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Carbon nanotube-based transparent thin film acoustic actuators and sensors

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Abstract

Transparent thin film acoustic transducers that can effectively work as both acoustic actuators (speakers) and sensors (microphones) are developed in this study. The developed transducer consists of a piezoelectric poly(vinylidene fluoride) (PVDF) thin film coated with compliant carbon nanotube (CNT) based transparent conductors, which are fabricated by CNT acid treatment and layer-by-layer nanoassembly based surface modification of the PVDF substrates. The developed thin film transducers show excellent acoustic response over a broadband frequency range, and have the advantages of being transparent, flexible, extremely thin, and lightweight. The developed transducers could make a significant impact on room acoustics by enabling windows, computer screens, touch panels and posters themselves to server as invisible speakers and microphones.

Keywords: Carbon nanotube; Thin film acoustic transducer; Transparent speaker; Transparent microphone

1. Introduction

The continued growth in urban population has led to high-density housing close to airports and highways. This has increased the exposure of the population to noise from a variety of sources, increasing the need to provide better sound insulation for the homes. Because windows constitute the primary path through which noise enters a home, window improvements provide the most satisfaction to home dwellers [1]. The idea of active noise cancellation (ANC) has been proven to be a promising solution for the noise attenuation for windows [2]. In ANC, a control algorithm drives a voice-coil actuator to vibrate the glass panel itself to generate the anti-phase canceling sound to cancel the primary noise wave. However, multiple actuators on the glass panel are needed to achieve global noise cancellation. Several actuators on a window pane would totally destroy the aesthetics of the window. Therefore, an optically transparent distributed actuation system needs to be developed in order to make the development of active noise blocking windows feasible.

Transparent thin film acoustic actuators and sensors also have many other diverse applications. For instance, thin film speakers can work as transparent compact and lightweight general-purpose flat-panel loudspeakers. Attaching transparent thin film speakers onto the surface of windows, computer screens, posters, and touch panels can enable them to be "speaker-integrated" devices. The thin film speakers can also be used for other ANC systems that need compact and lightweight actuators, such as aircraft cabins. Further, transparent thin film microphones can work as invisible sound monitors for military applications.

There are no fully transparent thin film speakers and microphones that have been previously developed, although several research groups have investigated different methods for the development of thin film acoustic actuators and sensors. Heydt et al. [3,4] developed an electroacoustic loudspeaker that uses the electrostrictive response of a polymer thin film. Over 80 dB sound pressure level can be produced from the "bubble" elements of their loudspeaker. However, the high resonant frequency (about 1500 Hz) and required high driving electric field (25 V/μm) will prohibit its use from most normal loudspeaker applications. Recently, piezoelectric PVDF has been investigated to fabricate acoustic transducers, either being used as a sensor [5], or an actuator [6], or both [7]. Their results show PVDF to be a promising solution for thin film acoustic transducers. However, although PVDF itself is transparent, the need of transparency for the electrodes poses a great challenge that has not been solved and is addressed in this paper.

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2. Review of results on transparent conductive thin films

Transparent conductive thin film electrodes are also widely used for liquid crystal displays (LCDs), touch screens, solar cells, and flexible displays. Indium tin oxide (ITO) thin films are often used in these applications because of their high electrical conductivity and high optical transparency. However, ITO thin films are brittle and need high processing temperatures [8,9]. For thin film speaker applications, the continuous vibrations have been found to crack the compliant metal electrodes after a short period of usage. An alternative material to ITO is poly(3,4-ethylenedioxythiophene)-poly(4-stryrenesulfonate) (PEDOT:PSS). Using PEDOT:PSS, flexible films can be made that can continue to conduct beyond 60% strain [10]. PEDOT:PSS-based flexible transparent speaker has also been developed by Lee et al. [11,12]. However, as will be shown in Section 4, the low transparency and conductivity (about 1 S/cm) of PEDOT:PSS significantly limit its performance.

