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光声换能器的材料组成及应用进展

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摘　要

光声换能器是近年来迅速发展的一种新型器件，它可以将吸收的光能转换为声能并以超声波的形式发射出去。相比于传统压电型超声换能器，光声换能器具有灵敏度高、带宽大、制作工艺简单等优点，在工业无损检测和医学成像领域具有巨大的应用潜力。本文就近年光声换能器的材料组成、制作方法和应用进展进行了综述。

关键词

光声换能器，复合薄膜，光声效应，医学成像，无损检测

Material Composition and Application Progress of Photoacoustic Transducer

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Abstract

Photoacoustic transducer is a kind of new device developing rapidly in recent years. It can convert absorbed light energy into sound energy and emit it in the form of ultrasonic wave. Compared with the traditional piezoelectric ultrasonic transducer, the photoacoustic transducer has the advantages of high sensitivity, large bandwidth, simple fabrication process and so on, thus leading to the great application potential in industrial non-destructive testing and medical imaging. In this pa-

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per, the material composition, fabrication methods and application progress of photoacoustic transducers in recent years are reviewed.

Keywords

Photoacoustic Transducer, Composite Film, Photoacoustic Effect, Medical Imaging, Non-Destructive Testing

1. 引言

随着时代发展和科技进步，超声波的应用已经渗透到社会各个领域。传统压电型超声换能器具有带宽窄、尺寸大、易受电磁干扰等缺点，应用场景受到相对限制[1]，不足以满足人们的日常需求。高灵敏度、抗电磁干扰的光声换能器的发展具备突破以上限制的可能。光声换能器是一种能够将光信号转换为超声信号的换能器件。相比于传统压电型超声换能器，光声换能器具有尺寸小、灵敏度高、带宽大、制作工艺简单等优点，已初步应用于工业无损检测及医学光声/超声成像领域。

为了使相关领域的科学研究人员详细了解这一快速发展的技术，本文综述了光声换能器的发展现状及应用进展。首先阐述了光声换能器的工作原理；然后对光声换能器的材料组成及制作方法进行介绍；最后介绍光声换能器在工业无损检测、医学成像等领域中的应用。

2. 光声换能器的工作原理

光声换能器将光信号转换为超声信号的工作原理是基于光声效应[2] [3]，如图1所示。光声效应是无机材料被激光照射时因吸收光能而局部温度瞬态增加，产生的高温传导至有机材料导致体积膨胀进而产生超声波的现象[4] [5]。

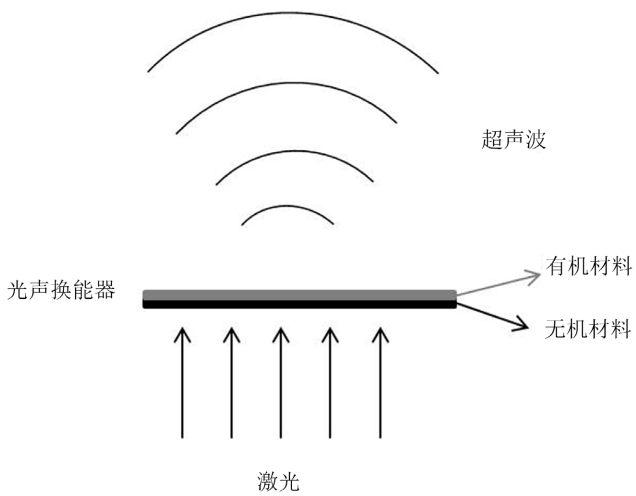

Figure 1. Schematic diagram of ultrasonic wave generated by the photoacoustic transducer
图 1. 光声换能器产生超声波原理示意图

常用的测试光声换能器复合薄膜产生超声波性能的实验装置如图 2 所示。激光脉冲穿过水箱壁照射在复合薄膜表面，使用针式水听器检测复合薄膜产生的超声信号，随后使用数字示波器对超声波信号进行记录并分析。

