

COF-based electrochromic materials and devices

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The transparency, reflectivity and color for electrochromic (EC) materials can be changed reversibly under low bias^[1]. EC materials find wide application in many fields like microelectronics, energy-saving buildings, automobiles, national defense and aerospace industry^[2]. Compared with inorganic EC materials, organic EC materials have advantages like easy modification of molecular structures, rich color changes and fast-switching speed^[3].

Metal-organic frameworks (MOFs) are one type of organic EC materials^[4]. Dinca *et al.* introduced the redox-active naphthalene diimide (NID) moiety into MOF-74 to achieve high EC performance^[5]. However, the coordination bonds of MOFs are unstable to some electrolytes, thus limiting the application of MOF-based EC materials. Covalent organic frameworks (COFs) are analogues of MOFs. The building units are connected *via* covalent bonds^[6]. COFs based on Schiff-base type linkages are highly stable in aqueous and most organic electrolytes^[7]. COFs show many advantages for EC application. The skeletons and pore structures of COFs can be facilely adjusted^[8]. The pores of COFs are permanent and continuous. Electrolyte ions can easily pass through the pores to realize fast switching and high cycle stability^[9]. The strong π - π interaction and periodic columnar array structures in 2D COFs facilitate charge transport^[10]. The optoelectronic properties of COFs can be facilely modulated by using different functional groups or side chains^[6]. Thus, COFs are a good platform for developing high-performance EC materials.

Schiff-base condensation reactions provide stable aromatic imine bonds and highly conjugated systems for COFs^[7]. Under the solvothermal reaction conditions, the imine exchange process can last for a long time and finally produce a thin crystalline COF film on the substrate^[11]. In 2019, Hao *et al.* first reported a COF_{TAPA-TTDA} with near-infrared (NIR) EC property^[12]. Tris(4-aminophenyl)amine (TAPA) and thieno [3,2-*b*]thiophene-2,5-dicarbaldehyde (TTDA) were chosen as building units (Fig. 1(a)). These building units render COFs rich color and high stability^[13]. The color of COF_{TAPA-TTDA} can be reversibly changed from red to brown by changing potential between 0 and 1.4 V (Fig. 1(b)). The NIR absorption at 1300 nm can be attributed to the intervalence charge transfer (IVCT) between triphenylamine cation radicals. Though COF_{TAPA-TTDA} only exhibits moderate coloration efficiency and

switching speed (Table 1), it proves the feasibility of COF-based EC materials. Xiong *et al.* reported a new EC material COF_{TAPA-TFPA} with reversible color change from yellow to brown^[14]. COF_{TAPA-TFPA} can be viewed as a 2D triphenylamine network with the C=N bond linkage. The adhesion of COF_{TAPA-TFPA} to substrate was improved by using an amine-functionalized ITO glass (Fig. 1(c)). The EC behavior is attributed to the reversible redox reaction of nitrogen in triphenylamine unit and C=N bond (Fig. 2(a)).

The EC performance of COFs can be further adjusted by introducing electron-donating (D) and electron-accepting (A) units. Yu *et al.* used a N,N,N',N'-tetra(*p*-aminophenyl)-*p*-phenylenediamine (TPBD) unit (D) and a 2,1,3-benzothiadiazole-4,7-dicarboxaldehyde (BTDD) unit (A) to construct D-A type material COF_{TPBD-BTDD} (Fig. 2(b))^[15]. Differing from previous materials, COF_{TPBD-BTDD} shows two absorption bands in the visible region. Under bias, cationic radicals and dications form, leading to dramatic color change (Fig. 3(a)). The excellent EC performance of COF_{TPBD-BTDD} is due to the large pore volume which facilitates the ion diffusion, and the reduced bandgap results from the D-A structure (Table 1). Efficient, fast-switching and stable EC COFs can also be realized by introducing D/A units into one building unit. Bessinger *et al.* designed a D-A-D building unit with a central thienoisindigo A moiety and two thienothiophene (or naphthalene) D moieties^[9]. The resulted COF_{Py-ttTh} shows strong light absorption in the visible and NIR regions and very fast switching. COF_{Py-ttTh} shows short coloration/bleaching times of 0.38 s/0.2 s, which outperforms previous COFs by at least an order of magnitude (Table 1).