Single-walled carbon nantotubes (SWNTs) have also been investigated for fabricating flexible transparent conductive thin films due to their high conductivity (in the order of 10^3–10^4 S/cm [13]) and high aspect ratio (>100). However, due to the aggregation of SWNTs, it is difficult to uniformly coat SWNT thin films on substrates. One approach that has been investigated is to add SWNTs into polymer matrixes [14,15], the resulted polymeric composites have good mechanical properties but low conductivity. Another approach is to disperse SWNTs in aqueous solution with the help of a surfactant (such as Triton X-100), thin films were then made by wet coating techniques [16]. However, the surfactant adsorbed on the surfaces of SWNTs is found to greatly affect electrical properties. To remove the surfactant, Wu et al. filtered the SWNT solution through a membrane, washed away the surfactant, and transferred the SWNT films to substrates thereafter [17]. Thin films made by these methods show much better conductivity. However, this fabrication process is not easy to scale up for large-size films, the films are easily broken during the washing and transferring processes, and the bonding between the SWNT film and the substrate is quite weak.

In the present work, we demonstrate the development of fully transparent thin film acoustic transducers using SWNTs as transparent electrodes. The developed fabrication processes and materials are described in detail in the next section. Briefly, the process is comprised of three steps: (i) oxidizing SWNTs with a mixture of sulfuric acid and nitric acid for an adequate length of time. The introduced negatively charged carboxylic groups on SWNT surfaces help SWNTs to be stably dispersed in water even without any surfactant; (ii) modifying the surface of the PVDF substrate using layer-by-layer (LBL) nanoassembly. Eventually, a positively charged and hydrophilic poly(diallyldimethylammonium chloride) (PDDA) molecular layer is deposited on the top of substrate surface; and (iii) coating pure SWNT thin films onto modified PVDF substrate surfaces using wet coating techniques, including wire-wound rod coating.

3. Prototype transparent PVDF thin film speaker

The high purity SWNTs (<10 vol.% impurity) for this study were synthesized using chemical vapor deposition (CVD) method and were supplied by Timesnanoweb (Chengdu, China).

A schematic of the fabrication process is shown in Fig. 1. In a typical acid treatment procedure, 100 mg nanotubes were added to 40 ml of acid mixture of sulfuric acid (98 wt.%) and nitric acid (69 wt.%) in a ratio of 3:1, and stirred for 45 min on a 110 °C hot plate. The suspension was then diluted to 200 ml. Finally, the SWNTs were collected by membrane filtration (0.45 μm pore size), and washed with enough deionized (DI) water to remove residual acids. The acid treated SWNTs (10 mg) were added into 10 ml of DI water and bath ultrasonicated for 1 h and settled for a few hours at room temperature. This well-known chemical treatment for nanotubes has been used to cut SWNTs into short tubes [18], and to functionalize SWNTs [19,20]. However, we found that, with an adequate acid treatment time, the introduced negatively charged carboxylic groups on SWNT surfaces can also help SWNTs to be stably dispersed in water even without any surfactant.

The substrate, a 250 mm × 28 μm PVDF thin film (Measurement Specialties Inc, VA), was firstly hydrolyzed with 6 M NaOH aqueous solution for 20 min at 60 °C. After rinsing with DI water, PVDF film was immersed in 1.5 wt.% PDDA solution

