

# 激光与光电子学进展

## 光纤荧光温度传感探针的研究进展

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**摘要** 温度是一种常见的物理量,对农业生产、工业制造、科学研究和人类生活能够产生巨大影响,因此温度检测具有重大意义。传统的电类温度传感器发展已较为成熟,但容易受到环境等因素的影响,尤其在高压和强电场磁场的恶劣条件下会产生温度检测精度降低及误差偏高等问题。光纤传感技术能够在恶劣环境下进行温度传感,可以弥补传统电类温度传感器易受环境影响的不足。而光纤荧光温度传感技术将光纤技术与荧光传感技术相结合,利用光纤进行传光并利用荧光物质对温度敏感的特性,进而实现在多种场合甚至恶劣环境下的温度检测,具有抗干扰性强、能实现远端探测和实时监测等优点。总结了掺杂法、化学修饰及物理沉积法、封装法、特种光纤填充法等主要的光纤荧光温度探针制备方法和荧光强度法、荧光强度比法、荧光寿命法、荧光发射峰位移法等常见的荧光测温信号处理方法,陈述分析了相关文献及现有成果,并对未来研究进行展望。

**关键词** 光纤; 荧光; 温度传感; 探针制备; 信号处理

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### Review of Research on Optical Fiber Fluorescence Temperature Probes

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**Abstract** Temperature is a common physical quantity that significantly affects agricultural production, industrial manufacturing, scientific research, and human life. Therefore, accurate temperature detection is crucial. Conventional temperature sensors are widely used; however, they are easily affected by environmental factors, particularly conditions of high voltage and strong electric and magnetic fields, which can cause problems such as reduced accuracy and high error. By contrast, optical fiber sensing technology enables sensing in harsh environments and can address the limitations of conventional temperature sensors. Optical fiber fluorescence temperature sensing technology combines optical fiber and fluorescent sensing technologies. It uses optical fibers for light transmission and the temperature-sensitive characteristics of fluorescent material to achieve temperature sensing capability. Moreover, it enables temperature detection in various conditions, including harsh environments, and offers advantages such as strong anti-interference, rapid response, good repeatability, and high sensitivity. This paper reviews optical-fiber probe preparation methods such as doping, coating and deposition, encapsulation, and special optical-fiber splicing methods. In addition, temperature-measurement signal processing methods such as fluorescence intensity, fluorescence intensity ratio, fluorescence lifetime, and fluorescence emission peak wavelength shift methods are discussed. Finally, we list and analyze the advancements in optical fiber temperature probes and present an outlook for future development.

**Key words** optical fiber; fluorescence; temperature sensing; fiber probe preparation; signal processing

## 1 引言

温度是一种表示物体冷热程度的物理量,对人类的生产活动具有重要意义。在工业制造过程中需要控制温度才能保证最终成品的质量;在农业生产过程中

需要对温度进行监测确保农作物能够适应环境;在生活中需要检测物品或环境的温度从而推测是否适合人类生存;这些方面均体现了温度检测的重要性和必要性。

传统的温度传感器主要有热电温度传感器和半导

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体温度传感器,如:基于热膨胀测温的温度传感器<sup>[1]</sup>;基于热电偶和热电阻的热电温度传感器<sup>[2-3]</sup>;基于半导体结的半导体温度传感器<sup>[4]</sup>;基于电容测温的温度传感器<sup>[5]</sup>;基于热噪声测温的温度传感器<sup>[6]</sup>;基于频率变化的温度传感器<sup>[7]</sup>;基于磁共振的温度传感器<sup>[8]</sup>等。这些方法虽然技术成熟,但容易受到环境因素的影响,尤其是在高压和强电场磁场的恶劣条件下会产生温度检测精度降低及误差偏高等问题。光纤温度传感器由于光纤具有抗电磁干扰和抗腐蚀的优点<sup>[9-13]</sup>,非常适合弥补传统的电类温度传感器在恶劣环境下传感精度降低的不足,因此光纤温度传感器的发展至关重要。

光纤荧光温度传感技术是将荧光物质与光纤结合构成光纤探针,利用探针中荧光物质对温度敏感的特性实现温度检测。已报道的光纤荧光温度传感探针主要有4种制备方法:掺杂法、化学修饰及物理沉积法、封装法和特种光纤填充法。此外,测温方法对荧光温度传感技术的性能有着很大影响,目前荧光测温的主要方法包括荧光强度法<sup>[14]</sup>、荧光强度比法<sup>[15]</sup>、荧光寿命法<sup>[16]</sup>和荧光发射峰位移法<sup>[17]</sup>等。本文从探针的制备方法和测温方法的角度出发,简要总结了近年来光纤荧光温度传感探针的研究成果,分析了未来的发展前景和趋势,为光纤荧光温度传感技术的发展提供参考和借鉴。

## 2 光纤荧光温度传感方法

荧光强度法是出现最早、最简单快速的检测方法,通过检测荧光发射峰的强度可以直观反映出温度的高低,信号响应如图1(a)所示<sup>[18]</sup>,能够细分为直接计算荧光强度的绝对强度值法和对强度进行归一化计算的强度归一化法;强度法虽然具有简单、快速、高效等优点,但容易受到环境和荧光材料的影响出现波动,最终

导致传感器的稳定性和准确性下降。荧光强度比法是在荧光强度法的基础上改良的测温方法,主要是利用2个不同波长荧光强度的比值测量温度,信号响应如图1(b)、图1(c)所示<sup>[19-20]</sup>;强度比法能够大大消减环境和荧光材料自身的影响,具有良好的抗干扰能力,但也存在部分荧光材料发射峰波长随温度变化产生偏移导致准确性和灵敏度下降的情况。荧光寿命法也是发展较为成熟的方法,通过检测荧光物质发射峰强度衰减至一定值所用时间实现温度的传感,信号响应如图1(d)所示<sup>[21]</sup>,这种方法具有影响因素少和抗干扰性强的优势,但需要特定设备才能实现检测。荧光发射峰位移法是通过检测荧光物质的发射峰在温度影响下波长的位移量实现温度检测的方法,信号响应如图1(e)所示<sup>[22]</sup>,此方法具有较好的稳定性,但也存在部分荧光物质的波长偏移量较少导致灵敏度较低的情况。除了主要的测温方法,也涌现出一些新颖的方法,荧光信噪比法是通过检测荧光信号与噪声的比例实现温度测量的方法,信号响应如图1(f)所示<sup>[23]</sup>,与传统方法相比,其考虑了噪声的影响,能够更准确地分析传感器的性能并提高传感探针的灵敏度,但这类方法在噪声很强的场合下灵敏度和稳定性就会出现显著下降,从而导致探针的性能降低。效率信号转换法是一种将激发光与荧光的转换效率作为参数进行测温的方法,信号响应如图1(g)所示<sup>[24]</sup>,这类方法能够结合结构的影响分析并提升探针的温度传感性能,如锥形、楔形光纤等,但这种方法多用于具有特殊结构的探针,普适性较差。自参考相位偏移法通过检测光的相位变化实现对温度的检测,信号响应如图1(h)所示<sup>[25]</sup>,抗干扰能力强,但一般只适用于能产生相位差的荧光探针。上述方法的对比如表1所示。

表1 荧光测温方法的比较

Table 1 Comparison of fluorescence temperature measurement methods

Method	Sensitivity	Stability	Accuracy	Anti-interference	Signal processing	Detection difficulty
Fluorescence intensity method	high	low	low	low	simple	low
Fluorescence intensity ratio method	high	high	normal	high	normal	low
Fluorescence lifetime method	low	high	normal	high	simple	high
Fluorescence emission peak wavelength shift method	low	high	low	high	normal	normal
Fluorescence signal-noise ration method	normal	high	normal	normal	complicated	low
Efficiency signal conversion method	high	normal	normal	normal	complicated	low
Self-referenced phase shift method	low	normal	normal	high	normal	normal