Further, the EC performance of COFs can be improved by designing novel skeletons, post-modification and developing COF-based hybrid materials. By using N,N,N',N'-tetrakis(4-aminophenyl)-1,4-benzenediamine (TPDA) and terephthalaldehyde (PDA) units, Hao *et al.* developed a highly crystalline three-state NIR EC material COF_{TPDA-PDA} (Figs. 3(b) and 3(c))^[16]. The three-state mix-valence derives from the adjacent triarylamine redox moieties. It causes a strong electronic coupling and improves the EC performance in the NIR region. Owing to the porous structure and IVCT interaction in the mix-valence system, dramatic absorption change and fast-switching (subsecond response) were realized (Table 1). Loading functionalized graphene oxide (FGO) and carbon nanotubes to COFs can reduce the impedance and further improve EC performance^[17, 18]. A FGO-COF developed by Lv *et al.* showed excellent cycle stability^[17]. After 1800 cycles, the contrast reten-

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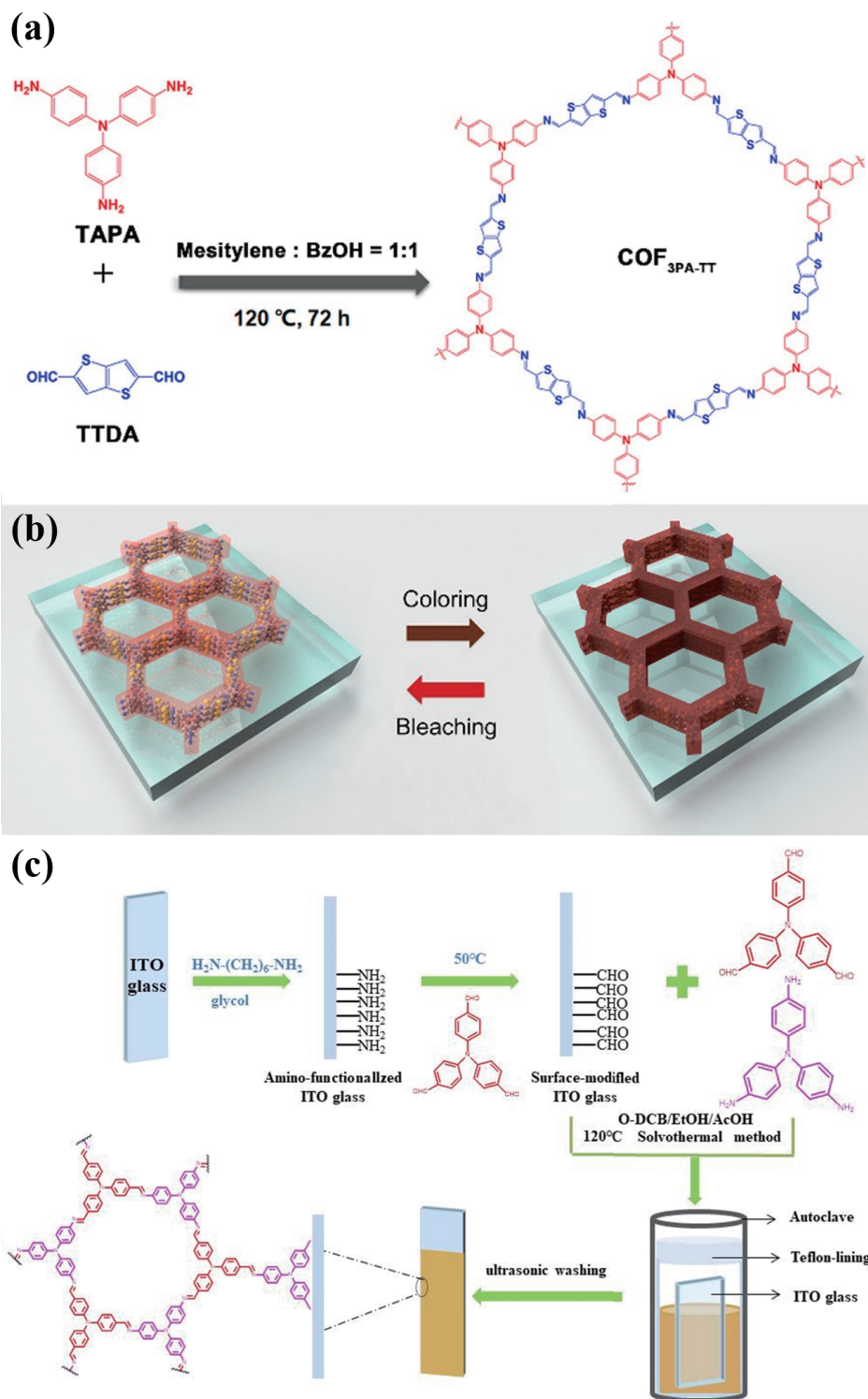