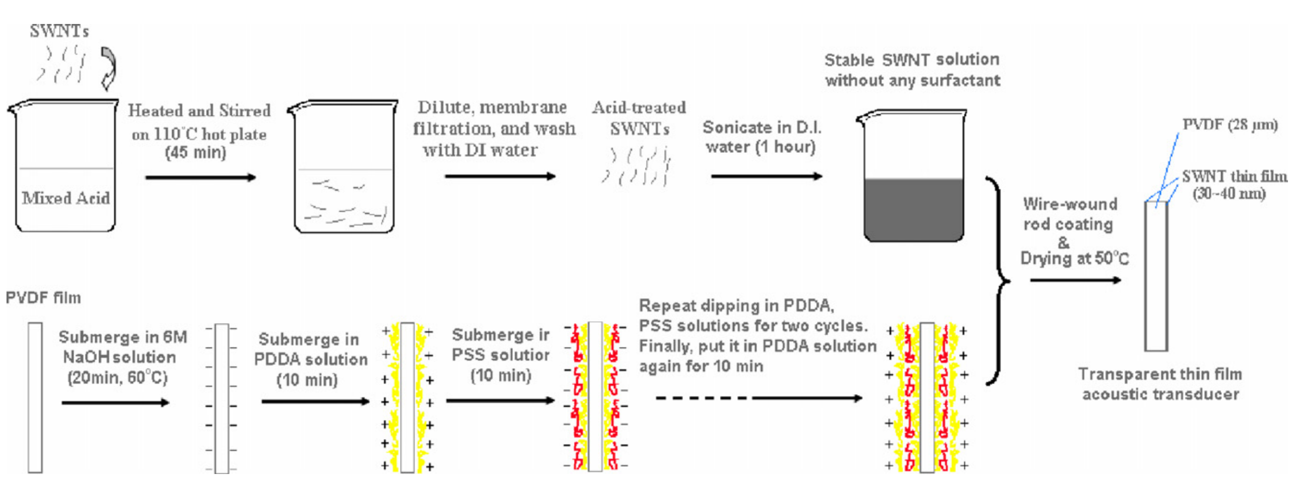

Fig. 1. Schematic diagram of the fabrication process of transparent thin film acoustic transducer.

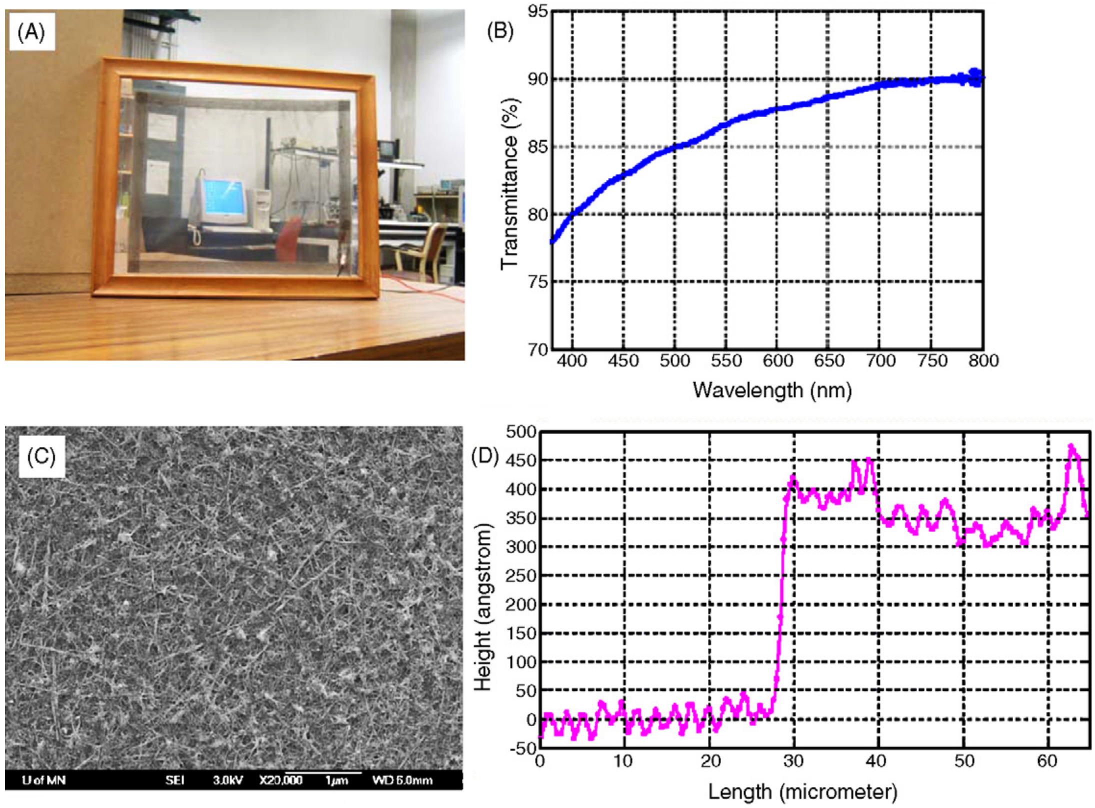

Fig. 2. (A) A 250 mm × 190 mm transparent thin film actuator/sensor. (B) Light transmittance spectrum of the SWNT thin film in the visible light range. (C) SEM image of the SWNT network of the transparent conductive thin film. (D) Thickness profile of the SWNT thin film.