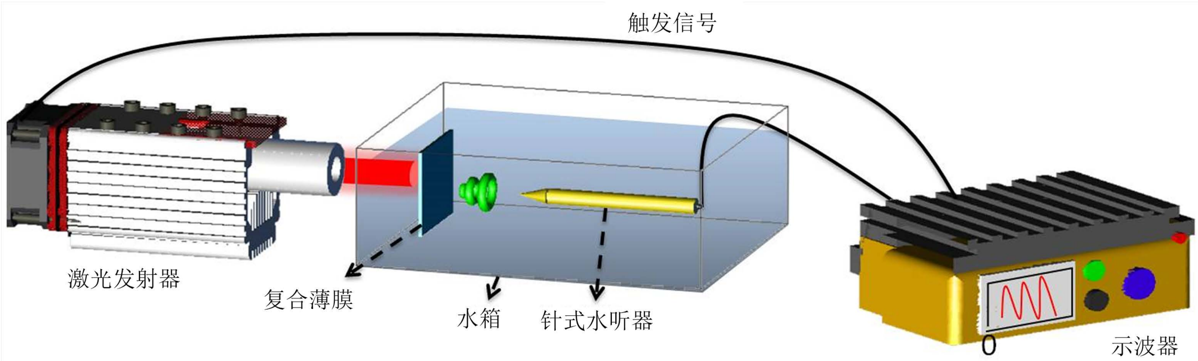

Figure 2. Schematic diagram of the experimental setup for testing the ultrasonic wave generation performance of the photoacoustic transducer composite film
图 2. 测试光声换能器复合薄膜产生超声波性能实验装置示意图

评价光声换能器工作性能的主要参数是光声能量转换率，影响光声能量转换率的因素有很多，例如照射光声换能器的激光脉冲能量及频率、组成光声换能器复合薄膜的材料、复合薄膜材料的厚度[6]以及形状[7]等，计算光声能量转换率的公式为：

$$\eta = \frac{E_a}{E_{optical}} \tag{1}$$

$E_{optical}$ 为无机材料吸收的激光能量，E_a 为输出的超声波能量。E_a 满足以下方程：

$$E_a = \frac{1}{\rho c} A \int_0^{\infty} p^2(t)\,dt \tag{2}$$

其中，ρ 为水密度；c 为水中超声波传播速率(1500 m/s)；p 为针式水听器检测到的声压；A 为声孔径面积，可近似认为是近场激光束面积。

现阶段针对不同复合薄膜材料组成的光声换能器，研究人员在特定参数下能够获得的最大超声波声压强度及能量转换效率如表 1 所示。

Table 1. Common composite film materials for photoacoustic transducers and their photoacoustic conversion
表 1. 组成光声换能器的常见复合薄膜材料及其光声转换情况

材料	峰值压力 (MPa)	激光能量 (mJ)	能量密度 (mJ/cm^2)	光声转换率 ($Pa/(W/m^2)$)	厚度 (μm)	基底
PDMS [8]	—	3×10^{-5}	—	2×10^{-4}	25	玻璃
CNFs-PDMS [1]	12.15	4.2	3.71	1.56×10^{-2}	57.9	玻璃
CNT-PDMS [9]	4.5	1.1×10^{-2}	36.3	—	<20	105 μm 芯光纤
CSNPs-PDMS [10]	4.8	2.8	3.57	4.41×10^{-3}	57.8	玻璃
Au [11]	2.7×10^{-3}	—	—	—	6×10^{-2}	62.5 μm 芯光纤
rGO [12]	7.5×10^{-5}	25	43.28	—	0.1	玻璃

3. 光声换能器复合薄膜的材料组成及制作方法

光声换能器复合薄膜的光吸收层使用的无机材料大致可分为金属复合材料[13]和碳纳米复合材料[14] [15]。聚二甲基硅氧烷(PDMS)具有较高的热膨胀系数 $\alpha = 9 \times 10^{-3}\ K^{-1}$，是当前最理想的复合薄膜热膨胀层材料。下面总结几种组成光声换能器的常用复合薄膜材料及其制备方法。

3.1. 碳纳米纤维–聚二甲基硅氧烷(CNFs-PDMS)复合薄膜

为了产生声压强度大于 10 MPa 的超声波，需要能够将光能高效率转化为声能的光声换能器复合材料[3]。Bao-Yu Hsieh 等人[1]制作了厚度为 57.9 ± 2.80 μm 的 CNFs-PDMS 复合薄膜，其中 CNFs 层的厚度仅为 132.7 ± 11.2 nm。该复合薄膜可以产生声压强度为 12.15 MPa 的超声波，光声能量的转换效率达到 15.6 $\times 10^{-3}$ Pa/(W/m^2)。因此，由 CNFs-PDMS 复合薄膜制作的光声换能器可用于产生高强度聚焦超声，应用于生物医学治疗。CNFs-PDMS 复合薄膜在激光脉冲照射下产生超声波的过程如图 3 所示，其中 CNFs 是光吸收层，PDMS 是热膨胀层。