## 3 掺杂法制备传感探针

将掺杂荧光材料的光纤用于温度传感是出现最早且运用最多的方法,从1990年开始就有研究人员采用掺杂法制备传感探针并用于温度传感,最常见的掺杂物质是 $\text{Er}^{3+}$ 、 $\text{Yb}^{3+}$ 、 $\text{Nd}^{3+}$ 、 $\text{Tm}^{3+}$ 及 $\text{Pr}^{3+}$ 等拥有温敏特性的稀土离子,主要制备方法有熔接法、化学气相沉积法

(CVD)、溶液掺杂法、激光加热基座法(LHPG)、溶胶凝胶法、共沉积法、电纺丝法、湿纺丝法、熔淬法、挤压法。熔接法<sup>[26]</sup>是通过将已经制备好的掺杂光纤与传光光纤利用光纤熔接机熔接制备传感探针的方法。化学气相沉积法是利用加热、等离子体激励或光辐射的方法,将含有薄膜元素的一种或几种气相化合物或单质在衬底表面上进行化学反应生成薄膜和晶体的方法,

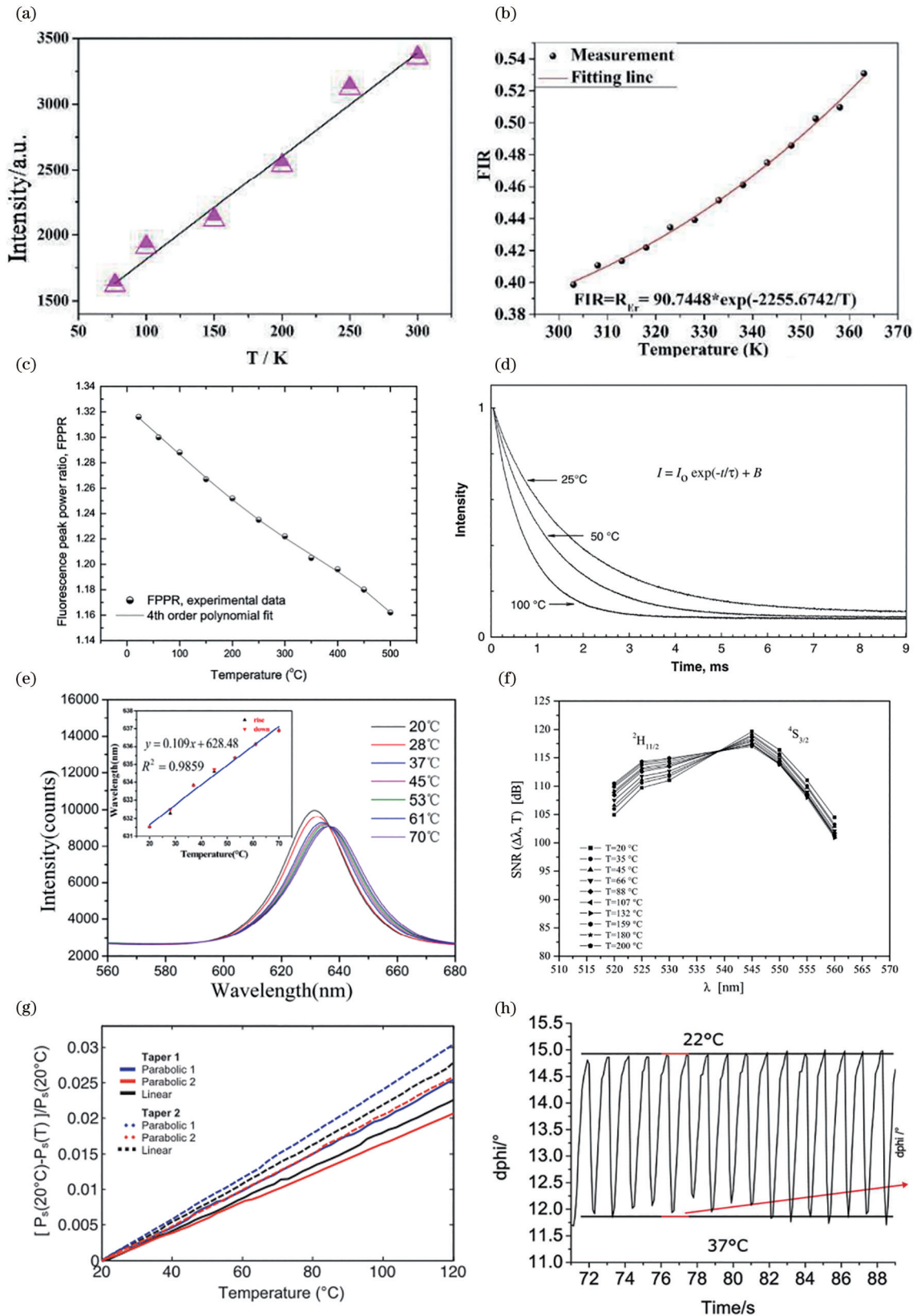


图 1 荧光信号处理方法。(a) 荧光强度法<sup>[18]</sup>；(b) 荧光强度比法<sup>[19]</sup>；(c) 荧光功率比法<sup>[20]</sup>；(d) 荧光寿命法<sup>[21]</sup>；(e) 荧光发射峰位移法<sup>[22]</sup>；(f) 荧光信噪比法<sup>[23]</sup>；(g) 效率信号转换法<sup>[24]</sup>；(h) 自参考相位偏移法<sup>[25]</sup>

Fig. 1 Fluorescence signal processing methods. (a) Fluorescence intensity method<sup>[18]</sup>；(b) fluorescence intensity ratio method<sup>[19]</sup>；(c) fluorescence power ratio method<sup>[20]</sup>；(d) fluorescence lifetime method<sup>[21]</sup>；(e) fluorescence emission peak wavelength shift method<sup>[22]</sup>；(f) fluorescence signal-to-noise ratio method<sup>[23]</sup>；(g) efficiency signal conversion method<sup>[24]</sup>；(h) self-referenced phase shift method<sup>[25]</sup>



广泛用于提纯物质,研制新品、淀积各种单晶、多晶或玻璃态无机薄膜材料。溶液掺杂法<sup>[27]</sup>是将温敏材料与可固化材料混合后固化制备光纤传感探针的方法。激光加热基座法<sup>[28]</sup>将荧光粉压制成药棒后采用激光加热源棒顶端使其融化形成熔区,用光纤作为籽晶插入熔区,不断插入和上提从而生长晶体纤维。溶胶凝胶法采用含有高化学活性组分的化合物作为前驱体,在液相下将发光原料均匀混合、水解、缩合后形成透明的溶胶体系,经过聚合形成三维网格结构的凝胶,可通过干燥、烧结固化制备出不同结构的晶体光纤。共沉淀法<sup>[29]</sup>在含有多种离子的溶液中加入沉淀剂,再将沉淀

形成的复合掺杂材料拉制成晶体光纤。电纺丝法<sup>[30]</sup>是利用高压静电场对溶液中的分子产生击穿作用,纺丝液在电场中被拉伸形成纳米纤维的方法。湿纺丝法<sup>[31]</sup>将荧光物质溶解在成纤高聚物的溶液中形成纺丝原液,通过喷丝孔将原液压成细流状,凝固形成光学纤维。熔淬法<sup>[32]</sup>采用激光或电子束将材料加热至熔融状态后冷凝硬化制成晶体光纤。挤压法<sup>[33]</sup>利用微挤压机对掺杂有荧光粉末的聚合物纤维挤压产生拥有轴向浓度梯度的光学纤维。部分方法的制备过程和制备结果如图 2 所示。

