低维碳材料水伏效应的传感应用

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摘要 以碳纳米管和石墨烯为代表的低维碳材料在与液体作用时, 表现出一系列新的生电效应, 如波动生电、射流生电、液滴生电、蒸发生电、湿度生电等, 这些现象被统称为水伏效应, 并成为近年低维功能材料领域研究的新热点. 这些发生在固-液界面或固-液-气界面的生电效应为基于新型能量转化原理的能量捕获技术开辟了新的方向, 也为基于固-液界面的传感探测提供了新的途径. 本文总结了水伏效应在流体运动、溶液浓度、湿度、温度等方面的传感应用潜力, 旨在为新型界面自驱动传感器件和传感系统的开发提供借鉴.

关键词 水伏效应, 低维碳材料, 界面, 传感器, 石墨烯

固-液界面是自然界中最普遍存在的一种界面, 也是与生命活动最为息息相关的界面, 在能源电池、化工合成、生物医学、环境处理等工业技术领域中, 固-液界面性能的调控也是关注的核心问题之一. 人们很早就发现, 在某些情况下, 固-液界面发生相对运动时会直接产生电信号, 但因这些电信号微弱, 甚少得到应用. 近年来, 随着纳米材料研究的推进, 人们在碳纳米管、石墨烯等低维碳材料中发现一系列新的固-液界面生电效应, 如波动生电、流体生电、液滴生电、蒸发生电等^[1~4]. 类比光在半导体中激发电子和空穴进而在p-n结内建电场作用下, 电子、空穴分离而在器件两端分别积累形成光伏电压的光伏效应(PV, 图1(a)), 这种运动的液相水、水溶液或气态水分子通过界面作用直接在低维材料中产生电压的现象被称为水伏效应(HV, 图1(b)). 利用水伏效应可以形成新的能量捕获方式, 相应地, 水伏效应产生的电压或电流信号也与固-液界面的物理特性、化学特性和流体特性等直接相关, 这为流速、溶液浓

度、湿度、温度等多种传感器的设计提供了新的技术途径.

以碳纳米管和石墨烯为代表的低维碳材料是目前研究水伏效应的最主要材料体系, 这一方面得益于低维碳材料十分优异的物理、化学特性, 如原子层级厚度、高强度、高导电性等; 另一方面也得益于近数十年来低维碳材料得到广泛的研究, 各种形貌结构可控的高质量制备技术被不断开发出来, 为水伏效应研究奠定了材料基础^[5~11]. 以石墨烯为例, 其平面六边形结构使所有的碳原子都是表面原子, 有极大的比表面积, 而其价键结构中的碳-碳sp²键由面内的σ键和面外的大π键构成^[12]. 暴露于面外的π键是石墨烯狄拉克载流子特性的主要来源, 同时也使其对光、电、热等外场的作用十分敏感^[13,14]. 当处于水环境时, 石墨烯表面容易吸附水分子或水合离子, 使本身物性受吸附水的调控, 形成不同程度的p型掺杂^[15,16]. 其他的低维碳材料, 碳纳米管可以看作是石墨烯卷成, 炭黑可以看作是有大量缺陷的纳米石墨

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图1 (网络版彩色)光伏效应和水伏效应的类比。(a)简化的光伏效应过程:电子和空穴被入射光子激发,被p-n结的内建电场分离,然后积累到半导体器件的两端形成光伏电压。(b)简化的水伏效应过程:正负离子在水运动和界面作用的协同作用下被分离,水运动包括体相水和分子的定向运动,也包括湿度的改变

Figure 1 (Color online) Schematic illustrations of photovoltaic effect (PV) and hydrovoltaic effect (HV). (a) A simplified photovoltaic effect process: the electrons and holes are excited by incident photons, separated by the built-in electric field at the p-n junction, and then accumulate at the two ends of the semiconductor to form a photovoltaic voltage. (b) A simplified hydrovoltaic effect process: the positive and negative ions are partially separated by the dynamic water (including moving bulk water, water molecules and changing humidity) with the aid of interface interaction

烯,因而与水都有比较容易的表面耦合。

1 低维碳材料水伏效应的典型机制

水伏效应的发生机制多种多样,早期的研究可以追溯到18世纪末19世纪初开创的现代电化学研究的一系列工作^[17]。1808年,德国科学家Reuss发现了电场作用使液体或溶液溶剂(通常为水)运动的电渗现象(electro-osmosis)和电场作用使电解质离子运动的电泳现象(electrophoresis)^[18,19]。1853年,德国物理学家亥姆霍兹(Helmholtz)首先认识到带电的电极进入电解质溶液后会排斥异种电荷,在固液两相的界面形成类似于电容的双电层(electrical double layer, EDL)。1859年,物理学家Quincke在柏林的实验中发现水在压力差作用下流过狭小的腔道缝隙或毛细管时,靠近管壁的某种电性的离子因管壁对其吸附作用而流速变慢,而管中心部分异种电性的离子流速则相对较快,使不同电性的离子受到流体的剪切作用而部分分离,从而在腔道两端产生电势差,即后来命名的流动电势(streaming potential),如图2(b)所示。Quincke分析了这些现象后,提出电中性固体与电解质溶液接触后也会形成双电层。1879年, Helmholtz基于热力学和静电学理论将双电层模型定量化,使其成为解释固-液界面动电效应(electrokinetic effect)的

