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氧化石墨烯/聚酰胺纳米复合材料研究进展

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摘要：石墨烯具有优异的光学、电学和力学性质，石墨烯/聚合物纳米复合材料受到了学术界和产业界的共同关注。近年来，氧化石墨烯/聚酰胺纳米复合材料在提高材料性能、拓展下游应用方面取得了突破。文中综述了氧化石墨烯、还原氧化石墨烯和功能化氧化石墨烯与不同聚酰胺复合的研究进展，总结了原位聚合、熔融复合和溶液共混等制备方法，讨论了氧化石墨烯的功能化方法以及纳米复合材料的化学结构、热性能、力学性能、电化学性能及应用，同时对该领域的发展和面临的挑战进行了探讨。

关键词：氧化石墨烯；聚酰胺；纳米复合材料；制备方法
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石墨烯是一种由碳原子以sp^2杂化轨道组成六角型呈蜂巢晶格的二维碳纳米材料，可以从天然丰富、低成本的石墨中提取获得[1~3]。石墨烯的制备方法包括直接剥离法、超声波处理和液相工艺剥离法等。石墨烯具有高的迁移率、弹性模量、大的比表面积、高导热率，以及优异的光学、电学等性能，在电子、生物技术、能量储能与转化及复合材料等领域发挥了重要作用[4~6]。

氧化石墨烯（GO）含有大量的羟基、环氧基、羰基、羧基等含氧官能团，是开发聚合物复合材料高力学性能和多功能性的重要增强体[7~12]。GO具有特殊的物理、化学性质，羧基、氨基的引入可改变氧化石墨烯的反应性和表面化学[13]，调节材料的电学性能，进一步拓宽其在电子、光电和电化学等领域的应用[14~16]。聚酰胺（PA）是一种性能优异的工程热塑性材料，具有良好的加工性能和耐化学性等[17~20]。聚酰胺与GO复合能够显著改善材料性能，因而得到广泛关注[21, 22]。结合文献报道与笔者课题组前期研究[23, 24]，本文总结了近年来氧化石墨烯、还原氧化石墨烯和功能化氧化石墨烯与不同聚酰胺的复合材料的研究进展，如Tab.1所示，讨论了材料的结构和性能，同时对该领域的发展和面临的挑战进行了探讨。

1 氧化石墨烯/聚酰胺纳米复合材料

1.1 原位聚合

原位聚合是指将纳米填料均匀分散在聚合物单体间，然后进行聚合反应制备纳米复合材料的一种方法，具有纳米材料分散性好和易放大生产等优势。在该方法中，单体存在于GO层间和层外，聚合形成氧化石墨烯基纳米复合材料。O’Neilla等[25]以己内酰胺（CLA）为单体，利用胶体状GO的高均匀分散性增强聚酰胺6（PA6）/GO纳米复合材料的力学性能。原位聚合反应后，氧化石墨烯薄片厚度由0.86 nm增加至约4 nm。在胶体分散状态下，当GO质量

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Tab. 1 GO/PA nanocomposites

Nanofiller	Synthesis methods	Polyamide		T_d/℃	TS/MPa	Ref.
GO	In situ polymerization	PA6	Colloidal dispersion GO	378	62	[25]
			GO/water slurry		482	[26]
			GO reduced self-assembly		76	[27]
			GO-PA6 covalent bonding		82	[28]
			GO-PA6 covalent bonding			[29]
	Melt mixing	PA66	Masterbatch dilution method		40	[30]
		PA6	wet-phase transformation method			[31]
		PA12	Introduction of POE-g-MA	480		[32]
	Solution mixing	PA6	Masterbatch dilution method			[33]
		PA66	GO-CNTs hybridization	300		[34]
			Electrostatic spinning technology			[35]
RGO	In situ polymerization	PA66	Ammonia pre-reduction-thermal reduction GO	390	84	[36]
			GO in situ thermal reduction	424		[37]
			CL open loop reduction GO	320		[38]
			GO in situ thermal reduction	380		[39]
	Melt mixing	PA12	GO high temperature thermal reduction	350	50	[40]
		PA66	GO chemical reduction		74	[41]
FGO	In situ polymerization	PA6	Synergistic enhancement of FG/FCNTs		668	[42]
			Chemically modified aminated GO		133	[43]
			Amide functionalized GO	420	41	[44]
		PA66	Chloride functionalized GO	310	40	[45]
		PA610	GO-Cl grafted PA610	420		[46]
	Melt mixing	PA12	PEI chemically modified GO	430	75	[47]

