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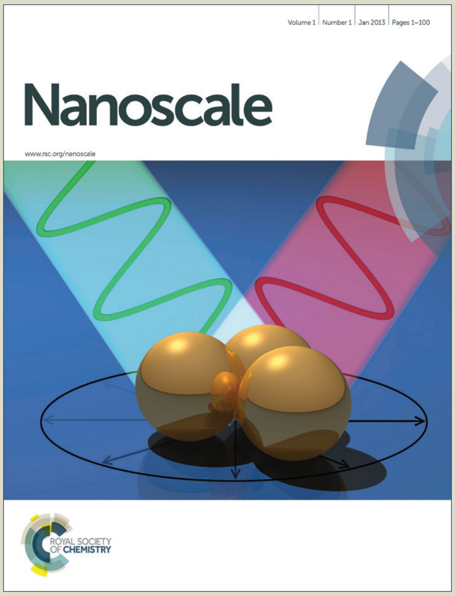

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Ultrasonication assisted preparation of carbonaceous nanoparticles modified polyurethane foam with good conductivity and high oil absorption properties

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Abstract: In this work, we report a facile, low cost and time-saving method for fabrication of compressible, electrical conductive, oil absorptive, cost-effective and flexible polyurethane (PU) foam through ultrasonication induced carbonaceous nanoparticles (CNP) onto flexible PU foam (CNP-PU foam). SEM pictures showed that the CNP could be firmly anchored onto PU foam, and made PU foam surface much rougher. Zero dimensional carboneous nanoparticles were easier to anchor onto PU foam surface than one dimensional nanoparticles (e.g., carbon nanotube) or two dimensional nanoparticles (e.g., graphene oxide). The CNP-PU foam exhibited excellent elasticity and high mechanical durability even if it is subjected to 500 cyclic compression. The CNP-PU foam had the excellent absorption of organic solvents up to 121 times the weight of the initial PU foam. In addition, the electrical conductivity of PU foams was greatly increased with the anchor of CNP onto the matrix. In addition, compression experiment confirmed that the electrical conductivity of

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CNP-PU foams changed with their compression ratios, therefore exhibiting excellent pressure sensitivity. The as-prepared materials have great potential as oil absorbent, elastic conductors, flexible electrode, pressure sensor, and so on.

Keywords: carbonaceous nanoparticles; PU foam; ultrasonication; oil absorption; electrical conductivity.

Introduction

Recently, polymer foams functionalized with different kinds of nanoparticles which possessed many excellent properties, have gained tremendous attention.[1-5] Owing to their high electrical conductivity[,1, 2] they have been applied in electronics sectors[3] and electromagnetic interference shielding materials.[4, 5] The excellent flexibility, compressibility and stretchability[1] make them useful in preparing stretchable displays/solar cells,[1] artificial skins[6] and sensors[7] and they are also used as oil absorbent [8-12] because of their high oil absorbing property. They have a lot of advantages over those three dimensional (3-D) graphene foams and carbon nanotube sponge[13-22] produced via costly and energy-consuming cryodesiccation or chemical vapor deposition (CVD) process, which have brittle mechanical property and relatively long preparation time. There are two methods to prepare multifunctional polymer foams with nanoparticles. One approach is directly distributing the nanoparticles into polymer matrix before the foam preparation. This method exists at least two disadvantages: (1) the nanoparticles are easy to aggregate during the processing, which will result in defect sites and limit the overall mechanical and the functional performance of the final product;[3] (2) the addition of nanoparticles into the polymer matrix may influence the processing parameter of the polymer, therefore affecting the formation of the foam. Another approach is physically coating the nanoparticles such as graphene or carbon nanotube onto the polymer foam surface.[6, 8, 9, 23, 24] Although the electrical conductivity and roughness of these polymer foams could be effectively enhanced, most of these properties could not sustain for a long time because the nanoparticles are just physically coated on the polymer surface. In previous researches, polydimethylsiloxane was usually used to cement the nanoparticles onto the polymer foam surface to enhance the stability of nanoparticles onto polymer foam,[8, 9, 23, 25] however, the electrical conductivity of the polymer foam was largely affected.