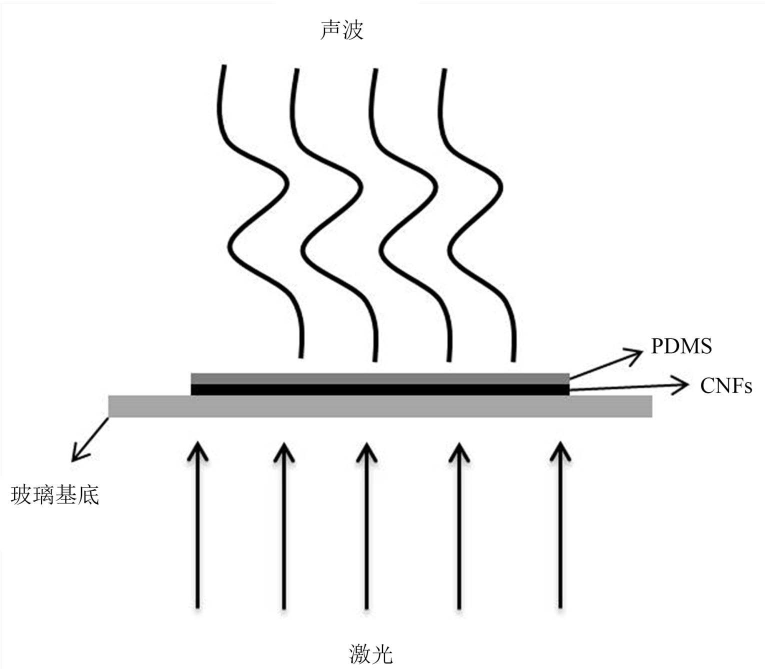

Figure 3. Internal structure diagram of the CNFs-PDMS composite film [1]
图 3. CNFs-PDMS 复合薄膜内部结构图[1]

CNF-PDMS 薄膜内部独特的结构成功实现了将光能转换为声能，并表现出高成像分辨率和高强度声压的性能使其在超声成像和聚焦超声治疗应用方面具有非常大的潜力。

3.2. 碳纳米管–聚二甲基硅氧烷(CNT-PDMS)复合薄膜

CNT-PDMS 复合薄膜具有非凡的热传递特性和光学特性[16] [17]，其中 CNT 具备高效吸收激光能量[18] [19]和热转换的能力[20]，并且能够快速将产生的热量传输到周围介质中。Richard J. Colchester 等人[9]采用浸沾法在直径分别为 105 μm 和 200 μm 的光纤末端端面上形成了 CNT-PDMS 复合薄膜层，超声激发效率分别为 0.1 MPa·mJ^{-1}·cm^2 和 0.13 MPa·mJ^{-1}·cm^2，−6 dB 带宽分别为 12 MHz 和 15 MHz。图 4 是使用扫描电镜(SEM)观察到的形成 CNT-PDMS 复合薄膜后的图像。

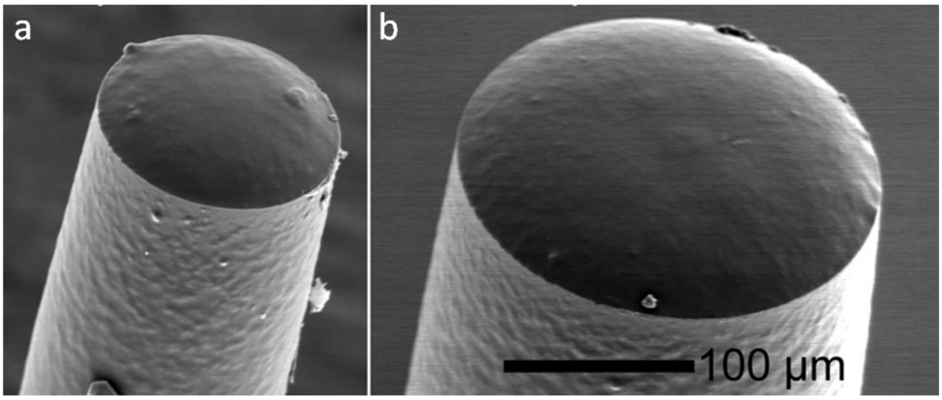

Figure 4. The CNT-PDMS composite film diagram. (a) 105 μm fiber core; (b) 200 μm fiber core [9]
图 4. CNT-PDMS 复合薄膜图。(a) 105 μm 光纤芯；(b) 200 μm 光纤芯[9]