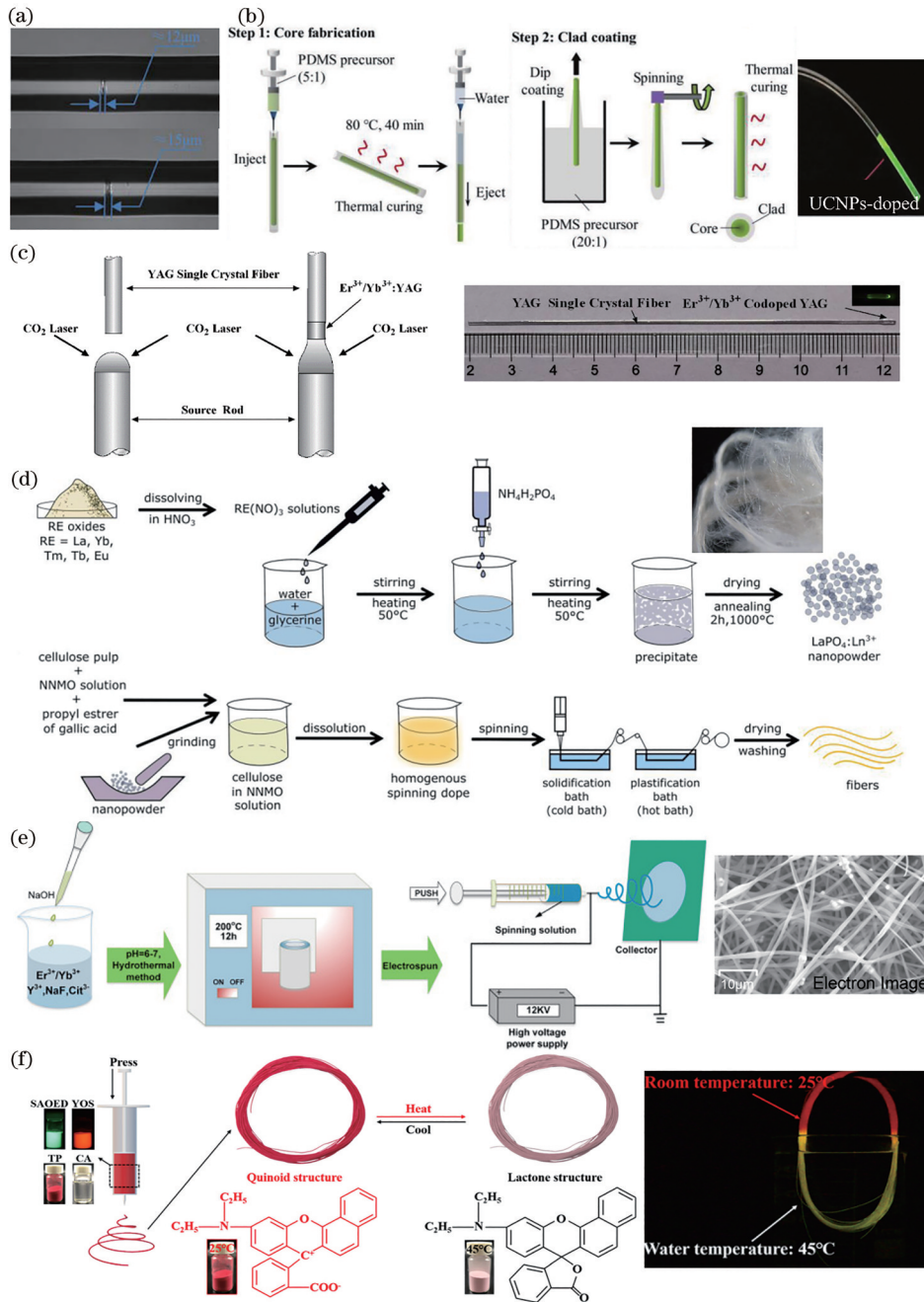


图 2 掺杂法制备的传感探针。(a)熔接法<sup>[26]</sup>; (b)溶液掺杂法<sup>[27]</sup>; (c)激光加热基座法<sup>[28]</sup>; (d)共沉淀法<sup>[29]</sup>; (e)电纺丝法<sup>[30]</sup>; (f)湿纺丝法<sup>[31]</sup>  
 Fig. 2 Sensing probes prepared by doping methods. (a) Welding method<sup>[26]</sup>; (b) solution doping method<sup>[27]</sup>; (c) laser heating pedestal method<sup>[28]</sup>; (d) codeposition method<sup>[29]</sup>; (e) electrospinning method<sup>[30]</sup>; (f) wet spinning method<sup>[31]</sup>

### 3.1 基于荧光强度法测温的掺杂型探针

掺杂法制备的探针最早采用荧光强度法进行温度检测,即通过直接检测荧光物质受激发射荧光峰的强度值变化检测温度变化,该方法是最便捷、高效的。Seat 等<sup>[34]</sup>采用激光加热基座生长结晶的方法制备了掺杂 Er<sup>3+</sup>和 Yb<sup>3+</sup>的蓝宝石光纤温度传感探针,分别实现了从常温至 1323 K 和 1423 K 的测温,灵敏度约为 0.0075 °C<sup>-1</sup>和 0.0045 °C<sup>-1</sup>。Guo 等<sup>[35]</sup>利用溶胶-凝胶工艺制备了掺杂 Eu<sup>3+</sup>的光纤温度传感探针,实现了 80~500 °C 的温度测量。

### 3.2 基于荧光强度比法测温的掺杂型探针

稀土材料是温度传感中常用的荧光材料,其通常

具有多个发射峰,同时掺杂 2 种及以上的稀土元素也能形成多个发射峰,因此,利用荧光强度比法进行温度传感成为掺杂稀土离子的光纤温度传感探针的主要数据处理方法,其最大优势是可以消减环境因素对测量结果的影响。制备这类传感探针的方法多为熔接法、化学气相沉积法、溶液掺杂法和激光加热基座法。此外,也可采用共沉积法、湿纺丝法、熔淬法、挤压法和电纺丝法制备这类传感探针,其性能对比如表 2 所示,测温范围和探针性能主要取决于材料本身和选择比值的波段,单一物质掺杂的探针测温范围普遍高于多物质掺杂的探针,而传感性能与制备方法之间没有明显的相关性。

表 2 掺杂法制备的荧光强度比光纤温度传感探针

Table 2 Optical fiber temperature sensing probes based on fluorescence intensity ratio prepared by doping methods