GO: graphene oxide; RGO: reduced graphene oxide; FGO: functionalized graphene oxide; TS: tensile strength; T_d: decomposition temperature

分数从0.10%增加到1.0%，弹性模量呈线性增加（11%~28%）。Tang等[26]以CLA和GO/水浆为原料，原位聚合制备了PA6/GO纳米复合材料，如Fig.1所示。当加入0.05% GO/水浆时，复合纤维的最大强度达到5.3 cN/dtex，断裂伸长率为38.8%。当添加到CLA熔体中时，水浆中的GO阻止了团聚，促进了PA6和GO之间的良好相互作用，增强了复合材料在体系中的分散性。

石墨烯具有优异的导热性，可作为一种理想的纳米填充剂改善材料的导热性能。Wang等[27]采用超声波处理，制备了GO含量较低的PA6/GO复合材料。PA6链作为间隔物，最大限度地减少了氧化石墨烯的聚集，提高了导热效率。0.25% GO复合材料的导热系数为0.69 W/(m·K)，约为纯PA6 (0.24 W/(m·K)) 的2.88倍。Zhao等[28]以PA6为共价功能化材料，将共价官能化氧化石墨烯纳米片均匀地分散在PA6基体中，采用原位聚合法制备了PA6/GO增强环氧树脂复合材料。添加量为0.015%的GO和1.50%的PA6时，复合材料断裂韧性显著提高了52.6%。随后，通过原位聚合和乙醇溶液沉淀法制备了一种新型层间增韧增黏剂PA6/GO。在低于0.05% GO用量的情况下，复合材料的层间断裂韧性进一步提高了80.6%[29]。

1.2　熔融复合

熔融复合法是在高温下将GO混入熔融状态的聚合物基体中，再通过挤压和注塑成型来制备复合

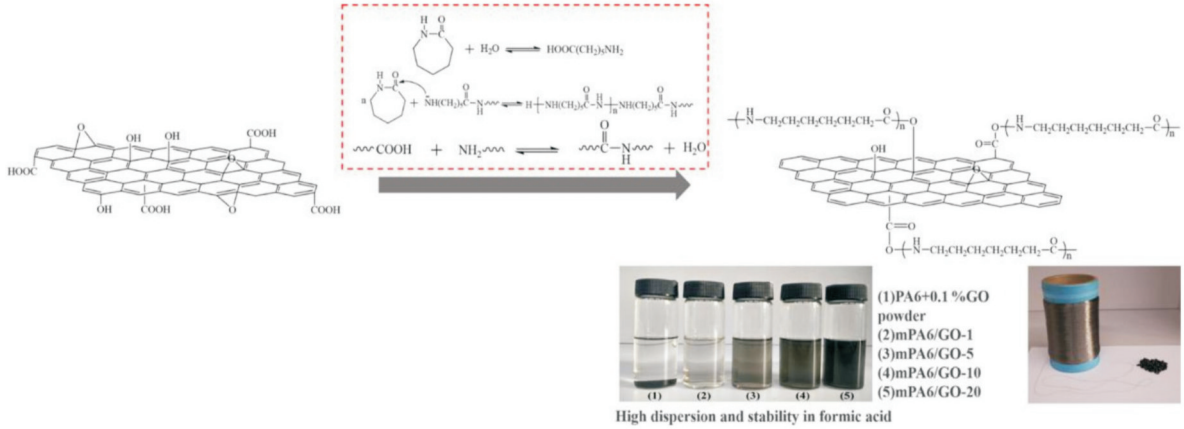


Fig. 1 Synthetic PA6/GO composites by in-situ polymerization and dispersion of the mixture in different solvents[26]

