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Review

Carbon nanomembranes from self-assembled monolayers: Functional surfaces without bulk

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ABSTRACT

In this topical review we describe the fabrication, characterization and applications of 1 nm thick, mechanically stable carbon nanomembranes (CNMs). They represent a new type of functional two-dimensional (2D) materials, which can be concisely described as "surfaces without bulk". Because CNMs are made by electron-induced crosslinking of aromatic self-assembled monolayers (SAMs), we start with an overview of SAMs with a special emphasis on aromatic SAMs. We describe the chemical modification of SAMs by electron, ion and photon irradiation, introduce the concepts of irradiation-induced crosslinking and chemical nanolithography of

Abbreviations: ABPT, aminobiphenylthiol; AFM, atomic force microscope; AMBPT, (4′-azomethylmalonodinitrile)-1, 1′-biphenyl-4-thiol; B1BPT, bis-1,1-biphenylthiol; B4BPT, bis-4,4-biphenylthiol; BBDS, bisbiphenyl-disulfanyl; BBPDT, bisbiphenylene-dithiol; BE, binding energy; BPT, 1,1′-biphenyl-4-thiol; cABPT, cross-linked aminobiphenylthiol; CBPS, 4′-[(3-trimethoxysilyl)propoxy]-[1,1′-biphenyl]-4-carbonitril; CNM, carbon nanomembrane; CV, cyclic voltammogram; DEA, dissociative electron attachment; DFT, density functional theory; DPN, dip pen nanolithography; EELS, electron energy loss spectroscopy; EFTEM, energy filtered transmission electron microscopy; ESI, electron spectroscopic imaging; EUV, extreme ultraviolet; EUV-IL, extreme ultraviolet interference lithography; FEBIP, focused electron beam induced processing; FRET, fluorescence resonance energy transfer; FWHM, full width at half maximum; GIXD, grazing incidence X-ray diffraction; HBP, 4-hydroxy-1,1′-biphenyl; HDT, hexadecanethiol; HIM, helium ion microscope; His-tag, histidine tag; HOPG, highly oriented pyrolytic graphite; HRTEM, high resolution transmission electron microscopy; IR, infrared spectroscopy; LB, Langmuir–Blodgett; LbL, layer-by-layer; LEED, low energy electron diffraction; LM, light microscope; MEMS, micro electro mechanical systems; μCP, micro contact printing; NBPT, 4′-nitro-1,1′-biphenyl-4-thiol; NEXAFS, near edge X-ray absorption fine structure spectroscopy; NPCF, *p*-nitrophenylchloroformiate; NTA, nitrilotriacetic acid; ODT, octadecanethiol; PE, primary electrons; PFBA, perfluoro butyric acid anhydride; PMMA, poly(methyl methacrylate); PS, polystyrene; RT, room temperature; SAM, self-assembled monolayer; SE, secondary electron; SEM, scanning electron microscopy; SIP, surface initiated polymerization; SIPGP, self-initiated surface photopolymerization and photografting; SIPP, surface initiated photo polymerization; STEM, scanning transmission electron microscopy; STM, scanning tunneling microscopy; TDS, thermal desorption spectroscopy; TEM, transmission electron microscopy; TEPA, tetraethylenepentamine; TFAA, trifluoro acetic acid anhydride; TMR, tetramethyl-rhodamineisothiocyanate; TMV, tobacco mosaic virus; TOF-SIMS, time-of-flight secondary ion mass spectrometry; UHV, ultra-high vacuum; UPS, ultraviolet photoelectron spectroscopy; VRH, variable range hopping; VUV, vacuum ultra-violet; XPS, X-ray photoelectron spectroscopy.

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aromatic SAMs and discuss the underlying physical and chemical mechanisms. We present examples for applications of these phenomena in the engineering of complex surface architectures, e.g., nanopatterns of proteins, fluorescent dyes or polymer brushes. Then we introduce a transfer procedure to release cross-linked aromatic SAMs from their original substrates and to form free-standing CNMs. We discuss mechanical and electrical properties of CNMs and demonstrate that they can be converted into graphene upon annealing. This transformation opens an original and flexible molecular route towards the large-scale synthesis of graphene sheets with tunable properties. Finally, we demonstrate the lithographic and chemical tailoring of CNMs to fabricate novel functional 2D carbon materials: supports for high resolution transmission electron microscopy (HRTEM) and nanolithography, nanosieves, Janus nanomembranes, polymer carpets, complex layered structures. Prospects of combining different types of nanomembranes made of SAMs (CNMs, graphene, nanosieves, Janus nanomembranes) towards the engineering of novel functional nanomaterials for a variety of electronic, optical, lab-on-a-chip and micro-/nanomechanical (MEMS/NEMS) devices are discussed.

Contents