经典理论。1880年,德国科学家Dorn发现了沉降电势(sedimentation potential)。至此,固液界面的4种经典动电效应:电渗、电泳、流动电势和沉降电势都被发现^[22~24],而其中通过液体流动剪切固液界面双电层而产生电信号的流动电势可以看作是被最早研究的水伏效应。

此后,随着电化学研究的深入,最初只有正负两个电荷层的简单双电层模型被不断改进。20世纪10年代, Gouy^[25]和Mooney^[26]认识到固液界面的双电层电容并非定值,而会随离子浓度和施加电场的不同而变化,因此他们在原本双电层模型的基础上引入了动态的扩散层(diffusion layer),使静电势在溶液中的分布随着离固液界面距离的增加而指数衰减。1924年, Stern^[27]针对高浓度溶液结合亥姆霍兹模型在界面处引入了吸附的固定电荷层(Stern layer),固液界面双电层模型的简单示意图2(a)。

在纳米材料研究兴起后,基于纳米材料表面特殊的结构和物性,人们就纳米结构的固液界面提出多种新的流体生电机理,其中代表性的有:

(i) 声子拖曳模型。2001年Kral和Shapiro^[20]通过理论分析提出,当有液体沿轴向流过金属性碳纳米管表面时,平衡状态下热运动液体分子对碳纳米管中碳原子撞击的对称性会被打破,液体分子的

图 2 (网络版彩色)典型水-固界面相互作用与水伏效应产生机制的模型。(a) 固液界面的双电层模型, 靠近界面处有Stern层, 之外是扩散层。(b) 经典纳米管道中的流动电势模型, 上下管壁的双电层发生交叠, 一种符号的离子吸附于管壁, 流体携带相反符号的离子流动同时在溶液中形成电流。(c) 声子拖曳或电子拖曳模型。水分子包覆金属性碳纳米管表面形成滑移层, 滑移层运动在碳管中激发声子风, 从而带动自由载流子在碳管中运动^[20]。Copyright © 2000 The American Physical Society。(d) 电摩擦模型, 碳管表面漂移的吸附离子通过电摩擦驱使碳管内自由电子运动^[21]。Copyright © 2004 The American Physical Society。(e) 在石墨烯表面拖动水滴产生电压的赝电容模型^[1]。Copyright © 2014 Nature Publishing Group。(f) 在石墨烯中产生波动势的双电层动边界模型^[2]。Copyright © 2014 Nature Publishing Group

Figure 2 (Color online) Schematic illustrations of typical water-solid interactions and models for hydrovoltaic effect. (a) An electric double layer forms at the solution-solid interface, consisting of Stern layer and diffusion layer. (b) Classical streaming potential effect in a nanochannel, in which the double layer overlaps, one type of ions is adsorbed at the interface and a pressure-driven flow carries counter-ions to form an electric current in the liquid. (c) Phonon drag or electron drag model for a metallic carbon nanotube immersed in a liquid. The water molecules coat the nanotube in a form of slipping layers, which generate a phonon wind to drive free carriers in the nanotube^[20]. Copyright © 2000 The American Physical Society. (d) Electronic friction Model. The drifting adsorbed ions will produce a voltage in the nanotube through electronic friction against free electrons inside the nanotube^[21]. Copyright © 2004 The American Physical Society. (e) Pseudocapacitance model for drawing a water droplet on graphene^[1]. Copyright © 2014 Nature Publishing Group. (f) Waving potential induced in graphene by one moving boundary of the electric double layer across a graphene sheet^[2]. Copyright © 2014 Nature Publishing Group

动量转移求和后不再为零, 会在碳纳米管表面激发“声子风”。“声子风”会拖曳一维的碳纳米管的载流子。被拖曳的正负载流子因浓度、迁移率等差异而在沿一维管道轴向的运动分量不能抵消, 即形成载流子定向运动的净电流, 如图2(c)所示。

(ii) 电摩擦模型。Persson等人^[21]在研究碳纳米管表面的溶液流动时, 提出了一个简单的离子“吸附-滑行-脱附”的摩擦模型, 溶液中离子吸附在碳纳米管表面后会被流体带动滑行一段距离后再脱附, 离子在碳管表面摩擦滑行时可以通过静电作用吸附纳米材料内部的载流子跟随运动, 从而形成一维纳米管道内部的定向电流, 如图2(d)所示。

(iii) 赝电容模型。当水滴在石墨烯表面运动时, 固-液界面处的双电层发生动态变化, 可以将运动界面前端和后端分别等效成2个赝电容 C_F 和 C_R , 液滴运动迫使后端电容 C_R 放电、前端电容 C_F 充电。这一液滴前端充电、末端放电的过程在与液滴接触的石墨