It is known that ultrasonication could provide a unique interaction between energy and matter.[28] When ultrasonication passes through a liquid medium, the transient cavitation including the process of formation, growth, and implosive collapse of bubbles will be generated in the liquid. It will lead to high temperature (5000 K) and pressure gradient.[29, 30] Ultrasonication has been extensively applied in many fields, such as dispersion, emulsifying, crushing, and activation of particles.[31-33] Herein, basing on the previous work in our research group that ultrasonication induced adsorption of carbon nanotubes onto electrospun polymer nanofiber,[26, 27] we propose a facile method for fabricating compressible, conductive, oil absorptive, cost-effective PU foam functionalized with carbonaceous nanoparticle (CNP-PU foam) by ultrasonication induced carbonaceous nanoparticles (CNP) onto flexible PU foam. The facile preparation method using ultrasonication treatment in this work not only guarantees the uniform dispersion of CNP into solution, but also greatly enhances the firmness of CNP anchored onto the PU foam surface. The CNP-PU foam with consolidated advantages of both flexible PU foam and CNP, exhibited not only excellent mechanical properties and oil absorption, but also high electrical conductivity. Thus, it holds great potential as oil absorbent, elastic conductors, flexible electrode, and pressure sensor.

Experimental

2.1. Materials

Carbonaceous nanoparticles (CNP) and carbon nanotube (CNT with product number of TNSS) were purchased from Chengdu Organic Chemicals, Ltd., Chinese Academy of Sciences. CNP were synthesized via chemical vapor deposition (CVD) method. Graphene oxide (GO) was exfoliated from graphite oxide in water. Graphite oxide was purchased from Nanjing XFNANO Materials Tech Co., Ltd. The morphologies of CNP, CNT and GO were shown in Fig. S1 (see supporting information). The polyurethane (PU) foam was commercial sponge from Top-china group. Chloroform and ethanol were purchased from Beijing chemical factory, and were used as received without further purification.

2.2. Preparation of CNP-PU foam

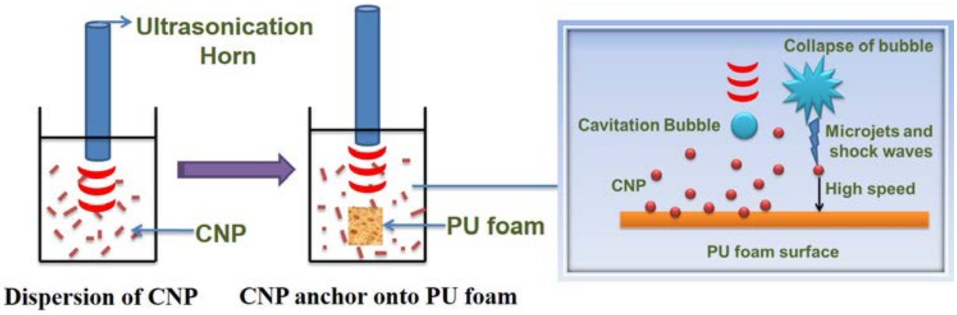
The pre-dispersion of CNP into chloroform and anchor of CNP onto PU foam were assisted by ultrasonication with a high-intensity ultrasonic horn (20 kHz, 950 W at 60 % efficiency) (Scientz-IID, Ningbo Scientz Biotechnology Co. LTD). 40 mg CNP were added into 40 mL chloroform, and then the suspension was pre-dispersed under ultrasonication for 60 min before the anchor of CNP onto PU form was performed. Then the PU foam was immersed into the CNP solution and subjected to ultrasonication treatment for 30 min to obtain CNP-PU foam. Finally, the CNP-PU foam was washed thoroughly with ethanol for 30 min to remove unanchored CNP and dried under vacuum at 50 °C in an oven for 24 h.