材料。该方法既可以改善聚合物基体内部的晶型结构，又可以在高温下充分混入GO提升聚合物基体的力学性能，是工业上制备GO纳米复合材料的首选方法。Rashmi等[30]利用母料稀释技术将PA11与氧化石墨烯混合制备了高填充（约15.0%）母料，随后将PA11和GO混合物在双螺杆挤出机中熔融复合制备得到了PA11/GO纳米复合材料。在5.0% GO负载量下，纳米复合材料的拉伸性能（强度和模量）分别提升了25%和56%，但其延展性有所降低（断裂伸长率从137%降低至50%）。Maio等[31]通过湿相转化法制备得到了GO母料，然后将母料研磨成粉末，添加到聚合物中，获得了PA6/GO复合材料。Yan等[32]通过熔融复合制备了聚酰胺12（PA12）/GO纳米复合材料。引入马来酸酐接枝聚乙烯辛烯橡胶（POE-*g*-MA）作为第二聚合物相以提高导电性，通过改变PA12，GO和POE-*g*-MA组分的复合顺序来优化微结构和性能，其电导率从2.8×10^{-14} S/m（PA12）增加到6.7×10^{-2} S/m。

1.3 溶液共混

溶液共混法是指先用适当的溶剂将聚合物或预聚物溶解，再通过给与特定条件（例如超声波处理和添加分散剂等方法）将GO分散在溶液中制备成复合材料。溶液共混法制备的复合材料，具有分散好、混合均匀充分、加工过程易控制等优点。Machado等[33]通过溶液共混制备了含有5.0% GO的母料，然后将其稀释到PA6基体中制备得到了PA6/GO纳米复合材料。由于GO的存在影响了PA6基体在熔融和结晶过程中的焓，从而增加了结晶度（32.4%~42.3%）。Wu等[34]将聚酰胺66（PA66）与GO在超声波下混合均匀。当GO质量分数为0.6%时，等温结晶活化能先降低后升高，并呈现最小值（ΔE=－337.95 kJ/mol）。Park等[35]通过改变聚合物溶液中GO的含量，对不同类型的复合纳米纤维进行静电纺丝，制备了PA66/GO复合纳米材料。在5.0 V电压下，与原始的PA66电流（1.6 μA）相比，纳米复合材料的电流提高了3个量级（达到0.1 mA）。当GO质量分数在5.0%以内时，PA66聚合物溶液可以通过静电纺丝获得性能优异的纳米纤维，在光电子器件等领域具有重要意义。

2 还原氧化石墨烯/聚酰胺纳米复合材料

还原氧化石墨烯（RGO）是氧化石墨烯的还原形式，通过氧化石墨烯还原获得，具有更高的力学性能、稳定性、导电性和导热性等。还原氧化石墨烯的制备方法主要包括热还原法和化学还原法。

2.1 力学性能

石墨烯是迄今为止人类发现的最坚固的材料之一，其弹性模量、固有强度和断裂强度分别可达到1.1 TPa，130 GPa和42 N/m[48]。因此，添加石墨烯是改善复合材料力学性能的有效方法。利用RGO其含氧官能团与PA66链末端氨基之间的缩合，可将PA66接枝到RGO上，一步原位聚合获得PA66/RGO纳米复合材料[36]（Fig.2）。加入少量的RGO（约1.0%）情况下，纳米复合材料的弹性模量和拉伸强度分别提高到660 MPa和84 MPa（提升约17%）。Hofmann等[40]通过将热还原氧化石墨烯（TRGO）分