烯区域两端产生电势差, 称之为“拖曳势”(drawing potential)^[1], 如图2(e)所示。拖曳势的大小和液滴的速度 v 以及数目 n 成正比, 且和溶液的浓度和种类相关。这个模型可以简单、定量地解释水滴在石墨烯表面的滑动生电现象, 也可以看作是经典流动势模型在纳米受限界面下的一种拓展情况。

(iv) 双电层动边界模型。当石墨烯插入电解质水溶液时, 在气-液-固动边界处的石墨烯双电层不断动态形成, 有充电电流流经石墨烯从而在石墨烯两端产生电势差; 当石墨烯被拉出溶液时, 气-液-固动边界处的石墨烯双电层动态解离, 有放电电流流经石墨烯从而在石墨烯两端产生相反的电势差^[2], 如图2(f)所示。这种液面波动导致双电层在动边界处动态形成和解离而产生的电势差被称为“波动势”(waving potential), 可以看作是上述水滴运动赝电容模型的集成形式。

在水受限于狭窄碳纳米管内部形成水分子链的

特殊情况下,赵亚溥研究组^[28,29]提出了一种偶极子与载流子的耦合流动模型,管内水分子偶极子与管壁载流子耦合流动形成定向输运的偶极链,使纳米管两端产生电势差,该电势差可用于单根碳管中水流位置和速度的探测.此外,在研究水与碳纳米材料界面的生电现象上,人们也提出库仑拖曳^[30]、库仑场非对称涨落等多种解释^[31~33].

2 传感应用

利用水伏效应的碳纳米材料传感器与常规传感器一样也可分为主动式和被动式.(1) 被动式传感:主要利用水伏生电的效应,水或溶液与碳纳米材料动态作用时,发生电荷转移、离子吸附-脱附、静电感生电荷、电子-声子相互作用等微观作用,通过固-液界面耦合直接在碳纳米材料中产生宏观可测量的电压或电流信号.利用电信号输出即可反向推测出固-液界面的性质,继而得知固体或液体的某些性质.如,利用石墨烯与海水波动耦合的电压输出可以监测海浪波动速度^[2],利用水凝胶吸收-释放水分子的伸缩变化监测湿度等^[34].这种传感无需外加电源,具有自驱动探测的效果.(2) 主动式传感:主要利用水或水溶液与碳纳米材料作用后,引起碳纳米材料本身性质的改变,如水或离子的表面掺杂引起石墨烯载流子浓度、电荷中性点(狄拉克点)等发生改变,测量石墨烯的电阻、转移曲线等就可以推测出溶液pH、浓度等信息.主动式探测需要外电源驱动的探测电路,并将碳纳米材料制成场效应晶体管等器件结构.同时,水伏效应产生的电压也可以同样形成环境偏压叠加在主动式传感器件的控制电路上,将此信号检测后可以对流动电势等进行标定^[35].

原则上说,只要溶液、水汽乃至水分子与碳纳米材料作用时产生可测量的信号,就可以利用这些信号认识其固-液界面的各种信息.但由于水伏效应涉及界面的各种动态物理、化学过程,发生机制多种多样,多种机制又常常同时起作用,导致实际应用中还有很多理论和技术问题需要解决.本文对基于低维碳纳米材料水伏效应的传感现象和传感性能进行简单的归纳,旨在为今后的相关研究提供参考.

2.1 对流体运动的探测

当液体流动时,会使静止状态下平衡的固液界面(如双电层)发生扰动,驱使溶液中的离子、分子等

带动碳纳米材料中的声子、载流子等微观粒子发生不对称运动,在不同位置产生净电荷积累,产生宏观可测量的电压和电流.通过检定测量到的电压或电流则可以反向推算出液体的流量、流速等流动状态参量,这就构成了微纳尺度的流量传感器.这种传感器从工作模式上看非常简单,但其尺度却可以突破常规传感器的体积限制,在微流体、生物环境探测等方面很有应用潜力.

Kral和Shapiro^[20]在提出声子拖曳效应的模型时,曾经做过理论估计,当水流流速为1 cm/s时可在一根碳纳米管中产生约0.7 nA的电流.Ghosh等人^[36]和Sood^[37]在实验中研究了水溶液流经单壁碳纳米管样品时的现象,他们将单壁碳纳米管用高压压实成毫米级大小的块体并夹在2个金属电极之间,发现水溶液低流速(10^{-6} ~0.1 m/s)流过时,两电极间会测量到与流速取对数后的值近似线性相关的电压信号,电压信号范围0~10 mV,如图3(a)所示.他们认为该电压信号来源于流体中库仑场涨落对碳纳米管中自由载流子的非对称的棘齿作用.但随后Cohen^[40]认为该现象更可能是由流动势引起.Persson等人^[21]则将这一实验中碳纳米管表面“吸附-滑行-脱附”的离子运动简化成一个经典的电摩擦模型,也给出了与实验观测量级相符的解释.由于该实验中金属电极和碳管都浸入在溶液里,金属电极与溶液表面势不同引起的电压波动就可达到数十乃至上百毫伏级别;另一方面,碳纳米管处理过程中也可能有纳米颗粒杂质等的引入,从而使样品浸入盐酸时产生电化学反应等干扰信号,因而这一早期研究中测量到的电信号的实际机制很难简单澄清.但这一将流体流速与碳纳米材料电信号直接关联的实验现象为流速传感、生理信号探测等提供了新的思路,激发了人们利用低维碳材料研究流体生电的热情^[41~44].

