate. As the stirring rate increased, the particle size of Aspirin@LTNP showed a decreasing trend, [1] which might be due to the fact that high-speed stirring can improve the mixing performance of deionized water and ethanol and reduce the coating rate of aspirin.[3] When the stirring rate was 500 rpm, the coating rate of Aspirin@LTNP reached the maximum of 72.44%.

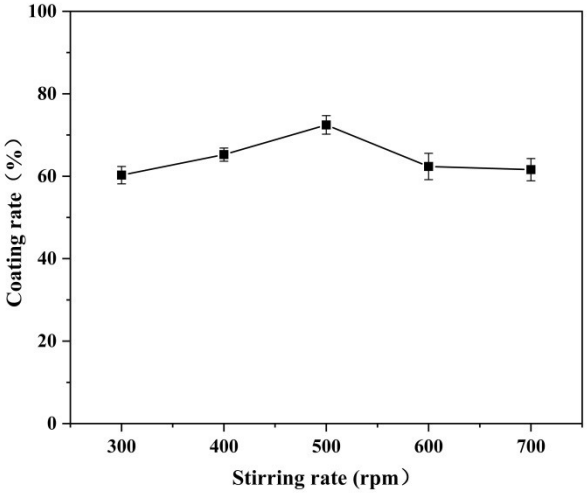

Fig.S5. Effect of stirring rate on coating rate

3.4 Effect of ethanol content on Aspirin@LTNP

Fig.S6 showed the coating rate of Aspirin@LTNP with ethanol content. It can be seen that the coating rate increased along with ethanol when the ethanol content was less than 40%. When the ethanol content was higher than 40% and lower than 60%, the coating rate decreased with the increase of ethanol. When the ethanol content was higher than 60% and lower than 80%, the coating rate increased rapidly with the increase of ethanol. When the ethanol content was higher than 80%, the coating rate decreased with the increase of ethanol. When the ethanol content was 60%, the coating rate decreased significantly, which might be due to the fact that electrostatic force and π-π interaction force were equal when the ethanol content was 60%, [4] resulting in the aggregation of some DES-lignin-g-PNVCL or destruction of nanoparticles formed, resulting in the inability to better coat aspirin. When the ethanol content was 80%, the coating rate of Aspirin@LTNP reached the maximum of 88.87%.

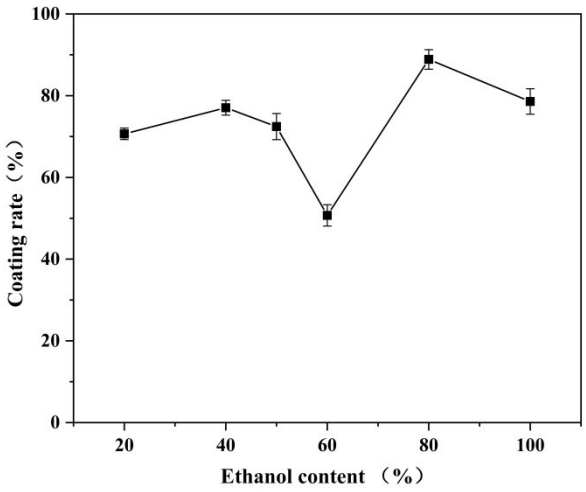

Fig.S6. Effect of ethanol content on coating rate

3.5 Effect of the mass of DES-lignin-g-PNVCL on Aspirin@LTNP

Fig.S7 showed the coating rate of Aspirin@LTNP with the mass of DES-lignin-g-PNVCL. It can be seen that the coating rate increased along with DES-lignin-g-PNVCL until it was stable. When the mass of DES-lignin-g-PNVCL was 30mg, the coating rate of Aspirin@LTNP reached the maximum of 88.87%. This indicated that its initial concentration and the degree of polymer aggregation in the system increased due to the mass of DES-lignin-g-PNVCL, resulting in the gradual increase of the particle size of the colloidal ball.[5] However, since the mass of APC remained unchanged, its coating rate tended to be stable after reaching the maximum. In order to save cost, 30mg of DES-lignin-g-PNVCL was considered as the optimal choice.