2.3. Characterization

SEM micrographs were obtained with a field emission scanning electron microscope (FESEM; XL 30, FEI Company) at a voltage of 20 kV. Thermogravimetric analysis (TGA) was carried out using a Pyris Diamond TG/DTA thermal analyzer. The experiment was performed in the range of 50-800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The compressive strength was conducted using an Instron mechanical Tester (Model 5567) with a crosshead speed of 5 mm/min at room temperature, and the strain was 80 %. The determination of water contact angle was conducted on a Drop Shape Analyzer DSA100 (KRÜSS company) with a water droplet of 2 μL. The oil absorption capacity (k) of the CNP-PU foam was calculated by weight measurements at ambient temperature according to the previous reports.[34] The alternating current conductivities of pure PU foam and CNP-PU foam were conducted by an Alpha high performance frequency analyzer coupled to a Novocontrol Broadband Dielectric Spectrometer, and the measurement frequency was set from 10^0 to 10^6 Hz.

Results and discussion

Scheme 1 is a schematic demonstration for ultrasonication induced CNP anchor onto the PU foam surface. The yellow PU foam became completely black after CNP anchor by ultrasonication treatment, indicating that the PU foam was successfully anchored by CNPs. The pure PU foam possessed a smooth surface, which can be confirmed from the SEM images in Fig. 2 (A1, A2). In contrast, from Fig. 2 (B1, B2 and B3), the PU foam surface was covered with the carbonaceous nanoparticles layers and became much rougher after CNP decoration. The possible mechanism of CNP anchored onto PU foam was given as following. Under ultrasonication treatment, cavitation bubbles were firstly formed in liquid. When the cavitation bubbles approached to carbonaceous nanoparticles, cavitation bubbles collapsed into asymmetric shape, and high speed jets and shock waves were generated. These jets and shock waves with high energy could push the CNP toward the PU foam surface at high speeds, and finally the interfacial collision between CNP and PU foam occurred. Meanwhile, these jets and shock waves could also hit the surface with a tremendous force, which rendered the PU foam softened or even partially melted at the impact sites. Under the synergy of the above actions, CNP could be firmly anchored onto the PU foam surface.[32, 35, 36] When CNP was just physically coated onto PU foam via dip coating method, the adsorbed CNP could be mostly washed away. After the sample was put into ethanol with agitation for 30 min, the PU foam almost become the initial yellow (Fig. 2D). In contrast, when the PU foam pre-treated by ultrasonication in the same CNP solution was also washed by ethanol under agitation for 30 min, the color of PU foam treated with ultrasonication was still black (Fig. 2E). Hence, the firmness of CNP anchored onto PU foam surface induced by ultrasonication was much higher than that attached onto PU foam surface just via physically deposition. In addition, the water contact angle of CNP-PU foam increased to 127.6°, compared with 103.8° for pure PU foam surface. It means the hydrophobicity of PU foam was further increased, which is attributed to both the increase of roughness by anchoring CNP onto PU foam and the more hydrophobic nature of CNP.