在石墨烯的研究兴起之后,Dhiman等人^[45]报道了石墨烯在浸入流动的盐酸溶液中时会有与流速正相关的电压信号输出,但之后被证明该信号可能是金属电极在盐酸溶液中产生的干扰信号,与石墨烯本身无关^[35,46].Yin等人^[2]在研究气相化学沉积的大面积单层石墨烯与液体作用时发现,人工配置的海水溶液(0.6 mol/L氯化钠溶液)上下波动时,竖直插入其中的石墨烯层上下两端会产生电压.该电压与溶液固液界面的波动速度有明显的近线性关系,液面波动速度越快,电压信号也越大,如图3(b)所示.这

图3 (网络版彩色)低维碳纳米材料对流体流速的传感. (a) 单壁碳纳米管样品中测量到的电压与水流速度的关系^[36]. Copyright © AAAS. (b1) 石墨烯在波动的盐水中的示意图, (b2) 测量到的峰值电压与波动速度的关系, 盐水中NaCl摩尔浓度为0.6 mol/L^[2]. Copyright © 2014 Nature Publishing Group. (c) 三维石墨烯泡沫样品中, 测量到的电流与流速变化的关系, 插图为测量装置示意^[38]. Copyright © 2014 Royal Society of Chemistry. (d) 乙醇与水混合溶液流过三维石墨烯样品时, 测量到的电流与流速的关系^[39]. Copyright © 2014 American Chemical Society

Figure 3 (Color online) Sensing the flow velocity using low-dimensional carbon materials. (a) Dependence of induced voltage in a single-walled carbon nanotube sample on the flow velocity of water^[36]. Copyright © AAAS. (b1) Schematic illustration of waving potential in graphene moving across the surface of seawater; (b2) peak voltage as a function of inserting velocity of graphene into 0.6 mol/L NaCl solution^[2]. Copyright © 2014 Nature Publishing Group. (c) The induced currents versus the velocity of the flow through three-dimensional graphene foam, the inset shows the test facility^[38]. Copyright © 2014 Royal Society of Chemistry. (d) The variation of induced currents as the velocity of the flow through a three-dimensional graphene foam changes^[39]. Copyright © 2014 American Chemical Society

是由石墨烯-溶液界面的双电层电容的动态充放电引起, 也可以看作是经典毛细管中流动势模型在半开放石墨烯膜表面结构上的拓展. 当固-液界面的动边界波动速度为cm/s级别时, 产生的电压信号为mV级; 波动更快时, 产生的电压信号可达百毫伏级别, 可以方便地将海浪等的波动行为转化为易监测和处理的电压信号. Huang等人^[38]将泡沫镍上化学气相沉积的三维石墨烯泡沫置于流体管道中, 当不同流速的水流流过时, 石墨烯泡沫两端产生了微安级别的电流; 在流速0~60 cm/s内, 电流从0~25 μ A单调增加, 之后流速再增加则电流饱和, 如图3(c)所示. 他们也测量了乙醇和水混合溶液对三维石墨烯泡沫的作用, 流

速不变时, 随着乙醇比例的增加, 测量到的电流逐渐减小^[39].

对水滴的探测是对流体探测的一种特殊情形, 但在自然界中, 水滴运动(如降雨)的现象又十分频繁. 在单层石墨烯表面, 0.6 mol/L氯化钠盐水液滴滑动时, 会产生与运动速度和液滴体积都成正比的电压信号(图4(a), (b)). 该现象可以用微电容充放电的模型来解释^[1], 由此产生的电压可以指示液滴大小和运动速度. 使用多个探测电极时, 液体在表面上运动的更详细信息都可以被很好地测量, 如使用正交的4个电极, 可以测量到蘸水毛笔的笔尖在石墨烯表面运动的方向和轻重缓急(图4(c), (d)). 使用化学气相

图4 (网络版彩色)石墨烯对水滴运动的传感. (a) 氯化钠盐水滴在石墨烯表面拖动的实验示意图. (b) 大小分别为43和86 μL 的2个盐水滴在不同拖动速度下对应的电压输出. (c) 毛笔蘸水在石墨烯上4个电极间书写的示意图. (d) 毛笔书写时在两对电极间测量到的输出电压随笔尖运动的变化^[1]. Copyright © 2014 Nature Publishing Group. (e) 水滴在石墨烯/PTFE结构表面运动时电压输出与水滴大小的关系, 插图为对应的实验示意图^[47]. Copyright © 2016 American Chemical Society. (f) 石墨烯表面模拟不同降雨量时测量到的电压谱图^[48]. Copyright © 2016 The Royal Society of Chemistry