(with 0.5 M NaCl) for 15 min at room temperature, followed by rinsing with DI water. PVDF film was then dipped into 0.3 wt.% poly(sodium styrenesulfonate) (PSS) (with 0.5 M NaCl) for 15 min and rinsed. The PDDA/PSS adsorption treatment was repeated for two cycles and finally treated with PDDA solution again. The outermost layer is thus the positively charged PDDA molecular layer. Here PDDA is chosen for its high hydrophilicity among common polycations [21]. The SWNT/water solution was then applied to both sides of the PVDF film by wire-wound rod coating and dried at 50 °C. After drying, additional SWNT layers could be coated above the initial SWNT layer to achieve a desired combination of electrical and optical properties. In this study, the final SWNT thin film has two layers with total thickness of 30–40 nm, 87% average light transmittance in the visible light range, and 2.5 kΩ/Da surface resistivity.

Fig. 2A shows a picture of a fabricated thin film acoustic actuator/sensor fixed in a photo frame (the gray lines on the edges of the film are 3M 9713 conductive tape which is used to reduce the electrode contact resistance). It is obvious that we can clearly see through this flexible thin film actuator/sensor. Fig. 2B shows the light transmittance spectrum for the SWNT thin film over the visible light range, which indicates an average transmittance of 87%. The thickness of the SWNT thin film is about 30–40 nm as measured by a profilometer (Fig. 2D). Fig. 2C is a scanning electron microscope (SEM) image of the SWNT thin film, which shows a randomly ordered tight carbon nanotube network formed on the surface (those spots in the SEM image are impurities and bundles of very short nanotubes). Since there is no surfactant in the SWNT thin film, the SWNT bundles contact each other directly which greatly enhances the conductivity.

4. Characterizing the transducer as a loudspeaker

The developed carbon nanotube-based transparent thin film acoustic transducer shows excellent acoustic response. First, it was characterized as a loudspeaker. The thin film transducer is excited to produce sound by a driving signal. Fig. 3 shows a typical frequency response from 50 Hz to 3 kHz generated from the thin film speaker excited by a 12 V_{rms} white noise signal. The response is measured at 50 mm from the speaker along the centerline axis. As can been seen from the figure, the speaker has a pretty smooth response over a broadband frequency range, and the resonant frequency is about 150 Hz which is low enough for general-purpose loudspeakers and most ANC applications. The results are also compared with a thin film speaker that uses PEDOT:PSS as the electrodes, which has the same size, same boundary conditions, and driven by the same signal. It shows that the CNT-based thin film speaker has a 15 dB higher response than the PEDOT:PSS-based thin film speaker over all frequencies. In other words, if want to produce the same sound level, the PEDOT:PSS-based thin film speaker needs a driving voltage 5.6 times of that of the CNT-based thin film speaker. The CNT-based speaker thus removes the need for expensive high-power voltage amplifiers and results in much less power consumption. The developed thin film speaker also shows good excellent durability. After being used for ten months, the speakers did not show

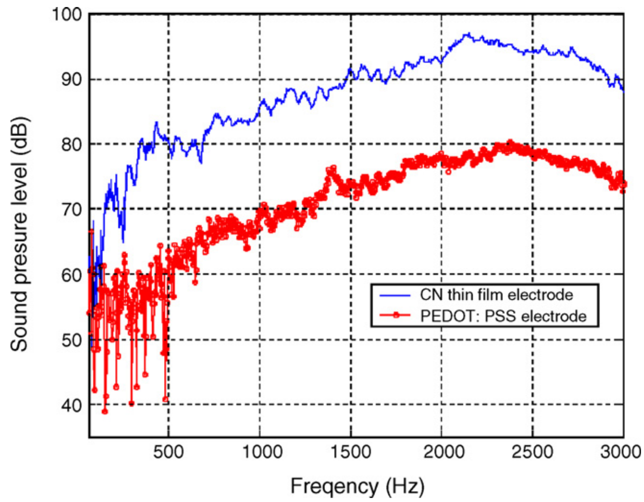

Fig. 3. Measured frequency response from the CNT-based thin film speaker that is excited by a 12 V_{rms} white noise signal, compared with a PEDOT:PSS-based thin film speaker.