Scheme1 Illustration of ultrasonication-induced CNP onto the flexible PU foam

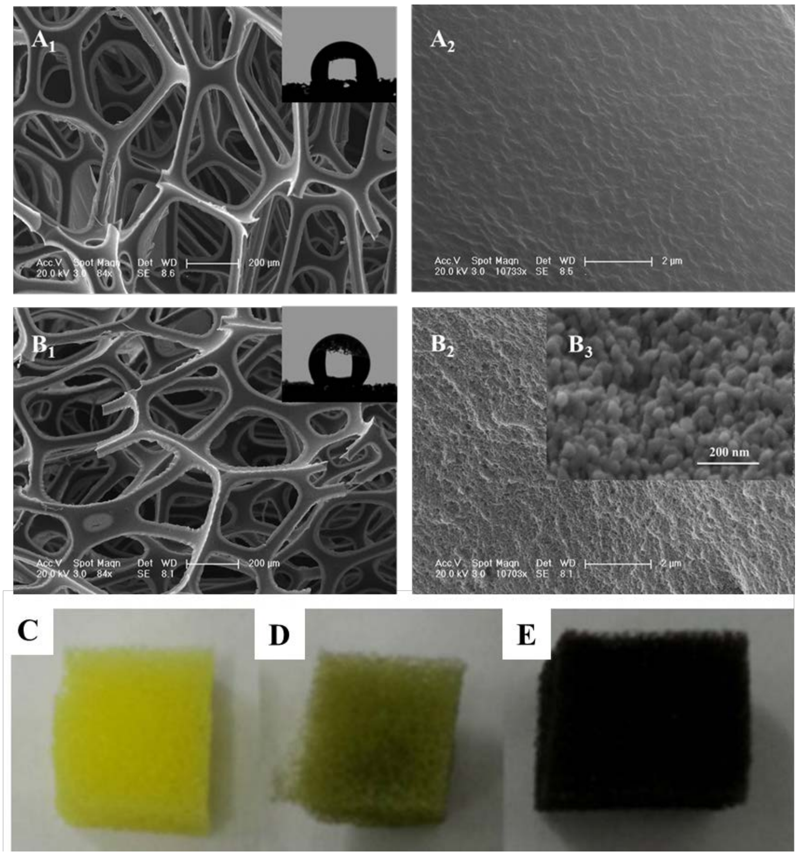


Fig. 2 SEM images, water contact angles and digital pictures of pure PU foam (A_1, A_2, C), CNP-PU foam (B_1, B_2, B_3, E) and dip coating method of CNP onto PU foam (D)

The effect of different nanoparticle dimensions on the efficiency of nanoparticle deposition onto PU foam under ultrasonication was also investigated. Under the ultrasonication, an average pressure by shock waves is exerted on the particles as the shock waves pass over the particles nearby the collapsed bubble. The actual velocity of a particle reaches during ultrasonication depends strongly on the particle size and shape.[37] As for the particles that have the same volume, the velocity of the quasi-zero dimensional CNP should be larger than those of one dimensional CNT and two dimensional GO (detailed analysis was shown in Section 2 in supporting information). The higher velocity nanoparticle has the higher kinetic energy, which leads to the more adhesion of particles onto the PU foam. Thus, the surface of CNP-PU foam was much rougher than those of CNT-PU and GO-PU foams because of the higher content of nanoparticles anchored on the surface, as shown in Fig. 3. In addition, the structure of CNP, CNT and GO were partially damaged by the mechanical shock waves and shear forces created by the collapse of cavitation bubbles under ultrasonication (Fig. 2S-4S and Table 1S in supporting information).

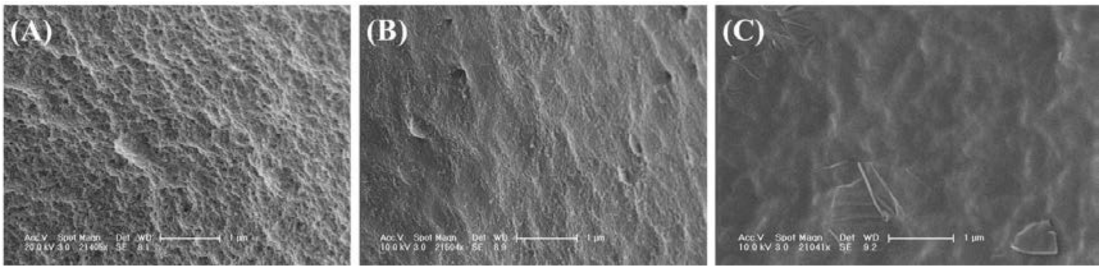


Fig. 3 SEM images for PU form anchored with different dimensional nanoparticles. (A) CNP, (B) Carbonaceous nanoparticles, (C) Graphene oxide

The thermal stability of PU foam and CNP-PU foam was investigated by TGA. As shown in Fig. 4, the quite similar TGA curves of CNP-PU foam and pure PU foam indicated that the CNP deposition did not change the thermal properties of the PU foam. The residue content difference between the two samples implied that about 2 wt% of CNP had been induced onto the PU foam surface under ultrasonication.