Fig. 1. (Color online) (a) Chemical structures for TAPA, TTDA, and $\text{COF}_{\text{TAPA-TTDA}}$. (b) Schematic for the electrochromic phenomenon of oriented $\text{COF}_{\text{TAPA-TTDA}}$ thin film. Reprinted with permission^[12], Copyright 2019, American Chemical Society. (c) The preparation of $\text{COF}_{\text{TAPA-TFPA}}$ nanofibers. Reprinted with permission^[14], Copyright 2020, Elsevier.

tion even reached 109.1%.

In short, COF-based EC materials can be synthesized by combining various redox units. The uniform porous structures guarantee fast ion diffusion, and the strong π - π stacking in COFs allows efficient charge transport. They present higher stability than conducting polymers, and they show fast switching. Large-area and cheap COF-based EC devices are expected.

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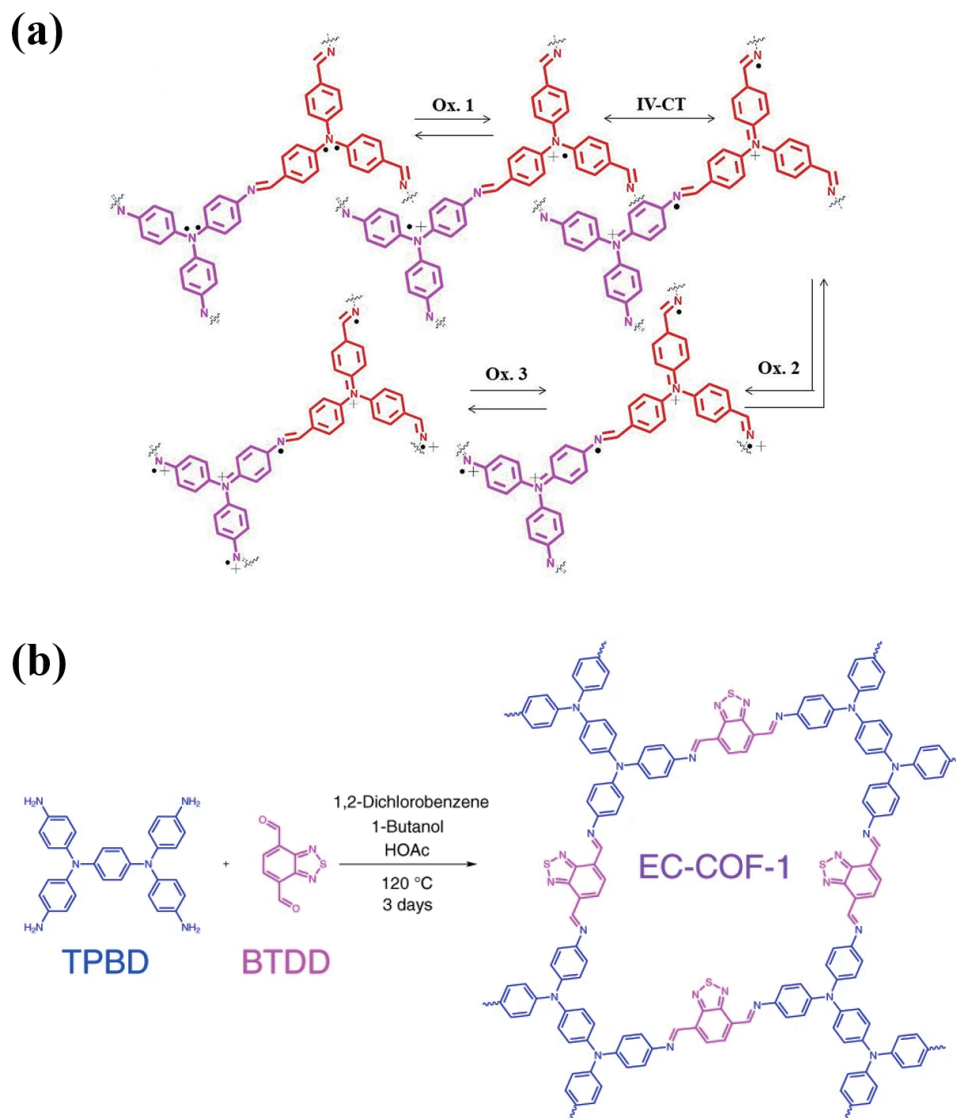