Figure 4 (Color online) Sensing the motion of water droplets on graphene. (a) A schematic diagram of a sodium chloride solution droplet sliding on graphene surface. (b) The induced voltages versus the moving velocities of a 43 μL droplet and an 86 μL droplet on graphene. (c) Photograph of hand-writing with a Chinese brush on graphene. (d) Sensing the stroke directions (arrows) by the drawing potentials between electrodes E1⁺–E1[–] and E2⁺–E2[–] as shown in (c)^[1]. Reprinted with permission from Ref. [1], Copyright © 2014 Nature Publishing Group. (e) The output voltages of water droplets moving on the surface of graphene/PTFE structure versus the size of water droplets^[47]. Copyright © 2016 American Chemical Society. (f) A voltage output diagram simulating different rainfall amounts^[48]. Copyright © 2016 The Royal Society of Chemistry

沉积的网络状石墨烯^[49,50], 或增加石墨烯和液滴间的黏性^[51], 得到的电压会显著增大. Kwak等人^[47]在石墨烯层下加入聚四氟乙烯(PTFE)增强静电摩擦效应, 结果表明0.1 mL的液滴可以产生大于100 mV的电压, 0.6 mL的液滴可产生0.4 V电压, 3个0.6 mL的液滴串联可以得到1.1 V电压(图4(e)). 在模拟降雨的条件下, 这类石墨烯传感器可以把不同的降雨强度转化为不同的电脉冲谱^[48], 如图4(f)所示.

2.2 对溶液浓度、液体成分的探测

水势信号除了与水的流速等运动参量密切相关外, 也与水中离子浓度密切相关. 水中通常溶解有各种盐类电解质, 盐类电离后以浓度不同的水合离子的形式存在于溶液中. 水或水溶液与低维碳材料接触形成的固-液界面按照离子浓度不同可能有几种类型: (1) 纯水, 固液界面只有水与碳纳米材料接触, 通常

发生在实验室去离子水或气态水分子吸附于固体表面的情况. 这种情况下只需考虑水本身的电离, 其 $\text{H}_3\text{O}^+/\text{OH}^-$ 离子浓度在25℃常温下只有 $1 \times 10^{-7} \text{ mol/L}$ (即pH 7), 对应水体的导电性很差, 阻抗在 $\text{M}\Omega \text{ cm}$ 量级(超纯水阻抗可达 $18.2 \text{ M}\Omega \text{ cm}$), 固液界面可以看作是极少量离子和大量水分子共存的状态. (2) 低浓度溶液, 如天然河湖水 and 地下水等淡水, 盐浓度通常小于1 g/L(对应氯化钠的摩尔浓度约17 mmol/L), 离子完全电离后水合离子浓度在 10^{-3} mol/L 量级, 阻抗一般在 $\text{k}\Omega \text{ cm}$ 级别. 考虑到界面对离子的吸附富集后, 固液界面处可以认为是少数离子和多数水分子共存的状态. (3) 较高浓度溶液, 如海水和盐湖, 盐浓度可达0.6 mol/L以上, 对应水溶液有良好的导电性, 如典型海水等效为0.6 mol/L氯化钠溶液的阻抗约 $23 \Omega \text{ cm}$ ^[52]. 考虑界面的吸附作用后, 固液界面处的水合离子占相当大的比例.

水溶液的离子浓度与其导电性密切相关, 我们可以将氯化钠溶液与晶体硅做类比分析. 从图5可以看到, 氯化钠溶液的离子浓度和阻抗分别取对数后有良好的线性关系: 当水溶液中离子浓度从纯水(去离子水)的 10^{14} cm^{-3} 增加到饱和氯化钠溶液的 10^{21} cm^{-3} 时, 阻抗也从 $10^7 \Omega \text{ cm}$ 降低到几个 $\Omega \text{ cm}$, 变化6个量级. 氯化钠溶液的“离子浓度-阻抗”曲线与晶体硅p型掺杂的“载流子浓度-电阻率”曲线极为相似, 只是在同等载流子浓度下, 氯化钠溶液的阻抗比晶体硅高5个量级, 这与氯化钠溶液中离子质量比硅中电子或空穴的有效质量高4~5个量级基本吻合.