Method	Mixed element	Range / °C	Wavelength /nm	Occasion	Sensitivity	Accuracy	Deviation	Resolution	Ref.
Welding	Er <sup>3+</sup>	26-60	545/532	thermocouple	0.01 °C <sup>-1</sup>	—	—	0.06 °C	[36]
	Er <sup>3+</sup>	30-100	1530/1565	heating platform	0.00056 °C <sup>-1</sup>	—	—	—	[37]
	Er <sup>3+</sup>	30-110	980/1540	lab	—	1.2 °C	—	—	[38]
	Er <sup>3+</sup>	18-150	515-533/ 543-561	oven	—	—	2.2 °C	0.3 °C	[39]
	Er <sup>3+</sup>	22-500	1535/1552	thermal chamber	0.000335 °C <sup>-1</sup>	—	6 °C	—	[20]
	Er <sup>3+</sup>	20-540	515-525/ 555-565	thermocouple	0.025 K <sup>-1</sup>	—	—	0.1 K	[40]
	Er <sup>3+</sup>	25-600	1133/1237	oven	0.008 °C <sup>-1</sup>	—	—	—	[41]
	Yb <sup>3+</sup>	22-160	905/1064	heating platform	—	1 °C	1.5 °C	—	[42]
	Yb <sup>3+</sup>	25-600	976/1030	oven	0.0095 °C <sup>-1</sup>	1 °C	0.6 °C	—	[43]
	Nd <sup>3+</sup>	25-900	820-840/ 880-930	oven	—	1.5 °C	—	—	[44]
	Nd <sup>3+</sup>	250-1500	820-840/ 895-915	oven	0.0102 °C <sup>-1</sup>	—	2.5 °C	—	[45]
	Er <sup>3+</sup> , Yb <sup>3+</sup>	30-150	520/550	lab	—	—	—	—	[46]
	NaYF <sub>4</sub> :Er <sup>3+</sup> , Yb <sup>3+</sup>	40-100	525/545	oven	0.0087- 0.0144 K <sup>-1</sup>	—	—	—	[26]
Chemical vapor deposition and solution doping	Pr <sup>3+</sup> , Nd <sup>3+</sup> , Yb <sup>3+</sup>	200-600	810-830/ 866-894 900-910/ 1051.5- 1076.5	oven	0.017 °C <sup>-1</sup>	—	—	1 °C	[47]
	Bi	25-500	950-1200/ 1200-1500	oven	0.0091- 0.0097 K <sup>-1</sup>	—	—	—	[48]
	Nd <sup>3+</sup> , Yb <sup>3+</sup>	10-140	920-930/ 1020-1030 820-840/ 880-930	heating platform	0.0156 °C <sup>-1</sup> 0.0112 °C <sup>-1</sup>	2 °C	—	—	[49]
Er <sup>3+</sup> /Yb <sup>3+</sup>	20-150	1040-1070/ 880-970	oven	—	0.3 °C	—	—	[50]	

表2 (续)

Method	Mixed element	Range / °C	Wavelength /nm	Occasion	Sensitivity	Accuracy	Deviation	Resolution	Ref.
	Er <sup>3+</sup> , Yb <sup>3+</sup>	25-300	1012.5/ 1537.5	oven	—	—	—	1 °C 10 °C	[51]
	Er <sup>3+</sup> , Yb <sup>3+</sup>	25-600	530/555	oven	0.016 dB·°C <sup>-1</sup>	—	1.1 °C	—	[52]
	Sb <sup>3+</sup> , Er <sup>3+</sup> , Ge <sup>3+</sup>	20-600	1535/1552	oven	0.000695 °C <sup>-1</sup>	2.8 °C	—	—	[53]
	Eu <sup>3+</sup>	25-100	615/450	thermocouple	—	—	—	—	[54]
	Er <sup>3+</sup> , Yb <sup>3+</sup>	22-51	—	organism	0.00526 K <sup>-1</sup>	0.1- 0.3 °C	—	—	[55]
	NaYF <sub>4</sub> :Yb, Er	25-70	525/545	organism	0.018 °C <sup>-1</sup>	—	—	—	[27]
Solution doping	β-NaLuF <sub>4</sub> :Yb <sup>3+</sup> / Tm <sup>3+</sup> /Er <sup>3+</sup>	30-90	521/542	lab	0.00311 K <sup>-1</sup>	—	—	—	[19]
	NaY <sub>0.77</sub> Yb <sub>0.20</sub> Er <sub>0.03</sub> F <sub>4</sub>	25-100	525/550	heating platform	0.00256 °C <sup>-1</sup>	0.3 °C	—	—	[56]
	NaYF <sub>4</sub> :(18%) Yb <sup>3+</sup> , (2%)Er <sup>3+</sup>	22-200	514-523/ 533-562	sand and air bath	0.0029 K <sup>-1</sup>	—	—	2.7 K	[57]
	Ho <sup>3+</sup> /Yb <sup>3+</sup>	25-350	549/667	oven	0.0489 K <sup>-1</sup>	—	—	—	[58]
Laser heating pedestal method	Tm <sup>3+</sup> /Yb <sup>3+</sup>	60-460	660-740/ 740-850	thermocouple	0.021 K <sup>-1</sup>	—	—	—	[59]
	Er <sup>3+</sup> , Yb <sup>3+</sup>	25-450	524/546	thermocouple	0.00486 K <sup>-1</sup>	—	—	—	[28]
	Er <sup>3+</sup> /Yb <sup>3+</sup>	室温 -600	502-542/ 542-592	electric furnace	0.0087 K <sup>-1</sup>	—	—	—	[60]
Codeposition	Yb <sup>3+</sup> /Tm <sup>3+</sup> , Eu <sup>3+</sup> , Tb <sup>3+</sup>	20-406	700/800	furnace	0.024 K <sup>-1</sup> 0.022 K <sup>-1</sup>	—	—	—	[29]
Melt quenching	Er <sup>3+</sup> /Yb <sup>3+</sup>	30-287	545/523	oven	0.012 K <sup>-1</sup>	1 K	0.2%	—	[32]
Wet spinning	SrAl <sub>2</sub> O <sub>4</sub> :Er <sup>3+</sup> , Dy <sup>3+</sup> , Y <sub>2</sub> O <sub>2</sub> S:Eu <sup>3+</sup> , Mg <sup>2+</sup> , Ti <sup>4+</sup>	25-45	512-596/ 616-626	thermal gravimetric analyzer	—	—	—	—	[31]
Electrospinning	Na (Y <sub>1-x-y</sub> Er <sub>x</sub> Yb <sub>y</sub> )F <sub>4</sub> / PAN(NYF-EY/ PAN)	30-150	523/542	lab	0.0148 K <sup>-1</sup>	—	—	—	[30]
Extrusion	Eu <sup>3+</sup>	20-95	623/585	gas flow cell	—	—	1%	—	[33]

### 3.3 基于荧光寿命法测温的掺杂型探针

荧光寿命法也是掺杂法制备的光纤温度传感探针常用的一种信号处理方法,主要制备方法包括熔接法、化学气相沉积法、溶液掺杂法和激光加热基座法,探针性能的比较如表3所示,探针的测温范围和传感性能主要取决于荧光材料,这类探针大多采用单一物质掺杂即可实现温度的检测,且与具体的制备方法没有特别明显的相关性。

### 3.4 基于其他方法测温的掺杂型探针

部分荧光物质的发射峰波长会随着温度的变化产生偏移,因此出现了荧光发射峰位移法。Shen等<sup>[85]</sup>采用熔接法分别将掺杂Er<sup>3+</sup>、Ge<sup>3+</sup>/Er<sup>3+</sup>、Sn<sup>3+</sup>/Ge<sup>3+</sup>/Er<sup>3+</sup>和Sb<sup>3+</sup>/Ge<sup>3+</sup>/Er<sup>3+</sup>的光纤与光纤布拉格光栅(Fiber Bragg grating, FBG)结合制备成光纤温度应变传感探针,采用荧光发射峰位移法实现了室温至900 °C的温度传感,在室温和800 °C时的灵敏度分别为12 μm·°C<sup>-1</sup>

表 3 掺杂法制备的荧光寿命光纤温度传感探针

Table 3 Optical fiber temperature sensing probes based on fluorescence lifetime prepared by doping methods