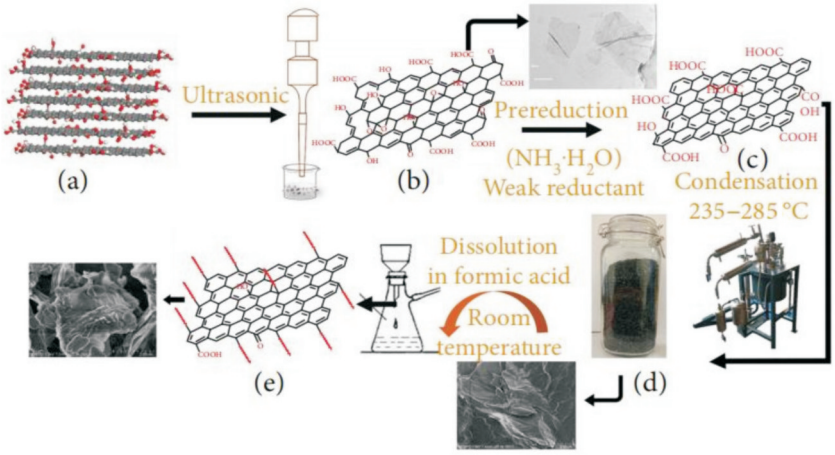


Fig. 2 Synthesis of PA66/RGO nanocomposites by in situ polymerization with simultaneous thermal[36]

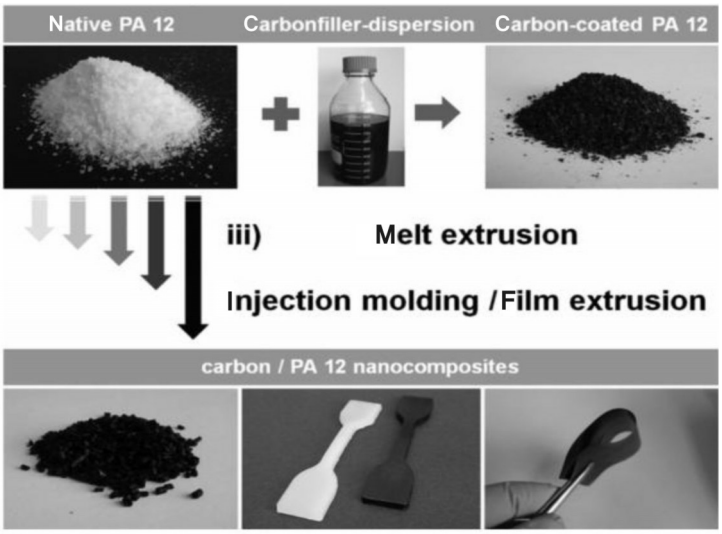


Fig. 3 Schematic illustration of PA12/GO nanocomposite fabrication[40]

散体喷涂到研磨后的PA12粉末上,熔融复合制备了PA12/RGO纳米复合材料,如Fig.3所示。在复合填料质量分数为10.0%时,TRGO增强了PA12的弹性模量(提升130%)和电导率(高达8.9×10^{-4} S/cm)。Elcin等[41]将高剪切热动力混合器用于石墨烯与PA66基体的混合分散,制备得到了石墨烯增强的PA66纳米复合材料。GO质量分数为0.5%时,纳米复合材料的结晶度增加至40.3%,弹性模量和拉伸强度分别提高了45%(3473 MPa)和16.1%(81 MPa)。

2.2　热、电性能

GO表面含有含氧基团,具有高度亲水性,但是其sp^2结构遭到破坏,导致其电绝缘性。为了改善材料的导电性,需要还原氧化石墨烯,去除其大部分含氧基团,恢复sp^2石墨网络。相对于化学还原方法,热还原能够避免大量有机溶剂的使用。Zheng等[37]通过对GO进行热还原和原位聚合制备了PA6/RGO纳米复合材料。在己内酰胺聚合过程中,分散的GO原位热还原,使复合材料的导电性增强。当RGO的体积分数由0.27%增加至1.09%时,其电导率从4.2×10^{-14} S/m提高至1.0×10^{-4} S/m。Yang等[38]在GO存在下,利用PA6/聚苯乙烯(PS)的反应诱导相转化,通过原位开环聚合制备了PA6/RGO复合材料。当RGO负载量为0.5%时,PA6/RGO复合材料的初始分解温度提升了43 ℃。Ding等[39]以CLA为单体,6-氨基己酸为引发剂,RGO为导热填料,通过原位聚合和GO的热还原获得了PA6/RGO复合材料,如Fig.4所示。