Fig. 2. (Color online) (a) Schematic for the redox process of $\text{COF}_{\text{TAPA-TFPA}}$ nanofibers. Reprinted with permission^[14], Copyright 2020, Elsevier. (b) Synthetic route for $\text{COF}_{\text{TPBD-BTDD}}$. Reprinted with permission^[15], Copyright 2020, Springer Nature.

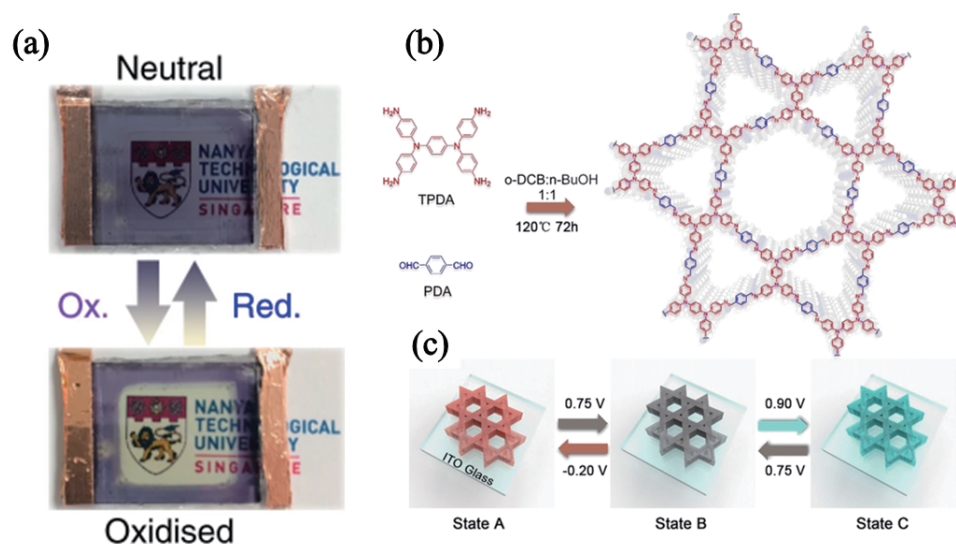


Fig. 3. (Color online) (a) Color switching of $\text{COF}_{\text{TPBD-BTDD}}$ device. Reprinted with permission^[15], Copyright 2020, Springer Nature. (b) Chemical structures for TPDA, PDA, and $\text{COF}_{\text{TPDA-PDA}}$. (c) The three-state electrochromic behavior of $\text{COF}_{\text{TPDA-PDA}}$ thin film. Reprinted with permission^[16], Copyright 2021, Wiley.

Table 1. Electrochromic properties of COF-based EC materials.

EC material	λ_{\max} (nm)	t_c/t_b (s)	Coloration efficiency (cm^2/C)	ΔT (%)	Ref.
COF _{TAPA-TTDA}	610	17.5/10.5	102	21	[12]
	1300	18/13	152	41	
COF _{TAPA-TFPA}	530	4.5/4.9	115	30	[14]
	574	1.8/7.2	284	33	
COF _{TPBD-BTDD}	730	2.6/3.5	246	12	[15]
	550	0.38/0.2	318	–	
COF _{Py-ttII}	660	0.29/0.14	620	–	[9]
	880	–	858	–	
	1050	1.3/0.7	320	52	
COF _{TPDA-PDA}	740	3.4/1.8	227	57	[16]

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