光伏效应中观测到的电压与溶液浓度的关系则通常是非单调变化的: 在低浓度溶液中, 适当的增加离子浓度会增加电压信号输出; 但超过一定浓度后(如 0.01 mol/L), 输出电压则会随离子浓度继续增加而降低. 在多个研究组的不同工作中都观测到了类似的现象: 如在单层石墨烯的表面观察不同浓度氯化钠液滴滑动的电压输出(图6(a)), 结果发现氯化钠浓度约 0.01 mol/L 时输出电压达到最大值^[1]. 将石墨烯的基底更换为压电聚合物聚偏氟乙烯(PVDF)后, “石墨烯/PVDF”上可以观察到输出电压得到大幅度增强, 但仍然是 0.01 mol/L 的氯化钠溶液有最大的电压输出(图6(b))^[53]. 这种光伏效应中的电压-浓度的关系可以简单地定性解释: 输出电压的产生来自于正负离子在外部作用下的分离, 这些外部作用可能是水流, 也可能是“固-液界面”, “固-液-汽界面”的不

断产生-破坏. 当水中离子浓度从纯水的极低浓度开始增加时, 单位面积吸附于界面的离子数目显著增加, 同样的水运动可以分离更多的正负离子对, 正离子或负离子有更大的集聚, 输出电压也随之增加. 但另一方面, 溶液中的离子本身也构成导电通路, 分离后的正负离子有通过溶液电路再平衡的趋势, 该过程与输出电压形成竞争关系. 当溶液浓度在较高浓度范围增加时, 溶液阻抗很小, 水势效应分离正负离子的速度小于已积累电荷通过溶液再平衡而消耗的速度, 输出电压随之降低.

图5 (网络版彩色)NaCl溶液(实线)和p型硅(虚线)中电阻率随载流子浓度的变化. 绘图数据来自于文献[52]

Figure 5 (Color online) The electrical resistivity versus carrier concentration for NaCl solution (solid line) and p-type silicon (dotted line). The data adapted from Ref. [52]

图6 (网络版彩色)低维碳纳米材料对溶液浓度的探测. (a) 氯化钠液滴在石墨烯上电压-流速曲线的斜率随溶液浓度的变化^[1]. Copyright © 2014 Nature Publishing Group. (b) 石墨烯-压电材料异质结上电压对氯化钠溶液浓度变化的响应^[53]. Copyright © 2016 Wiley. (c) 炭黑中水蒸发诱导电压随氯化钠水溶液浓度的变化^[4]. Copyright © 2017 Nature Publishing Group

Figure 6 (Color online) Sensing the solution concentration using low-dimensional carbon materials. (a) Slopes of the voltage-velocity curves for droplets of NaCl solution on graphene with various concentrations^[1]. Copyright © 2014 Nature Publishing Group. (b) The voltage on graphene-piezoelectric material heterostructure responds to the flow of NaCl aqueous solution with various concentrations and deionised (DI) water^[53]. Copyright © 2016 Wiley. (c) The evaporation induced voltage in a carbon black sheet responds to NaCl concentration in water^[4]. Copyright © 2017 Nature Publishing Group

但对于其他产生机制的水伏效应,输出电压与浓度的关系则会不同.在水蒸发电的例子中,溶液浓度越低,炭黑中产生的电势越高,接近纯水时电势可达1.0 V;溶液浓度越高,炭黑中的电势则越小,1 mol/L的盐水溶液中,观测到的电势已经趋近于零(图6(c))^[4],其中具体的微观机制还需进一步揭示.

水溶液流动中的流动势本身也可以辅助溶液流速和浓度的测量,Newaz等人^[35]利用石墨烯场效应晶体管构造了液体流动势的测量装置,他们发现当流体流过石墨烯表面时,石墨烯晶体管转移曲线的电荷中性点的移动与流体溶液的离子浓度和流速有重复性很好的相关性,流体在石墨烯表面附近产生的电化学流动势起到栅压的作用,引起电荷中性点的位置改变.利用这种水溶液流动与石墨烯场效应管的耦合作用,可以测量低至70 nL/min的流量或

40 nmol/L的溶液浓度.

2.3 对湿度的探测

湿度是自然环境最基本的指标之一,不仅广泛用于气象、地质、环境监测等领域,也可以用于生物生理信息的获取.湿度的探索与液态水的探测不同,需要材料与气态的水分子有密切作用.近期一系列研究中发现,纳米碳材料与气态水也会发生多种作用,从而产生可用于湿度监测的信号.

孙连峰研究组^[54]发现在单壁碳纳米管上顺次布置4个电极,当右端2个驱动电极(Motor部分)有驱动电流流过时,左端2个电极(Generator部分)会产生对微量水蒸气浓度敏感的毫伏级电压,产生的电压与水蒸气浓度在0~0.03%(300 ppm)范围内有接近线性的相关性,超过这一浓度则趋于饱和(图7(a)).他们

