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Recent advances in covalent organic frameworks for separation and analysis of complex samples

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ABSTRACT

Covalent organic frameworks (COFs) is two- or three-dimensional crystalline porous structures constructed by strong covalent bonds between organic subunits. As a new fascinating crystalline porous material, COFs have become a rapidly rising star in various fields such as gas separation and storage, catalysis, drug delivery, sensing and so on. Recently, COFs materials show great potential in analytic chemistry due to their low density, large surface areas, tunable pore size and tailored functionality. Considering that COFs have received considerable attention during the past years and will continue to be one of the interesting and hot research topics. This review describes the application of the porous COFs and their derived materials in proteomics analysis, separation and determination of various substances including harmful substances, isomers and pharmaceuticals. We also discuss the challenges and opportunities of COFs in these applications.

1. Introduction

Covalent organic frameworks (COFs), as an emerging new type of porous materials, is two- or three-dimensional (2D or 3D) crystalline porous structures constructed by strong covalent bonds between organic subunits [1–4]. Since the first two 2D COFs materials were tactfully constructed by Yaghi and co-workers in 2005 via the dehydration reactions of 1,4-benzenediboronic acid itself (COF-1) or with hexahydroxytriphenylene (COF-5), respectively, COFs has been developing rapidly and making great progress in the past decade or so [5–7]. In comparison with traditional crystalline porous materials, the COFs consisting of organic building units with different groups by covalent bonding possess many unique advantages including large surface areas, good chemical and thermal stability, tunable porous structure and low density [8–11]. These advantages together with the highly ordered pore structures make the COFs attract intensive interest of researchers [12–15]. To efficiently synthesize COFs with increased crystallinity and in large scale production, many research groups have explored the synthetic possibility in different ways such as the solvothermal [16–18], ionothermal [19,20], mechanochemical [21] and microwave synthesis [22–24]. In addition, the different reversible reactions containing the dehydration reaction of boronic acid itself or with catechol, the cyclotrimerisation reaction of the nitrile, and the dehydration reaction of aldehyde with amine or hydrazide have been developed to construct novel COFs that mainly includes boron-based COFs, triazine-based COFs, imine-based COFs, respectively, and thus expand the type of COFs [25–30].

With the development of the synthetic strategies, more and more COFs materials with different function and properties have been reported [31–33]. The diversity of COFs materials together with its unique advantages such as tunable pore size and functionality make it show great potential in various applications for gas storage and adsorption, catalysis, sensing and biomedicine [34–37]. Recently, COFs materials with various functionality also were widely in analytic chemistry [38,39]. For example, some COFs have been applied as novel solid carrier or sorbent for the immobilization of enzymes or capture of target analytes including peptides and other small molecules in complex samples, respectively [40,41]. Some COFs-based composites have been synthesized as novel stationary phases for separation and detection of important analytes such as isomers and drug molecules [42–45].

Considering that COFs, as a new member of porous materials, have received considerable attention during the past years and will continue to be one of the interesting and hot research topics in analytic chemistry. This review will give an overview on the current

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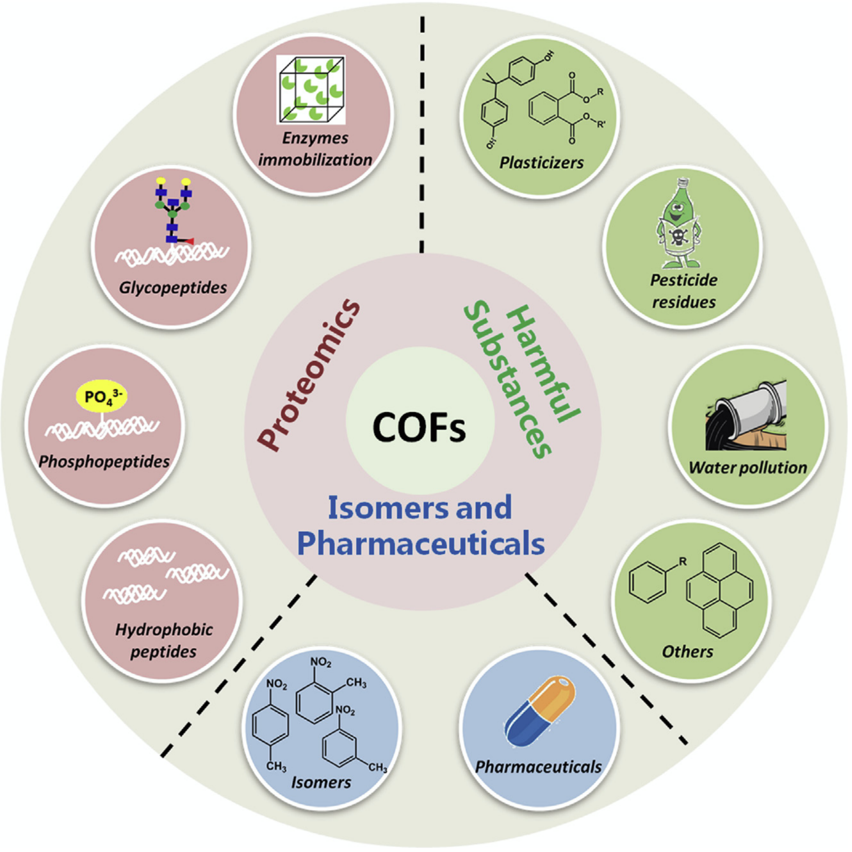
Abbreviations

Azo	4,4-azodianiline
Bd	benzidine
BD-Me_2	*o*-tolidine
BPA	bisphenol A
BPs	bisphenols
BSA	bovine serum albumin
BUs	benzoylurea insecticides
COFs	covalent organic frameworks
CSPs	chiral stationary phases
CTFs	covalent triazine-based frameworks
ECD	electron capture detector
EDMA	ethylene dimethacrylate
GC-FID	gas chromatography-flame ionization detector
HPLC	high performance liquid chromatography
HRP	horseradish peroxidase
ICP-MS	inductively coupled plasma mass spectrometry
IgG	immunoglobulin G
IMAC	immobilized metal affinity chromatography
MA	methacrylic anhydride
MICOFs	molecularly imprinted covalent organic frameworks
MG	magnetic graphene
MMA	methyl methacrylate
MNPs	magnetic nanoparticles
MOAC	metal oxide affinity chromatography
MS	mass spectrometry
MSPE	magnetic solid-phase extraction
NSAIDs	nonsteroidal anti-inflammatory drugs
OA	okadaic acid
Pa-1	paraphenylenediamine
Pa-2	2,5-dimethyl-1,4-benzenediamine
PAEs	phthalate acid esters
PAHs	polycyclic aromatic hydrocarbons
PFCs	perfluorinated compounds
PTMs	post-translational modifications
SPE	solid-phase extraction
TAPB	1,3,5-tris(4-aminophenyl) benzene
Tb	1,3,5-triformylbenzene
Tp	1,3,5-triformylphloroglucinol
TPA	terephthaldicarboxaldehyde
2D	two-dimensional
3D	three-dimensional

research of COFs used as carrier, solid sorbent or stationary phases for sample pretreatment, separation and determination of various substances (Scheme 1). We start with the survey of the COFs and their derivatives applied for proteomics analysis in Section 2. It is then followed by the description of the application of COFs and their composites in the separation and analysis of harmful substance in Section 3. Section 4 summarises the applications of COFs materials in the separation and detection of isomers and



Scheme 1. Overview of the COFs used in various samples pretreatment, separation and determination.