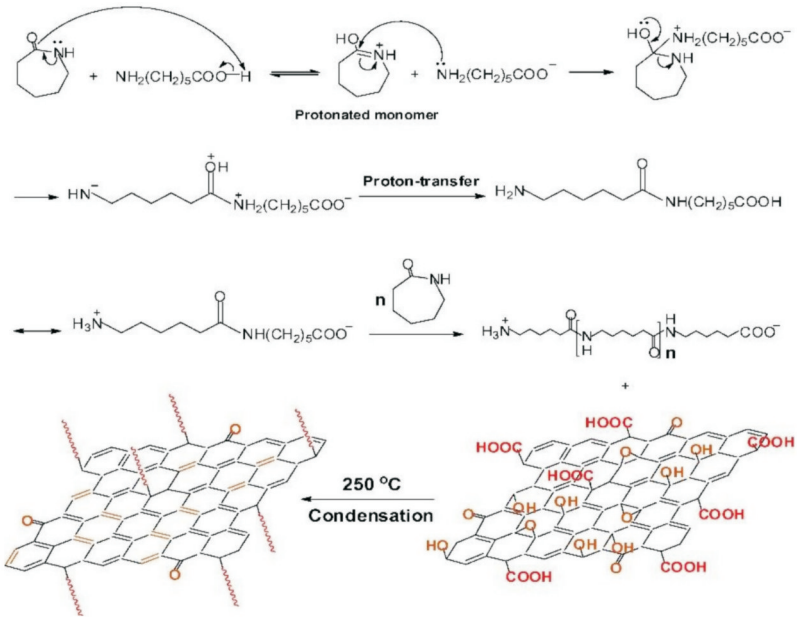


Fig. 4 Synthesis of PA6/RGO composite by in situ polymerization with simultaneous thermal reduction from GO to RGO[39]

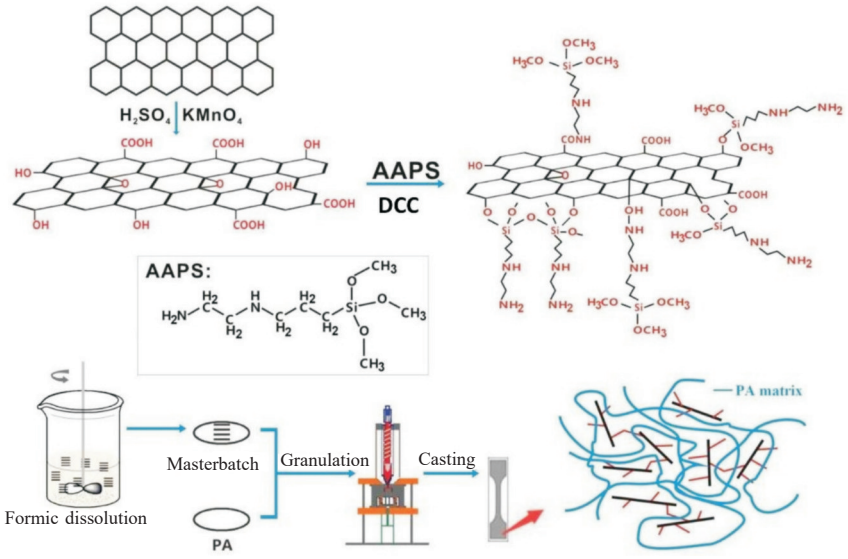


Fig. 5 Illustration of the synthesis of AMG/PA composites[50]

该方法有利于形成连续的导热路径，从而将热导率从0.196 W/(m·K)提高到0.416 W/(m·K)。

3 功能化氧化石墨烯/聚酰胺纳米复合材料

功能化是实现GO分散、溶解和成型加工的重要手段，可以赋予GO新的特性，使其在聚合物复合材料领域具有更好的应用前景。Eigler等[49]首先提出了功能化的概念，在GO中引入叠氮化物，赋予其功能化，同时可以有效防止GO的分解。