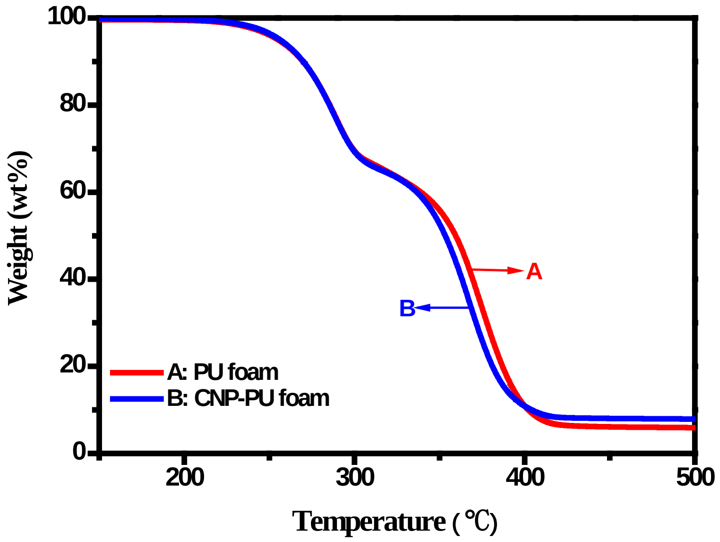


Fig. 4 TGA curves of (A) PU Foam and (B) CNP-PU foam

The cyclic compressing tests of the CNP-PU foam were conducted to evaluate the mechanical property as shown in Fig. 5. The unloading curve of CNP-PU foam almost return to the initial points even after 500 cycles of compressing at 80 % compressing strain suggested that CNP-PU foam had excellent elasticity and complete shape recovery without plastic deformation after the release of the pressure. In contrast, 3-D graphene foam and carbon nanotube sponge could be totally destroyed at this strain. The compressive stress only had 6 % loss after 500 compressing cycles, which confirmed the good elasticity and flexibility of the CNP-PU foam. The excellent mechanical properties are very important for CNP-PU foam to be applied in oil absorbent, elastic conductors, flexible electrode, pressure sensor, etc.

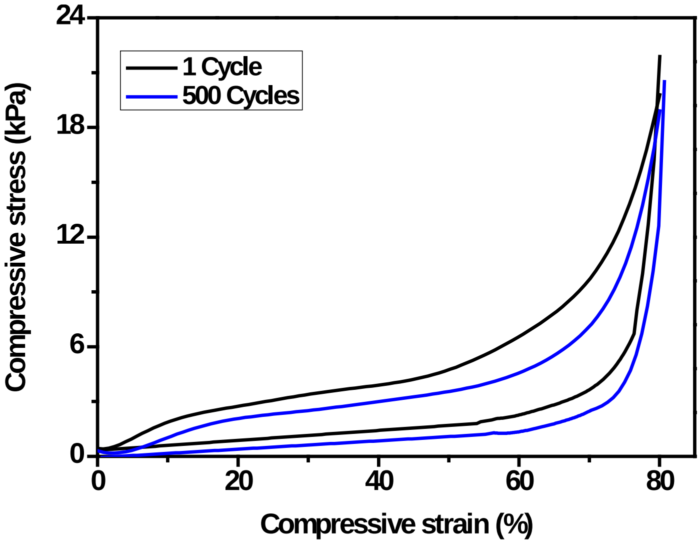


Fig. 5 Cyclic stress-strain compressive curves of CNP-PU foam at 80 % strain

The hydrophobic foams could be used for absorbing oils and organic solvents, which is a significant feature for practical applications. The absorption capacity (k) was used to measure how much organic solvent that the CNP-PU foam could absorb. $k=(W_{saturated\ absorption}-W_{initial})\ /W_{initial}$. Fig. 6 demonstrated that the absorption capacities of the CNP-PU foam for various organic solvents were 50-121 times its own weight, predominantly depending on the density of organic solvents. Especially, the CNP-PU foam exhibited the much better absorption for chloroform, dichloromethane, and toluene, which are well-known toxic organic contaminants in water. The k of chloroform, dichloromethane, DMF and toluene could reach 121, 117, 75, and 68, respectively. Taken chloroform (with Sudan III) as organic solvent in selective absorption experiment (Fig. 7), the CNP-PU foam without employing external force could selectively absorbed a high-density organic solvent (chloroform) from water. Once the CNP-PU foam contacted with chloroform in water, the red chloroform could be quickly sucked into the CNP-PU foam within a few seconds. The absorbed chloroform in the foam can be readily collected by a simple squeezing process. No water in the collected chloroform can be found in Fig.7F, which presented a very high separation efficiency of the CNP-PU foam. Due to the cost-effective preparation, highly selective absorption of the as-prepared PU foam, it may have great potential application in removing oils and toxic organic contaminants from water.