图7 (网络版彩色)不同水伏器件对湿度的传感性能。(a) 单壁碳纳米管中产生电压对通入水蒸气量的响应,其中通入水蒸气为600 μL时(水蒸气浓度为0.075%或750 ppm),输出电压饱和^[54]。Copyright © 2008 Wiley。(b) 相对湿度变化时氧化石墨烯薄膜中产生的电压^[55]。Copyright © 2015 Wiley。(c) 相对湿度变化时三维聚吡咯中产生的电压^[56]。Copyright © 2016 Wiley。(d) 相对湿度变化时氧化石墨烯器件的电容响应^[57]。Copyright © 2013 Nature Publishing Group。(e) 氧化石墨烯器件的湿度传感性能与商业化高精度湿度传感器性能相当^[58]。Copyright © 2013 American Chemical Society。(f) 枯草芽孢杆菌涂覆的聚吡咯胶带在湿度增加时因吸水膨胀而伸长^[34]。Copyright © 2015 Nature Publishing Group

Figure 7 (Color online) Humidity sensing performance of different hydrovoltaic devices. (a) Dependence of the induced voltage difference along single-walled carbon nanotubes on the quantity of water into a 0.8 L chamber (water vapor 0~0.075%)^[54]. Copyright © 2008 Wiley. (b) Voltage output of a device of graphene oxide film in response to the relative humidity (ΔRH) variation^[55]. Copyright © 2015 Wiley. (c) Voltage output cycles of a device of 3D-polypyrrole in response to the periodic RH variation ($\Delta RH \sim 85\%$)^[56]. Copyright © 2016 Wiley. (d) Capacitance of a graphene oxide device versus RH at 100 Hz, 1 and 10 kHz^[57]. Copyright © 2013 Nature Publishing Group. (e) Sensing performance of a 15 nm thick graphene oxide sensor compared to the response of a commercial high precision RH sensor^[58]. Copyright © 2013 American Chemical Society. (f) Elongation of individual strips as a function of relative humidity^[34]. Copyright © 2015 Nature Publishing Group

将这一现象归因于碳纳米管内侧类似于库仑拖曳的电动力驱动效应,因而增加驱动电流可以增加水蒸气反馈电压的输出。曲良体研究组^[55]制备了内部含氧基团呈梯度分布的氧化石墨烯膜,研究发现当水分子吸附于石墨烯膜表面时能引起内部离子的重新分布,从而在膜两侧产生电势差。该膜能监测到低于5%的湿度变化,在湿度变化30%时,对应输出电压变化~20 mV(图7(b))。他们将氧化石墨烯膜组装成三维泡沫结构后进一步增强了湿度敏感性,湿度变化75%时,样品两端的电势差可在2 s内上升到260 mV^[59]。他们也发现引入锂离子浓度梯度的三维聚吡咯泡沫对湿度非常敏感,当湿度增加时,水分子吸引锂离子向暴露表面迁移,在材料两端产生电势差;当湿度降低时,锂离子又回到材料内部。在他们的实验中,当相对湿度(ΔRH)变化为85%时,材料两端测量到的电势差达60 mV,且该材料经过数百个“湿润-干燥”循环后,仍保持稳定的湿度响应性能(图7(c))^[56]。

除了光伏作用直接产生电压信号外,纳米碳材料也会因水分子吸附而发生电阻等本身电学性质的改变,从而可以指示湿度等信息^[60,61]。Yavari等人^[16]研究了绝对湿度对石墨烯电阻的影响,发现石墨烯的稳定电阻会随着绝对湿度升高而变大:在每kg空气中水分子含量为0.312 kg的高湿度下,石墨烯样品电阻会从34 Ω 上升到84 Ω 。Bi等人^[57]利用氧化石墨烯吸附水的阻抗-频率关系构筑了灵敏的湿度传感器,其在15%~95%湿度范围内的灵敏度比传统湿度传感器高1个量级,如图7(d)所示。诺基亚研究院Borini等人^[58]发现15 nm厚的氧化石墨烯具有最佳的

湿度敏感性,这种氧化石墨烯制备的透明柔性湿度传感器可以实现30 ms内的快速湿度响应,湿度测量精度与商业化的高精度湿度传感器相当(图7(e))。

在湿度变化时,除了输出电信号外,碳纳米材料也可产生伸长、扭转等其他作用。如一些聚合物和氧化石墨烯水凝胶有显著的吸水膨胀、脱水收缩效应,以之纺成纤维的水敏效应会被放大:当环境湿度变化引起“吸水-脱水”过程时,纤维会发生快速的旋转^[62-65]。这在一些生物体系尤其显著,如枯草芽孢杆菌涂覆的聚酰亚胺胶带,在相对湿度从10%变化到90%时,细菌的吸水膨胀会使胶带长度有数倍的伸长(图7(f))^[34,66],以之构造成水轮机结构可在湿度差的驱动下生电。若进一步将碳纳米材料的水伏效应与湿度变形效应结合,则可能获得湿度驱动的新型自驱动微纳机电系统。

2.4 对其他信号的探测

利用水伏效应构造的器件也会对其他物理场的变化,如温度、风速等,产生直接或间接的响应。如用碳纳米管构成表面能捕获器(surface-energy generators, SEGs),当乙醇在表面张力的作用下流过碳纳米管时,在碳管中会产生纳瓦级别的持续电功率输出,以之驱动1个热敏电阻可构成自源的温度传感器(图8(a))^[67],在室温附近温度变化1℃时,电压变化约3 μV 。在炭黑蒸发发电器件中,输出电压与液面风速有明显的关系,当风速在1.8~2.8 m/s之间规律变化时,输出电压也在1.0~1.5 V之间规律变化^[4],以此可作为液面处风速的指示(图8(b))。