3.1 氨基化氧化石墨烯

氨基作为一种重要的官能团，能够与聚酰胺链末端或单体的羧基发生反应，实现聚酰胺和石墨烯的高效复合。陈美龙等[43]用氯化亚砜将其活化得到酰氯修饰氧化石墨烯，再与氨气反应制备氨基化氧化石墨烯。在负载量0.1% GO情况下，PA6/GO的拉伸强度和弹性模量分别达到133 MPa和736 MPa。聚乙烯亚胺（PEI）具有多个反应胺位点，可以有效地与GO表面官能团的活性位点反应，有助于增强石墨

烯在尼龙基体中的分散和相互作用。Roy等[47]采用聚乙烯亚胺(PEI)对GO进行化学改性,通过熔融复合增强GO在PA12基体中的界面作用。添加0.35% GO,拉伸强度提高了54%(75 MPa),弹性模量提高了74%(801 MPa),储能模量增加了约63%(2466 MPa)。如Fig.5所示,Chen等[50]通过溶液共混在石墨烯表面成功接枝N-(2-氨乙基)-3-氨丙基三甲氧基硅烷(AAPS),制备了氨基改性氧化石墨烯(AMG)。AMG与溶剂甲酸具有较强的氢键作用,从而获得良好的分散性。研究发现,AMG/PA6复合材料的拉伸强度达到73.01 MPa,比纯PA6增加了87.1%;AMG能够显著降低聚合物复合材料的摩擦系数(由0.428降至0.237),提高其耐磨性。

3.2　酰化官能化改性氧化石墨烯

酰化官能化改性氧化石墨烯,能够更便利的实现原位聚合,调控材料性能,制备复合材料。O'Neilla等[44]通过酰胺($CONH_2$)官能团制备得到功能化酰胺氧化石墨烯,与己内酰胺进行原位聚合,首次制备了酰胺官能化GO/PA6复合材料。随着GO质量分数从0.1%增加至0.75%,复合材料屈服强度提升了30%。Zhou等[42]采用原位聚合法制备了聚(苯乙烯-马来酸酐)官能化石墨烯和碳纳米管。通过碳材料上的马来酸酐基团与PA6链的末端氨基之间的缩合反应,实现了己内酰胺的原位开环聚合制备PA6/FG/FCNTs复合材料。PA6/FGO纳米复合材料的拉伸强度提高2.4倍(668 MPa),弹性模量提升132%(从1.32 GPa提高至3.06 GPa)。

此外,可以通过亚硫酰氯对GO进行官能化,得到酰氯官能化氧化石墨烯(AGO)。AGO和PVP减少了颗粒絮凝,得到了分散良好的悬浮液。同时原位界面聚合能够避免PA66原位聚合复杂工艺(例如抽真空等),有效获得PA66/GO纳米复合材料(Fig.6)[45]。同时,酰氯功能化氧化石墨烯与聚酰胺610(PA610)链上的氨基之间进行原位聚合制备了PA610/GO纳米复合材料[46]。GO和PA610基体之间的强界面黏合阻碍了PA610链的流动性,从而促使复合材料的降解温度提高了72.2 ℃,导热系数提高了36.9%,且结晶度明显低于纯PA610。

4　总结与展望

高性能新材料对于科技进步、经济发展和社会生活起到了至关重要的作用。GO作为近年来发现的新型碳材料,具有高模量、高导电、高导热等优异性能,与聚合物复合是开发高性能新材料的重要途