CNT-PDMS 复合薄膜产生的聚焦超声具有高声压强度和大带宽的特点，利用此特点可以将 CNT-PDMS 复合薄膜制作为光声透镜，该透镜产生的超声波带宽高于 15 MHz，可以应用于靶向治疗[21]。并且使用连续多层 CNT 纱线将金纳米颗粒与弹性聚合物结合在一起可以制成一款新型独立式光声换能器，该换能器无需聚焦即可产生高强度声压(约为 33.6 MPa) [22]。此外，CNT-PDMS 复合薄膜产生超声波的输出声压强度与入射激光强度、复合薄膜材料的厚度以及衰减系数有关[23]。CNT 的比热容和热扩散率与直径成反比，与长度成正比。因此，当前制作 CNT-PDMS 复合薄膜选择 CNT 的最佳长度和直径分别为 10~30 μm 和 8 nm [7]。

3.3. 蜡烛烟尘纳米颗粒–聚二甲基硅氧烷(CSNPs-PDMS)复合薄膜

蜡烛烟尘纳米颗粒具有较高的光吸收系数和热转换性能，适合用于制作光声换能器复合薄膜的光吸收层。在 CSNPs-PDMS 复合薄膜中，蜡烛烟尘纳米颗粒的直径在 30~45 nm 之间[24]。当照射激光波长为 532 nm 时，蜡烛烟尘纳米颗粒涂层的光吸收率达到了 96.24%，能量转换效率为 4.41×10^{-3}，−6 dB 带宽为 21 MHz [10]。

CSNPs-PDMS 复合薄膜的光学吸收、体积分数和厚度是影响光声传导效率的主要因素。当激光能量处于 0~1.1 mJ 时，CSNPs-PDMS 复合薄膜输出超声波信号的正峰值压力与输入激光能量呈正相关关系，输出超声波信号的负峰值压力与输入激光能量呈负相关关系。并且 CSNPs-PDMS 复合薄膜的最佳厚度为 2.15 μm，当厚度超过 2.15 μm 时，光声转换效率将会呈现指数衰减的趋势[25]。

3.4. 金纳米孔薄膜

金在等离子体共振频率下具有很高的光学吸收性能[26]，在光声换能器中也发挥着非常重要的作用。由金属夹层制作而成的复合薄膜可以实现高效的光声转换[27]。金纳米孔薄膜是指利用聚焦离子束对金薄膜进行打孔形成间距 200 nm、直径 80 nm 的金纳米孔，然后将激光脉冲经光纤照射在金纳米孔上。由金纳米孔薄膜组成的光声换能器产生的超声波 3 dB 带宽为 7 MHz，声压强度为 2.73 kPa [11]。图 5 为涂覆有金纳米孔薄膜层的光纤端面产生超声波的示意图。

3.5. 复合薄膜的制备方法

根据材料的不同，光声换能器复合薄膜的制作方法主要有浸沾法[9] [28]、旋涂法[1] [29]、化学气相沉积法[16] [30] [31]、金属蒸镀法[22] [32]、蚀刻法[33] [34] [35]。

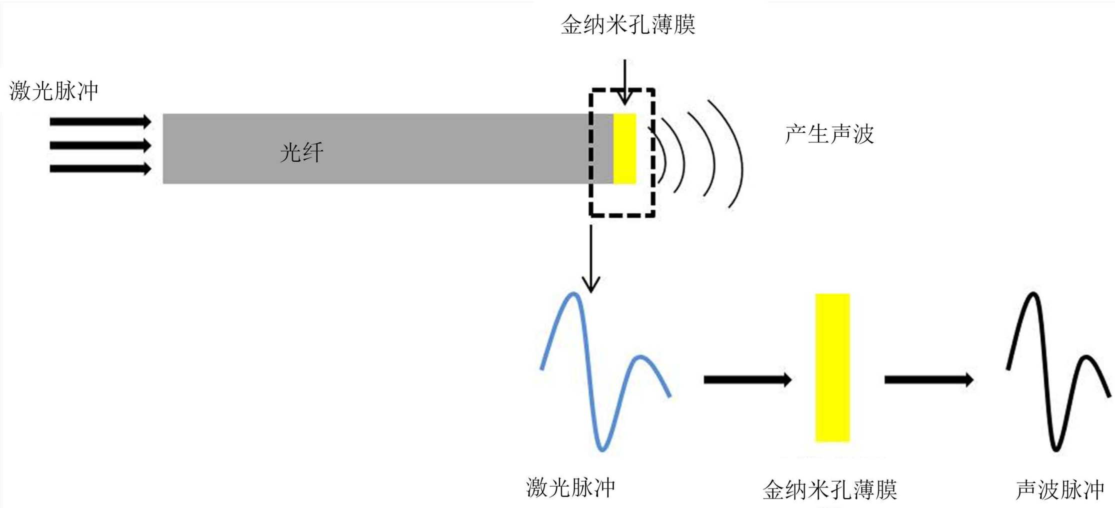

Figure 5. Schematic diagram of the gold nanopore film photoacoustic principle [11]
图 5. 金纳米孔薄膜光声原理示意图[11]