Method	Mixed element	Range / °C	Occasion	Sensitivity	Accuracy	Deviation	Resolution	Ref.
Welding	Er <sup>3+</sup>	25–120	oven	—	—	1.2 °C	—	[61]
	Er <sup>3+</sup>	30–150	oven	0.07 μs·°C <sup>-1</sup>	—	0.02%	—	[62]
	Er <sup>3+</sup>	25–150	oven	0.000247 K <sup>-1</sup>	1.8 °C	—	—	[63]
	Er <sup>3+</sup>	0–600	lab	—	—	—	—	[64]
	Er <sup>3+</sup>	500–600	oven	—	—	50–100 °C	—	[65]
	Yb <sup>3+</sup>	—	lab	—	—	—	—	[66]
	Yb <sup>3+</sup>	–196–170	oven	0.00013 ms K <sup>-1</sup>	—	—	—	[67]
	Yb <sup>3+</sup>	23–977	tube furnace	—	—	—	—	[68]
	Pr <sup>3+</sup>	300–500	oven	—	—	—	—	[69]
	Nd <sup>3+</sup>	20–90	temperature control room	—	—	0.98 °C	—	[70]
	Tm <sup>3+</sup>	25–800	oven	7 μs·°C <sup>-1</sup>	—	1 °C	1 °C	[71]
	Tm <sup>3+</sup>	25–1350	oven	—	—	6 °C	—	[72]
	Er <sup>3+</sup> /Yb <sup>3+</sup>	30–150	oven	—	—	0.8 °C	—	[73]
	Er <sup>3+</sup> /Yb <sup>3+</sup>	0–850	oven	—	5 °C	—	—	[74]
	Yb <sup>3+</sup> , Tb <sup>3+</sup>	25–977	furnace	—	—	—	—	[75]
Chemical vapor deposition and solution doping	Pr <sup>3+</sup>	20–80	hot water	—	5%	—	—	[76]
	Er <sup>3+</sup> /Yb <sup>3+</sup>	25–300	oven	0.0145 ms·°C <sup>-1</sup>	—	0.35 ms	—	[77]
Solution doping	Nd <sup>3+</sup>	0–150	microwave oven	—	—	0.3 °C	—	[78]
	Cr <sup>3+</sup>	25–100	battery	10 μs·°C <sup>-1</sup>	0.3 °C	0.06 °C	—	[21]
	Cr <sup>3+</sup>	27–277	electric oven	0.625 μs·°C <sup>-1</sup>	—	—	—	[79]
Laser heating pedestal method	Er <sup>3+</sup>	25–1274	tube furnace	0.003 K <sup>-1</sup>	—	—	—	[80]
	Tm <sup>3+</sup>	25–1200	oven	3 μs·°C <sup>-1</sup>	5 °C	—	2.5 °C	[81]
	Cr <sup>3+</sup>	–20–500	copper block heating device	1–250 μs·°C <sup>-1</sup>	—	—	—	[82]
	Cr <sup>3+</sup>	0–600	electric stove	—	—	0.2 °C	—	[83]
	Cr <sup>3+</sup>	0–923	oven	—	—	4.62%	2.4 K	[84]

和 18 μm·°C<sup>-1</sup>, 偏差在 0.02 nm 以内。Zhang 等<sup>[22]</sup>采用喷墨打印的方法制备出量子点光纤荧光温度传感探针, 采用荧光发射峰位移法实现了 20~70 °C 的温度检测, 敏感度达到 109 pm·°C<sup>-1</sup>, 误差小于 1.4%。

测温过程中可能存在噪声的影响, 因此衍生出荧光信噪比的信号处理方法。Castrellon-Urbe 等<sup>[23]</sup>采用熔接法将掺杂 Er<sup>3+</sup> 的石英光纤与多模光纤结合制备了可实现远程温度检测的光纤温度传感探针, 利用荧光信噪比法实现了 20~200 °C 的温度测量, 信噪比分别为 110 dB 和 111 dB, 灵敏度可达到 0.035 °C<sup>-1</sup>。

此外, 随着温度的变化, 激发光功率与荧光信号功率的转换比也会发生变化, 因此衍生出效率信号转换法。Alvarez-Chavez 等<sup>[24]</sup>制备了锥形的掺杂 Yb<sup>3+</sup> 的光纤温度传感探针, 研究了光纤锥度对温度传感的影响, 采用效率信号转换实现了 30~120 °C 的温度传感, 在 0.1 W 激发光功率下灵敏度达到 0.4203 °C<sup>-1</sup>。

自参考相位偏移法是通过检测光的相位变化实现对温度检测的方法。Steinegger 等<sup>[25]</sup>将温敏有机染料溶于聚(偏二氯乙烯-共丙烯腈)后涂覆于玻璃光纤末端, 完全凝固后再涂覆炭黑形成光学隔离层制备出光纤荧光温度传感探针, 利用自参考相位的移动实现了 22~37 °C 的温度检测, 相位移动约为 3°, 响应速度为 0.5 s。

掺杂法制备的光纤荧光温度传感探针发展时间长, 原理简单, 技术成熟, 可采用的荧光温敏物质种类丰富, 具有良好的重复性和稳定性、较广的测温范围等优势。荧光物质主要采用稀土离子形成的化合物和上转换纳米粒子, 因其热稳定性好, 且在超高温下仍能保证稳定性能, 可实现大范围的温度检测。然而, 早期的掺杂法制备传感探针对设备要求高, 耗时长, 对环境要求较为严苛。随着材料科学的迅猛发展, 新的基体材料和温敏材料不断出现; 未来采用掺杂法制备探针可以选择具有特定性能的功能性材料作为基体, 如水



凝胶、聚合物凝胶等,能够提高制备效率和生物相容性,甚至无需特殊设备就能实现探针制备,降低制备成本;也能够采用具有特殊荧光性能的温敏材料制备传感单元,如有机荧光材料和金属复合材料,从而提升传感探针的性能。仪器科学的发展也使得多种掺杂法的制备工艺更精湛、效率更快且重复性更好。大量科研团队的报道证明掺杂法是目前光纤荧光温度传感探针主流的制备方法,未来有望进行规模生产并在日常生活和生物医学中实现广泛应用。

## 4 化学修饰及物理沉积法制备传感探针

除掺杂法外,许多团队也采用物理沉积和化学修饰光纤表面的方法制备温度传感探针。物理沉积主要是用浸涂、滴涂等方法将温敏物质沉积在光纤端面;化学修饰主要是通过化学键的方式在光纤侧表面或端面将光纤与荧光物质结合。

### 4.1 基于荧光强度法测温的修饰型探针

荧光强度法通常只需在光纤表面修饰单一荧光温敏物质即可,利用其荧光强度随温度变化的特性进行传感。García 等<sup>[86]</sup>采用溶胶-凝胶法在光纤表面制备衍生抗反射涂层,并通过浸涂法将荧光素沉积在衍生涂层上制备成光纤荧光温度传感探针,基于荧光强度法实现了 30~250 °C 的温度检测,敏感度达到 1 °C,响应时间在 8 s 内。Chu 等<sup>[87]</sup>将四氯化铂五氟苯酚和 5(6)-羧基荧光素掺杂封装在氟化干凝胶中,采用浸涂法将其涂覆在光纤末端制备成光纤荧光氧气温传感探针,基于荧光强度法实现了 25~66 °C 的温度检测。Zhao 等<sup>[88]</sup>采用化学修饰法对光纤表面进行硅烷化,并将 Zn<sub>x</sub>Cd<sub>1-x</sub>S 量子点连接到光纤表面制备成光纤荧光温度传感探针,如图 3(a)所示,实现了 25~105 °C 的温

度传感。此外,还通过酰胺键将带有羧基基团的量子点固定修饰在硅烷化处理后的光纤表面,实现 26~42 °C 的温度检测,并用于大鼠脑切片的温度检测<sup>[89]</sup>。