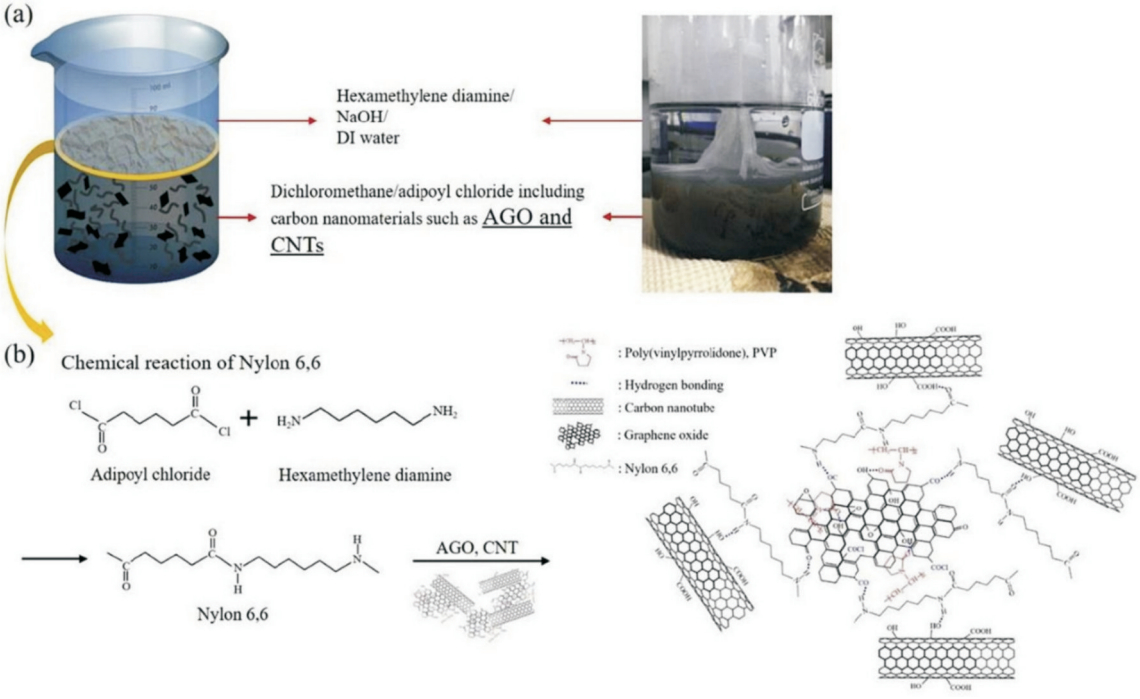


Fig. 6　Schematic of in situ interfacial polymerization process of nylon 66[45]

径。本文系统综述了氧化石墨烯/聚酰胺纳米复合材料的原位聚合、熔融复合和溶液共混等制备方法。基于PA/GO，PA/RGO和PA/FGO纳米复合材料，探讨了不同制备方法对力学性能、热性能和电性能的作用关系。还原氧化石墨烯能够有效改善复合材料的力学性能，并且在有机材料中有良好的相容性；氨基化氧化石墨烯在反应体系中具有良好的分散性和均匀性；酰化官能化改性氧化石墨烯，可便利的实现原位聚合，调控材料的性能，极大拓展了其在特种材料领域的应用。

通过GO表面改性增强基体与纳米填料之间的相互作用已成为目前研究的热点。展望未来，进一步开发高性能PA/GO纳米复合材料仍存在以下亟待解决的问题：(1) 开发更安全和更可控的氧化石墨烯的大规模制备新途径，降低成本，为复合材料研究奠定基础；(2) 强化氧化石墨烯表界面性能研究，改善氧化石墨烯在聚合物基体的相容性和分散性，阐明材料的构效关系，拓展应用领域；(3) 设计合适的加工方法，改善在极低负载水平下的性能。通过不断改进制备方法和技术，期待发现更多低成本、高质量，可满足大规模生产需求的PA/GO纳米复合材料。

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Recent Advances on the Graphene Oxide/Polyamide Synthesis of Nanocomposites

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ABSTRACT: Graphene exhibits excellent optical, electrical and mechanical properties, and graphene/polymer nanocomposites have attracted the attention of both academia and industry. In recent years, great breakthrough has been made in graphene oxide/polyamide nanocomposites for improving material properties and expanding down-stream applications. In this paper, the research of graphene oxide, reduced graphene oxide and functionalized grapheme oxide composite with different polyamides was reviewed. The preparation methods of in- situ polymerization, melting composite and solvent mixing were summarized. The methods of functionalization of graphene oxide, structure, properties and applications of nanocomposites were summarized, and the development and challenges in this field were discussed.

Keywords: graphene oxide; polyamide; nanocomposites; preparation method