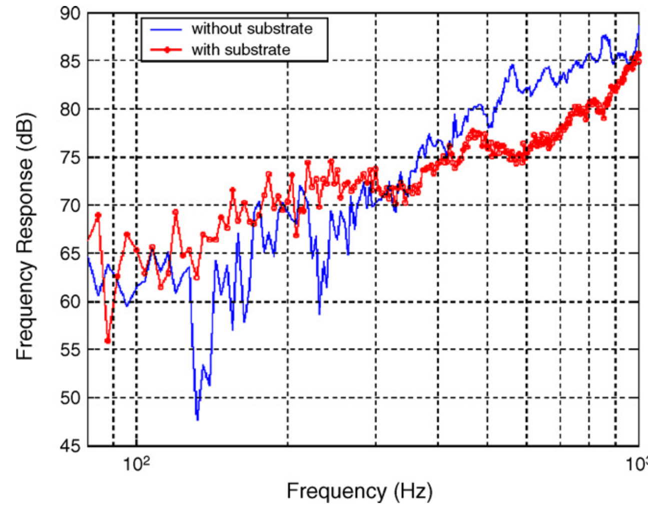

Fig. 4. The effect of the soft substrate on the frequency response of thin film speakers.

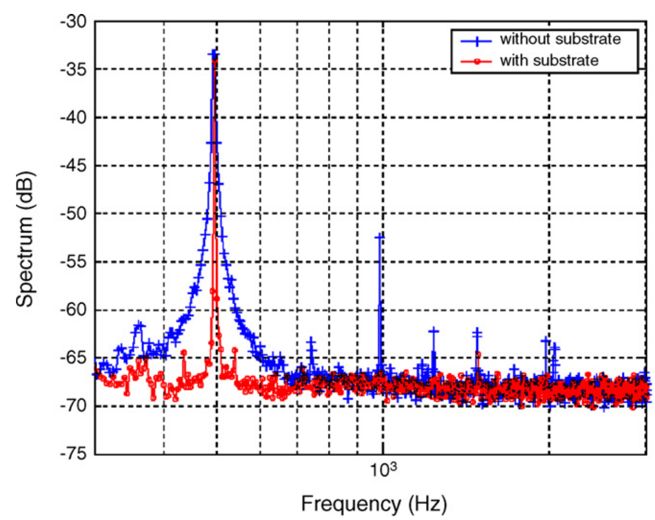

Fig. 5. The effect of the soft substrate on the harmonics of thin film speakers.

any degradation on their acoustic performance. No changes in electrical resistivity were observed on the carbon nanotube network.

Compared to traditional loudspeakers, the developed transparent thin film speaker has the advantages of being transparent, extremely thin and lightweight. For instance, the above thin film speaker is less than 30 μm in thickness and less than 10 g in weight, both of which are significantly less than traditional speakers. In addition, the sound propagation mechanism of the thin film speaker is fundamentally different from traditional loudspeakers. For thin film speakers, the sound is produced from everywhere over a large-size panel, unlike traditional speakers that project sound from one point where the actuator is installed. This property gives the thin film speakers better stereo height and width.

It was also found that the performance of the thin film speaker could be optimized for some specific applications, such as their use as actuators for active noise cancellation (ANC) systems, by attaching a soft substrate to modify the thin film dynamics. Here, a transparent soft layer (3 M VHB4910 tape, Young's modulus = 105 kPa) was cleaved to the film as the substrate to make an ANC actuator. The first effect of the substrate is on the frequency response. As shown in Fig. 4, although the acoustic output is lowered down at the high frequencies by the added mass, the frequency response is improved at lower frequency range that will be beneficial for ANC.

The other important effect of the soft substrate is that it can help to eliminate the nonlinear harmonics of a bare film speaker. Fig. 5 shows the response of the film speakers to a 500 Hz tonal signal. The film speaker without substrate produces harmonic sounds. A speaker with many harmonics is not appropriate as a control source for ANC, because it will produce other frequency harmonics at the same time as canceling the primary noise. On the contrary, the film speaker with soft substrate has no harmonics due to the added damping, which makes it possible for it to be used for active noise control applications.