### 4.2 基于荧光强度比法测温的修饰型探针

在化学修饰及物理沉积法制备的探针中,通常采用稀土离子作为温敏物质,主要由于其具有多个发射峰,因此也能采用荧光强度比法进行传感,可以有效消除环境因素造成的干扰,提高化学修饰及物理沉积法制备传感探针的检测稳定性。Zhang 等<sup>[90]</sup>利用水热法合成 Er<sup>3+</sup>/Yb<sup>3+</sup>共掺的 NaYF<sub>4</sub> 纳米粒子,用沉积法将这种粒子沉积在石英光纤端面制备成探针,如图 3(b)所示,采用荧光强度比法实现了 258~423 K 的温度传感,灵敏度可达到 0.0168 K<sup>-1</sup>,绝对误差为 1 K,不稳定性为 0.187 K,相对标准偏差为 0.133%。Ren 等<sup>[91]</sup>采用水热法合成 NaBi(WO<sub>4</sub>)<sub>2</sub>:Er<sup>3+</sup>/Yb<sup>3+</sup> 荧光粉,将其沉积于光纤端面制备成探针,同样采用荧光强度比法实现了 253~423 K 的温度传感,绝对灵敏度达到 0.014 K<sup>-1</sup>,绝对误差为 -0.5~0.6 K,可用于人体体温的检测。

### 4.3 基于荧光寿命法测温的修饰型探针

Zhao 等<sup>[92]</sup>利用滴涂法将 Mg<sub>6</sub>As<sub>2</sub>O<sub>11</sub>:Mn<sup>4+</sup> 荧光粒子均匀溶于乙醇溶液后,用移液管涂覆在微型光纤的表面制备成光纤荧光温度传感探针,将另外两根光纤分别用于输入激发光和输出荧光,通过计算荧光寿命实现了 30~210 °C 的温度传感,敏感度达到 7.2 μs/°C,误差控制在 1 °C 以内,精度达到 2 °C。

化学修饰及物理沉积法制备光纤荧光温度传感探针的方法是近几年发展起来的,具有对设备要求低及成本低的优点;稀土离子、量子点和有机荧光材料都可以作为温敏材料被固定在光纤侧表面或端面,因此荧光物质的选择较为丰富,可根据应用需求实现多个领域的温度检测。然而,该方法也具有一定的缺陷,如化学修饰法的修饰过程繁琐且耗时长,重复性差;而物理沉积法在检测时温敏物质易脱落,易受环境因素影响,稳定性差。目前这种制备方法在生化传感领域应用较多,而在温度传感方面的研究较少。随着技术进步,化学修饰法将以更加简单、稳定的修饰过程为发展方向,将繁琐的化学键连接修饰以更加便捷且牢固的方式实现;物理沉积法以改善沉积的均匀性和稳定性为发展方向,可通过开发新型功能性材料实现。此外,在更加细微的光纤上进行修饰能够制备出微型的温度传感探针,实现微小区域的温度检测。

## 5 封装法制备传感探针

早期的掺杂法制备光纤荧光传感探针对设备要求较高,封装法成为了一种可替代掺杂法的制备方法,被封装的敏感材料有稀土离子、量子点、有机分子以及上转换纳米粒子,常见的封装材料为毛细玻璃管、塑料管、合金、聚合物基质及玻璃等,将封装体与光纤结合即可形成温度传感探针。

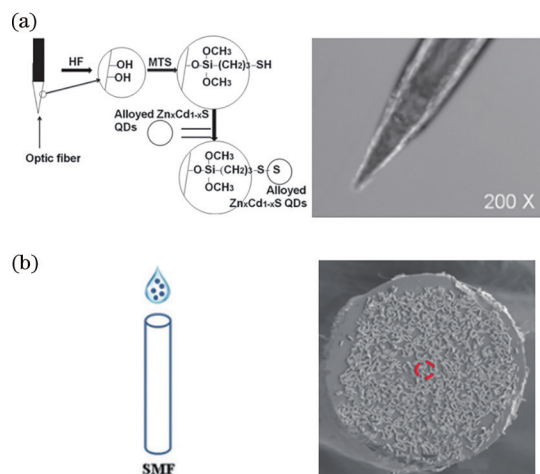


图 3 化学修饰及物理沉积法制备传感探针。(a) 化学修饰法<sup>[88]</sup>; (b) 物理沉积法<sup>[90]</sup>

Fig. 3 Preparation of sensing probes by chemical modification and physical deposition methods. (a) Chemical modification method<sup>[88]</sup>; (b) Physical deposition method<sup>[90]</sup>



### 5.1 基于荧光强度法测温的封装型探针

采用荧光强度法进行信号处理对封装法制备的温度传感探针同样适用。Tao 等<sup>[93]</sup>利用环氧胶中对温度敏感的多环芳香族化合物作为温敏物质,并将用于输入激发光和输出荧光的双光纤与温敏物质一起封装在石英毛细管中制备成荧光温度传感探针,如图 4(a)所

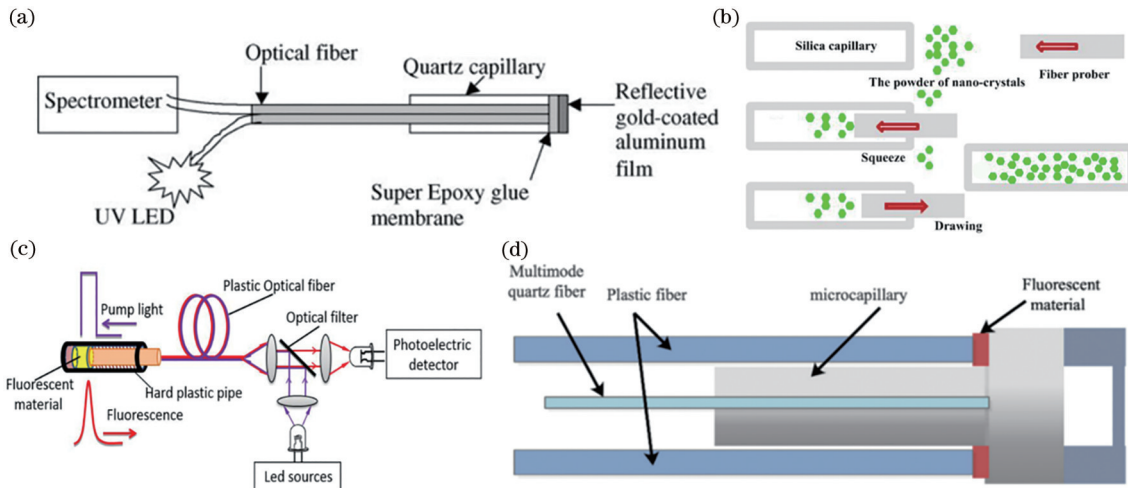


图 4 封装法制备传感探针。(a)封装环氧树脂<sup>[93]</sup>;(b)封装纳米晶体颗粒<sup>[94]</sup>;(c)封装荧光体<sup>[95]</sup>;(d)与法布里-珀罗干涉腔结合封装<sup>[96]</sup>  
Fig. 4 Encapsulation methods for preparing sensing probes. (a) Encapsulated with epoxy resin<sup>[93]</sup>; (b) encapsulated with nanocrystalline particles<sup>[94]</sup>; (c) encapsulated with phosphor<sup>[95]</sup>; (d) combined package with Fabry-Perot interference cavity<sup>[96]</sup>