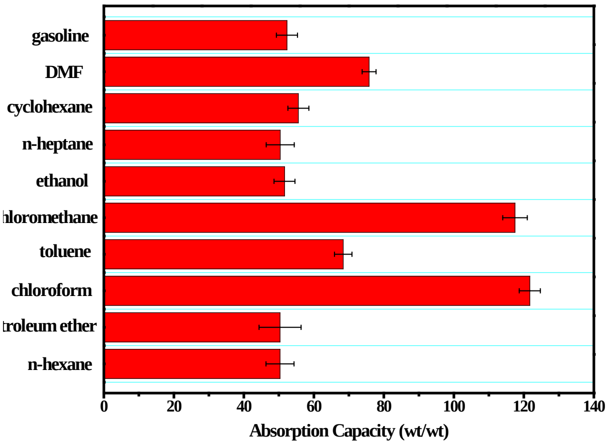


Fig. 6 Absorption capacity of CNP-PU foam for various organic solvent

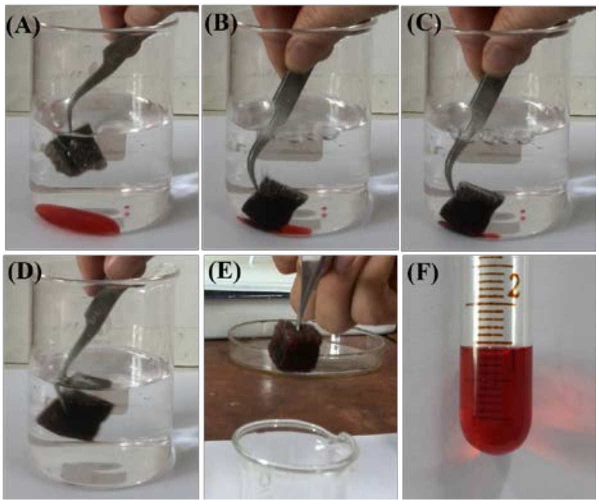


Fig. 7 Selective absorption of chloroform (dyed with Sudan III) in water by the CNP-PU foam

The CNP-PU foam combined the advantages of both flexible PU foam and CNP, exhibited not only excellent mechanical properties and oil absorption, but also high electrical conductivity. As shown in Table 1, the electrical conductivity of PU foam increased from 8.56×10^{-12} S/m to 9.43×10^{-5} S/m at the frequency of 1 Hz after CNP anchored onto the PU foam. In addition, the electrical conductivity of CNP-PU foam increased with increasing compression ratio, ranging from 9.43×10^{-5} S/m for compression ratio of 1 to 1.44×10^{-3} S/m for compression ratio of 8. It could be attributed to that the density of contact spots between CNP increases rapidly with increasing the compression ratio, bringing about the increase of the electrical conductivity of CNP-PU foam. Hence, this material could be applied as press sensitive sensors

Table 1 Alternating current conductivity under different compression ratio at the frequency of 1 Hz

Compression ratio	1	2	8
CNP-PU foam (S/m)	9.43×10^{-5}	2.54×10^{-4}	1.44×10^{-3}
PU foam(S/m)	8.56×10^{-12}	7.31×10^{-13}	1.10×10^{-12}

Conclusions

The compressible, conductive, oil absorptive, cost-effective polymer-based carbonaceous nanoparticle foam was facilely fabricated by ultrasonication induced carbonaceous nanoparticles onto flexible PU foam. Compared with one and two dimensional nanoparticles, zero dimensional carbonaceous nanoparticles are easier to anchor onto PU foam surface. The CNP could be firmly anchored onto PU foam surface under ultrasonication, therefore rendering the surface of PU foam became much rougher. The CNP-PU foam exhibited excellent mechanical properties and high stability, even if the foam was compressed by repeating 500 times. The as-prepared CNP-PU foam displayed good organic solvent absorption with up to 121 times its own weight. In addition, the CNP-PU foam had the obviously increased conductivity and the much better pressure sensitivity, compared with the native PU foam. The as-prepared materials hold great potential as oil absorbent, elastic conductors, flexible electrode, pressure sensor, and so on.

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