5. Characterizing the transducer as an acoustic sensor

The transparent PVDF thin film can also be utilized as an acoustic sensor, since the PVDF is a piezoelectric material. As acoustic pressure acts on the film surface, the piezoelectric effect will create an electrical signal that can be monitored. Fig. 6 shows the comparisons of the output voltages from an Audio-Technica ATR35s microphone and the developed piezoelectric PVDF thin film sensor when they are used to measure the same 600 Hz sound. Fig. 7 is the comparison in frequency domain when they are used to measure a wide band noise. As can see from the figures, the PVDF film can effectively and reliably measure acoustic frequency components. Although giving out smaller voltage output at high frequencies due to low energy transfer efficiency, the PVDF film can work almost as efficiently as a regular microphone for frequencies below 900 Hz where ANC systems are useful. More importantly, when used in ANC systems, the PVDF thin film sensor will help to achieve global

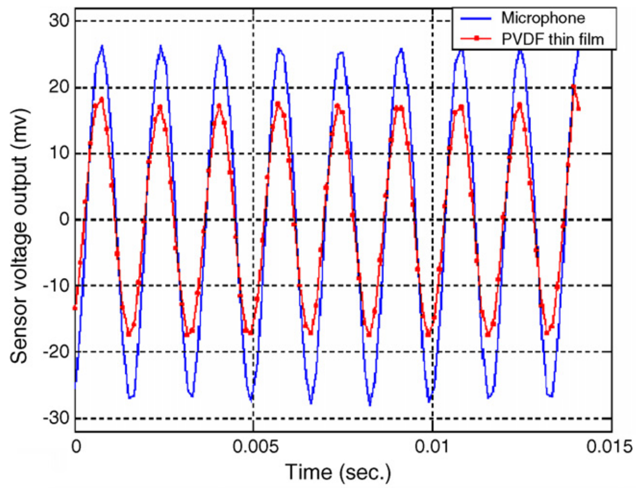

Fig. 6. The comparison of outputs of a regular microphone and the transparent thin film sensor when they are used to measure a 600 Hz sound.

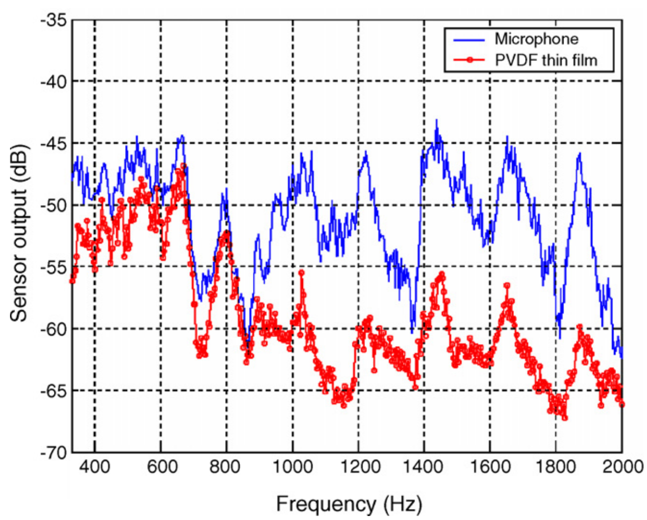

Fig. 7. The comparison of outputs of a regular microphone and the PVDF thin film sensor when they are used to measure a 320–2000 Hz wide band sound.

sound reduction, because it will pick up the acoustic signal over a large area instead of just one point as a regular microphone. Being transparent, the transparent thin film sensors can also be used as invisible sound monitors for military applications.

6. Conclusions

Transparent thin film acoustic transducers that can effectively work as both acoustic actuators (speakers) and sensors (microphones) have been developed by CNT acid treatment and layer-by-layer (LBL) nanoassembly-based surface modification of the PVDF substrates. The developed thin film transducers showed excellent acoustic response over a broadband frequency range, and have the advantages of being transparent, flexible, extremely thin, and lightweight. The developed transducers could make a significant impact on room acoustics by enabling windows, computer screens, and posters themselves to server as invisible speakers and microphones. The developed transducers can also be used as actuators for active noise control systems and invisible sound monitors for military applications.

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