### 5.2 基于荧光强度比法测温的封装型探针

封装多种稀土离子作为温敏物质的探针通常采用荧光强度比法进行传感。Li 等<sup>[94]</sup>采用溶剂热法合成了  $\beta\text{-NaLuF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}$  的纳米晶体颗粒,封装在毛细玻璃管中制备成光纤荧光温度传感探针,如图 4(b)所示,采用荧光强度比法实现了 300~500 K 的温度检测,灵敏度可达  $0.0153\text{ K}^{-1}$  和  $0.0009\text{ K}^{-1}$ 。

### 5.3 基于荧光寿命法的封装型探针

采用封装法完成制备后,只要荧光物质的荧光寿命对温度敏感,同样可以采用荧光寿命法进行温度传感,并不会受到封装材料的影响。Zhao 等<sup>[95]</sup>将掺杂  $\text{Mn}^{4+}$  的氟氧锗酸盐荧光体作为荧光材料封装在坚硬的塑料管中,与塑料光纤一起封装制成光纤荧光温度传感探针,如图 4(c)所示,采用荧光寿命法实现了 0~90 °C 的温度传感,标准误差为 0.45 °C。Jiang 等<sup>[96]</sup>将温敏荧光材料与法布里-珀罗干涉腔结合制备了光纤温度压力传感探针,如图 4(d)所示,采用荧光寿命法实现了 25~80 °C 的温度检测,灵敏度达到  $0.0048\text{ ms}\cdot\text{C}^{-1}$ 。

采用封装法制备光纤荧光温度传感探针,制备过程简单,耗时短,封装制备过程不需要特殊设备,成本低廉,灵活性强;通常采用荧光粉、有机荧光物质和量子点作为传感材料,传感物质可以以多种形式存在,便于制备;可以利用不同的封装材料实现不同领域的温度检测,应用领域广。但该方法对封装的严密性和避光性要求较高,探针的性能易受封装材料的影响。封装法未来的主要发展方向为运用耐热性能、导热性能

示,采用荧光强度法实现了 25~100 °C 的温度传感。Sun 等<sup>[18]</sup>将含 Nd 的荧光粉(LIFM-42(Nd))通过激发态分子内质子转移(ESIPT)调制后采取毛细管进行封装,并与光纤结合制备了近红外发射的光纤荧光温度传感探针,实现了 77~300 K 的温度传感,随温度变化呈现出良好的线性关系。

以及密封性能更好的材料对温敏材料进行封装,例如合金材料、柔性胶体等,从而实现更大范围的测温 and 更多领域的运用。

## 6 特种光纤填充法制备传感探针

随着光纤技术的发展,特种光纤的出现也为光纤温度传感探针的制备提供了新思路,光子晶体光纤和空芯光纤是常用的特种光纤,常采用量子点、有机荧光溶液等温敏材料进行填充,再与传光光纤熔接实现传感探针的制备。

### 6.1 基于荧光强度法测温的特种光纤型探针

特种光纤内封装的量子点或单种有机荧光物质通常只有一个发射峰,采用荧光强度法进行温度检测是最简单高效的。Bravo 等<sup>[97]</sup>将 CdTe 量子点(QDs)涂覆在空芯光纤(HCF)内部形成纳米薄膜,其两端再与多模光纤熔接即构成全光纤结构的光纤荧光温度传感探针,如图 5(a)所示,采用荧光强度法实现了 -20~70 °C 的温度测量,不同量子点的敏感度分别为  $0.0013\text{ }^{\circ}\text{C}^{-1}$  和  $0.0014\text{ }^{\circ}\text{C}^{-1}$ 。Mai 等<sup>[98]</sup>将罗丹明 6G(R6G)涂覆于抗共振光纤(ARF)内部形成薄膜制备成光纤荧光温度传感探针,如图 5(b)所示,在末端形成二氧化硅球增加荧光的收集效率,采用荧光强度法实现了 30~80 °C 的温度传感,灵敏度可达  $501.106\text{ }^{\circ}\text{C}^{-1}$  和  $50.6827\text{ }^{\circ}\text{C}^{-1}$ ,分辨率可达  $0.03946\text{ }^{\circ}\text{C}$  和  $0.003991\text{ }^{\circ}\text{C}$ 。

### 6.2 基于荧光强度比法测温的特种光纤型探针

将拥有多个发射峰的荧光材料填充或嵌入特种

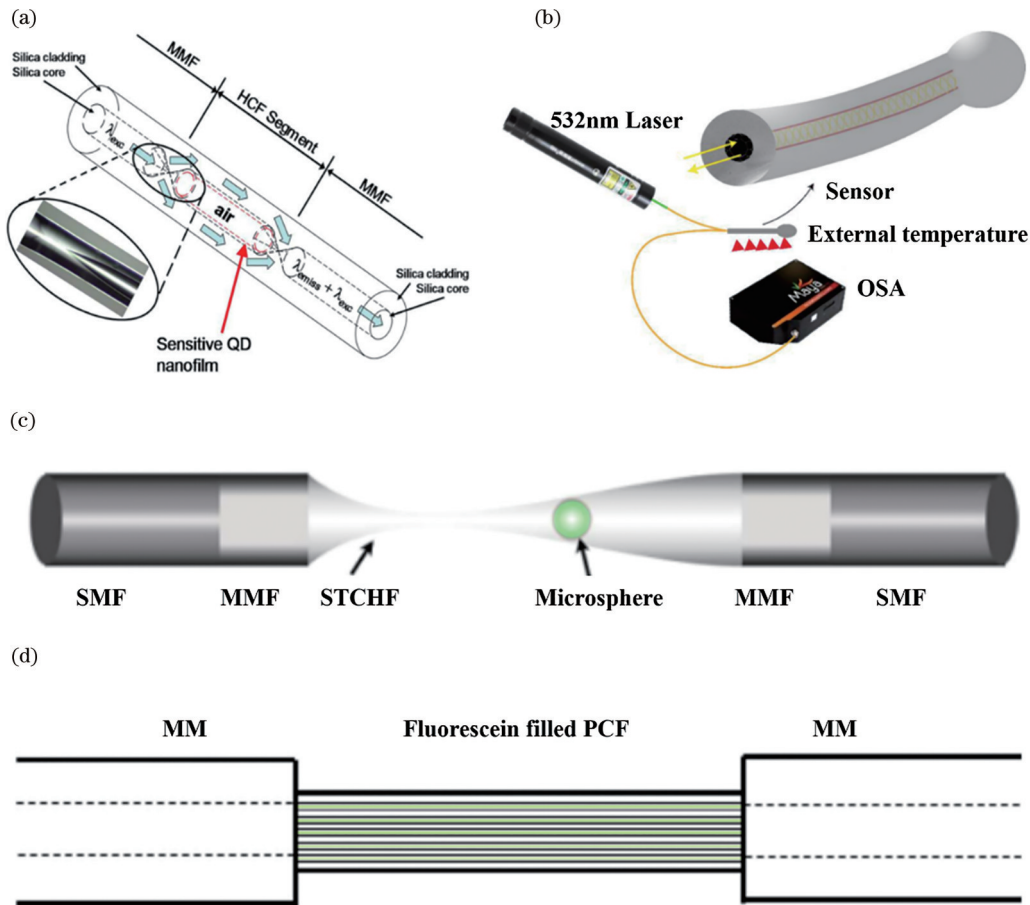


图5 特种光纤填充法制备传感探针。(a)填充量子点<sup>[97]</sup>;(b)填充R6G薄膜<sup>[98]</sup>;(c)嵌入玻璃微球<sup>[99]</sup>;(d)填充荧光素<sup>[100]</sup>  
Fig. 5 Special optical fiber filling methods to prepare sensing probes. (a) Filled with quantum dots<sup>[97]</sup>; (b) filled with R6G film<sup>[98]</sup>;  
(c) embedded with glass microspheres<sup>[99]</sup>; (d) filled with fluorescein<sup>[100]</sup>