浸沾法是指将光纤末端插入含有碳纳米复合材料的溶液中并缓慢取出，碳纳米复合材料固化后形成复合薄膜；旋涂法是指在玻璃基底上依次涂覆、旋涂光吸收材料和热膨胀材料，制备出复合薄膜；化学气相沉积法首先将多壁碳纳米管利用化学气相沉积在熔融石英衬底上面，再将金和 PDMS 分别旋涂在多壁碳纳米管上面形成复合薄膜；金属蒸镀法是在真空室中，利用喷镀系统将金属镀在碳纳米薄膜上形成复合薄膜；蚀刻法是利用化学反应原理将 PDMS 与固化剂按照一定比例掺杂进金盐中，经过一系列处理形成金纳米复合薄膜。

4. 光声换能器的应用

光声换能器主要应用于医疗领域和工业领域，在医疗领域的应用主要包括超声成像[36]与超声治疗[37]。在工业领域的应用主要包括无损检测，利用光声换能器产生的超声波检测设备内部是否有缺陷，从而避免事故的发生[38]。

4.1. 在医疗领域的应用

光声换能器产生的高强度聚焦超声可以将药物精确地传送到靶向细胞内[39] [40]，从而对肿瘤进行无创治疗[41]。并且由 CNT-PDMS 复合薄膜制作而成的光声透镜可以实现将靶细胞从周围细胞中去除的单细胞手术[30]。

光声换能器可以利用光声成像研究哺乳动物深层组织中细胞遗传过程[42]。这使得利用光声换能器研究细胞遗传机制成为可能，但是该研究系统目前处于初级阶段，还存在成像分辨率低和成像范围具有局限性等不足，需要进一步改进。另外，光声换能器还可以用于检测人体皮肤肿瘤[43]、进行超声溶栓[44] [45]、利用空化效应切割细胞团[46] [47]、调控神经系统[48] [49] [50] [51]等方面。这些都表明光声换能器对医学领域的发展具有重要作用。

4.2. 在工业领域的应用

传统的压电换能器具有电磁干扰等问题，在工业检测中会对结果产生影响。光声换能器从根本上解决了这个问题，在工业检测领域主要用于无损检测，其原理是根据待测物内部缺陷处与边缘处的超声回波信号计算出缺陷位置和尺寸。

光声换能器产生的超声波强度能够满足无损检测的要求。利用光声换能器对铝板进行无损检测时，可以通过调节入射激光能量改变产生超声波强度的方法检测缺陷位置[52] [53]，利用超声波非线性参数随着裂纹长度变化而变化的特点可以探测出裂纹的长度[54]。光声换能器还可以探测铜–铝不同金属连接面处的分层缺陷[55] [56] [57]，甚至能够针对宽度较小的裂缝进行修复，对于航空航天领域机器零部件的安全检测具有重要意义。

5. 讨论与展望

光声换能器具有光声转换效率高、灵敏度高、品质因数高等优点，产生的超声波声衰减系数随着复合薄膜厚度的降低而减少。研究结果表明，在产生的超声波声压强度大小方面，碳纳米结构类的复合薄膜远大于金属薄膜和还原氧化石墨烯类的薄膜。但是，碳纳米结构类的复合薄膜却比其它复合薄膜厚，这在一定程度上限制了碳纳米结构类复合薄膜的使用范围。因此，光声换能器的复合薄膜制作技术还有待进一步优化，在不影响产生的超声波声压强度大小的前提下，应使其厚度尽可能小；在薄膜的制作工艺、材料选择等方面，光声换能器还有很大的优化空间，使其更加微型化、轻型化和集成化。

光声换能器与传统换能器相比虽然具有很多优势，但是对于光声换能器来说还有许多技术瓶颈需要亟待解决。在激光诱导复合薄膜产生超声波的过程中，如果激光能量过高，复合薄膜容易灼伤损坏。因此，需要研究出耐高温的复合物薄膜材料，进而提高光声换能器的性能。目前光声换能器薄膜的形状较为单一，一定程度上限制了其应用领域以及应用场景。因此，需要研究人员开发出多元化形状的光声换能器薄膜。

虽然光声换能器在医疗领域及工业领域中有了一定的应用，但是目前仍处于初级阶段。在成像分辨率、产生的超声波声压强度等方面，光声换能器的性能有待进一步提高。

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