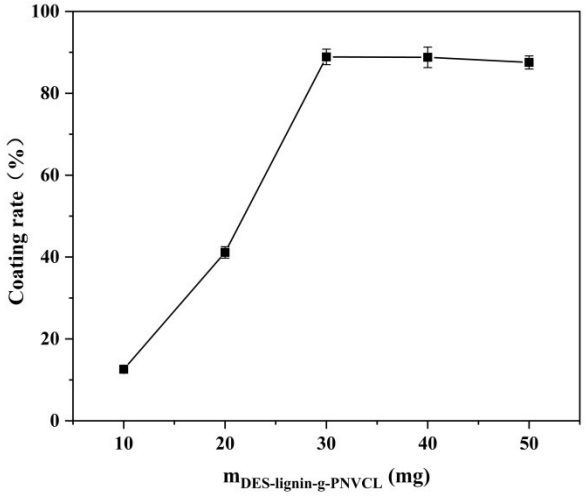

Fig.S7. Effect of the mass of DES-lignin-g-PNVCL on coating rate

3.6 Effect of the mass of APC on Aspirin@LTNP

Fig.S8 showed the coating rate of Aspirin@LTNP with the mass of APC. It can be seen that the coating rate increased along with APC when its mass was less than 10 mg. When the mass of APC was greater than 10 mg, the coating rate decreased with the increase of APC. This might be attributed that the excessive APC cannot be coated by DES-lignin-g-PNVCL when the ratio of DES-lignin-g-PNVCL to APC was lower the critical point. So the coating rate would decrease. When the mass of APC was 10 mg, the coating rate of Aspirin@LTNP reached the maximum of 88.87%.

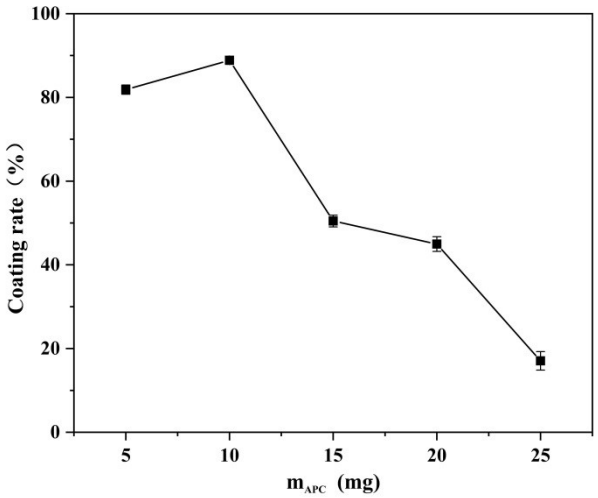

Fig.S8. Effect of the mass of APC on coating rate

3.7 HUVEC-Aspirin@LTNP light microscope cell

HUVEC-Aspirin@LTNP light microscope cell was illustrated in Fig. S9. The results showed that the Human Umbilical Vein Endothelial Cells (HUVEC) structure was not damaged when the concentration of Aspirin@LTNP less than 30μg/mL.

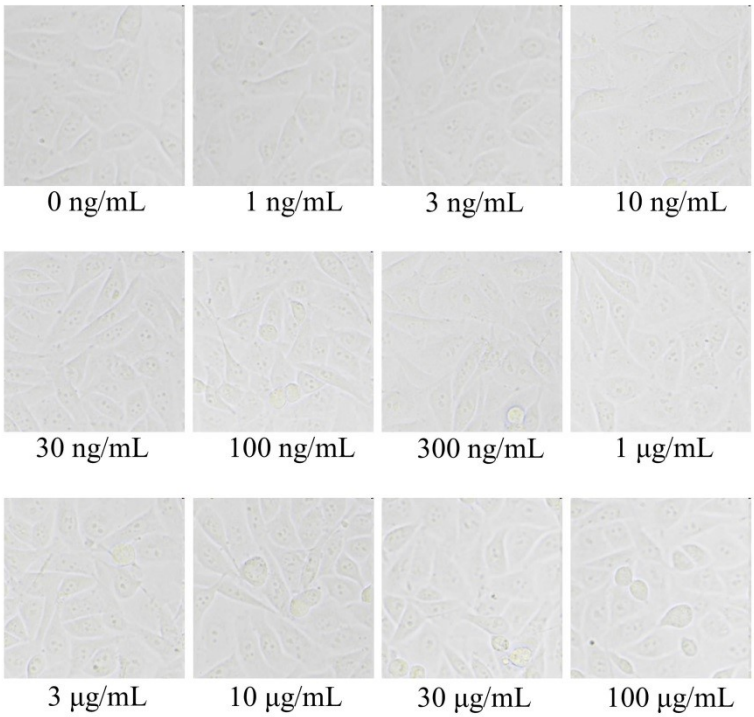

Fig.S9. HUVEC-Aspirin@LTNP light microscope cell

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