光纤中,采用荧光强度比法对信号进行处理,能够最大程度减少环境的干扰,提升传感探针的检测稳定性。Zhang等<sup>[99]</sup>制备了一种 $\text{Er}^{3+}/\text{Yb}^{3+}$ 共掺硝酸盐玻璃微球嵌入悬浮式三芯中空光纤(STCHF)中,与单模光纤(SMF)和多模光纤进行熔接制备成光纤荧光温度传感探针,如图5(c)所示,利用荧光强度比法实现了 $30\sim 110\text{ }^{\circ}\text{C}$ 的温度测量,灵敏度最高可达 $0.00547\text{ K}^{-1}$ 。

### 6.3 基于荧光发射峰位移法测温的特种光纤型探针

量子点和部分有机染料的荧光发射峰波长会随着温度变化而产生位移,通过检测发射峰波长的变化也能够实现温度传感。Tatar等<sup>[100]</sup>将荧光素水溶液填充于掺杂 $\text{GeO}_2$ 的二氧化硅光子晶体光纤中,两端与多模光纤熔接制成光纤荧光温度传感探针,如图5(d)所示,利用荧光发射峰位移法实现了 $24\sim 80\text{ }^{\circ}\text{C}$ 的温度检测,峰位波长偏移量约为 $9\text{ nm}$ 。Wu等<sup>[17]</sup>将 $\text{CdSe}/\text{ZnS}$ 量子点水溶液填充于空芯光子晶体光纤中,端面与多模光纤进行熔接,制备了全光纤反射式荧光温度传感探针,利用发射峰位移法实现了 $-10\sim 120\text{ }^{\circ}\text{C}$ 的温度检测,灵敏度达到 $126.23\text{ pm}\cdot^{\circ}\text{C}^{-1}$ 。Zhao等<sup>[101]</sup>将石墨烯量子点(GQDs)封装于空芯光纤中,两端采用多模光纤熔接形

成荧光温度传感探针,同样基于发射峰位移法实现了 $10\sim 80\text{ }^{\circ}\text{C}$ 的温度传感,灵敏度达到 $123.7\text{ }\mu\text{m}\cdot^{\circ}\text{C}^{-1}$ 。

特种光纤填充法制备的光纤荧光温度传感探针具有较高灵敏度,这类传感探针的特殊性体现在光纤结构上,与一般光纤有较大差异导致传感探针的多样性,而改变结构参数就可以改变传感探针的性能。填充物质的形式多种多样,液体和固体状态的荧光物质均可以被填充在光纤的特殊结构内,还可以轻松实现分布式温度传感,这是其他制备方法较难实现的。但是该方法所需要的特种光纤通常制备复杂且困难,依赖于特殊设备,成本高,此外探针的重复性和稳定性也有待提高。目前特种光纤填充法制备传感探针虽然有很多文献报道,但普适性较差,仅适合特殊场合使用。随着光纤制备技术提高和设备普及,未来此类方法主要以继续优化特种光纤的结构及参数为主要发展方向,满足更多应用需求从而提升探针的应用价值,此外,运用光纤拼接技术构建级联式特种光纤探针以实现分布式传感也是一个发展趋势。

## 7 结论与展望

光纤荧光温度传感探针是一种既可以进行接触式

温度传感也可以进行非接触式温度传感的温度传感探针,能够实现远端探测和实时监测,可以弥补传统热电式温度传感器的不足。在本文中,总结了光纤荧光温度传感探针的制备方法如掺杂法、化学修饰及物理沉

积法、封装法和特种光纤填充法,对比如表 4 所示,以及信号处理方法如荧光强度法、荧光强度比法、荧光寿命法、荧光发射峰位移法等,分析了各自的优缺点,并对未来的发展方向进行了展望,总结和展望如下。

表 4 制备方法的比较

Table 4 Comparison of preparation methods

Method	Preparation method	Measurement range	Stability	Repeatability	Cost
Doping	normal	large	high	normal	high
Chemical modification and physical deposition	complicated	normal	low	low	low
Encapsulation	simple	normal	high	high	low
Special fiber filling	complicated	small	normal	low	high

掺杂法制备的传感探针是最常见的,其具有较宽的测温范围和良好的传感性能,由于制备技术较为成熟且能够检测高温,因此目前主要被应用于工业生产和环境监测等领域。但早期掺杂法采用玻璃作为掺杂基体,需要特殊的设备才能实现光纤探针的制备。近些年来出现了无需特殊设备也可制备的水凝胶、凝胶和有机聚合物等新型材料,弥补了传统掺杂法的不足,采用新型材料制备探针将成为目前乃至未来掺杂法的主要发展方向,以降低制备难度和增加经济效益作为目标,具有生物亲和性和柔性的材料能够使得掺杂法制备的探针在生物和医疗等领域得到广泛应用。

化学修饰及物理沉积法是在一定的化学反应和物理沉积基础上实现的,对设备要求较低,客观上降低了制备的难度,扩充了温敏材料的种类,但化学修饰过程繁琐、物理沉积稳定性和重复性差,由于目前不能够很稳定地制备探针且制备工艺与技术优化空间较大,因此该类探针还处于实验室研发阶段并未得到广泛应用,未来将对化学制备过程和沉积工艺进行优化,以实现更加简易和稳定的制备作为目标,通过更加优秀的工艺制备出更加稳定的探针,应用拓展至医学、生化和环境温度监测等。

封装法是将温敏物质封装于容器内的一种制备方法,成本低廉,对设备要求低,但密封性一直是一个难点,封装材料的性能也是重要的影响因素,由于封装材料能够使敏感材料与外界环境相隔绝,大大降低了除温度外其他环境因素的干扰,主要被应用于环境温度的监测。目前乃至未来的发展趋势是采用具有更好性能的封装材料(如合金、柔性聚合物等)和密封材料(紫外固化胶)进行制备,以提升密封效果增强传感探针的稳定性和重复性作为目标,采用具有更好性能的材料制备探针实现更宽范围的测温,赋予探针在复杂环境下保持正常工作的能力,并有望在工业、生化、日常生活、航空航天等领域实现应用。

光纤的内部结构也能够影响传感探针的性能,特种光纤填充法制备的传感探针具有高敏感度,但特种光纤的制备依赖特殊设备,精细的结构也使得温敏材料的吸附具有一定的随机性,导致重复性差,与其他制

备方法相比优势并不大,因此目前仍处于实验室研发阶段。未来的主要发展方向是探针的结构设计与优化以及发展分布式传感技术,以提升稳定性和重复性为发展目标,通过研制不同的结构探针满足不同场合对传感性能的需求,在工业、航空航天、能源运输等领域具有较大的应用潜力。

不同的荧光材料具有不同的温敏特性,可以通过改善或开发新的温敏荧光材料提升探针的灵敏度、稳定性、重复利用性和测温范围等性能,如上转换纳米粒子和新型量子点等。

此外,信号的处理方法也会很大程度地影响探针的稳定性和准确性,因此,研究和开发更稳定有效的信号处理方法也是光纤温度探针的一个发展方向。

不同的光纤荧光温度传感探针拥有自己独特的优势,体积小和抗干扰能力强是最突出的特点,在一些特殊场合能够代替传统的温度传感器进行温度检测。未来将把更简易的制备流程、更多的温敏材料、更高的灵敏度和精度、更好的稳定性和重复性、更低廉的成本和更完善的测温方法作为整体的发展方向,使光纤荧光温度传感能在更多的领域得到更广泛的应用。

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