图 8 (网络版彩色)(a) 单壁碳纳米管表面能自驱动器件对温度的响应^[67]. Copyright © 2010 Wiley. (b) 炭黑中水蒸发电势对风速的响应^[4]. Copyright © 2017 Nature Publishing Group

Figure 8 (Color online) (a) Self-powered temperature sensing system with a SEG of single-walled carbon nanotubes^[67]. Copyright © 2010 Wiley. (b) Evaporation-induced potential in carbon black responses to the velocity of wind^[4]. Copyright © 2017 Nature Publishing Group

3 结论和展望

低维碳材料经过近30年的发展,已经发展出以富勒烯、碳纳米管、石墨烯为代表的庞大家族,其材料分布广泛、形式多样,便于加工和修饰.以低维碳材料为开端发展的水伏装置可以构成非常简洁的传感系统,特别是流体环境和生物环境的传感系统.如前面我们利用液滴和液面的“曳势”,可以直观地测量液体流动方向、流速乃至离子浓度等流体信息.受波动势的启发,人们最近发现血液流经1根置于细长管中的碳纳米管/聚合物纤维可产生准伏级电

信号^[68],初步展示了生物体系应用的端倪.

将水伏装置从碳材料体系拓展到其他功能结构,如与柔性电路、生物传感器等结合,有可能构造出全新的、自驱动的植入式生理监测装置;与光电等微纳传感器件结合可以构成自供能、自驱动的自源传感系统等^[69];进一步与微逻辑器件结合则可形成集信号传感、处理、分析于一体的水伏智能网络.现有的电子器件大多在固体结构或固体-固体界面工作,水伏器件在原理上工作于固体-液体或固-液-气界面,是对传统电子器件工作模式在维度上的补充,具有巨大的发展空间.

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Summary for “低维碳材料水伏效应的传感应用”

Sensing applications of hydrovoltaic effect in low-dimensional carbon materials

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A variety of phenomena observed in low-dimensional carbon materials, such as waving potential, moving droplet induced drawing potential, flow-induced voltage, water-evaporation-induced electricity, moisture-enabled electricity, have exhibited that low-dimensional carbon materials can generate electrical signals by interaction with dynamic water. This series of phenomena, which is termed as hydrovoltaic effect, has the potential of developing advanced technologies for water energy harvesting and enables the design of flexible sensing systems. This review focuses on the sensing ability of low-dimensional carbon materials to transform those physical/chemical parameters such as flow velocity, ion concentration, humidity, etc. into electrical signals through the hydrovoltaic effect.

Generally speaking, as long as dynamic water (including water solutions, water vapor or water molecules) interacts with low-dimensional carbon materials and simultaneously produce a measurable electrical signal, the signal then can be utilized to monitor various information of the solid-liquid interface. In the first section, we describe the fundamental properties of water-solid interfaces, look back the history of widely used electrical double layer model and four classical electrokinetic effects: electro-osmosis, electrophoresis, streaming potential and sedimentation potential. Then we discuss the recently proposed water-carbon interaction mechanisms, including phonon dragging, electrical friction, pseudocapacitance and dynamic boundary at the liquid-gas interface. Among these mechanisms, the latter two, pseudocapacitance and dynamic boundary, can be considered as an expandedness of streaming potential model under confinement low-dimensional space.

The second section reviews the phenomena of moving water induced voltage and its applications for dynamic water detecting. Diverse kinds of bulk water movement such as flowing, waving and drops sliding, can partially separate the positive ions from negative ions to produce an electrical potential difference along a nano-carbon sample under proper interface conditions. This electrical potential difference is usually proportional to the velocity and mass of the moving water near the solid-liquid interface and thus can be used as an indicator to measure these physical quantities.

The third section introduces several examples of detecting ingredients and concentration of water solution using hydrovoltaic effect. For drawing potential of moving droplets on graphene, the induced voltage increases with increasing ion concentration over a low concentration range (10^{-7} – 10^{-2} mol/L). However, for the electrical potential produced by water evaporation on carbon black film, the output voltage decreases rapidly as the ion concentration increases.

The next section presents the humidity sensing performance of different hydrovoltaic devices of low-dimensional carbon materials. Graphene and graphene oxide devices can be utilized as humidity and temperature sensors with convenient features such as flexibility and transparency. Single-walled carbon nanotubes can output a millivolt level of voltage in response to humidity variation at parts per million level.

Finally, this review makes suggestions for developments in this field by highlighting the potential of hydrovoltaic sensors to be applied in the fields of physiological nanodevices, wearable electronics and self-powered intelligent systems.

hydrovoltaic effect, low-dimensional carbon materials, interface, sensor, graphene

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