2024「中技社科技獎學金」
2024 CTCI Foundation Science and Technology Scholarship
境外生生活助學金
Living Grant for International Graduate Students

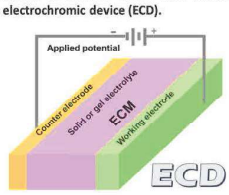
Demonstration of a Conjugated Microporous Polymer-Based Electrochromic Framework Through Metal Catalyst Free Route

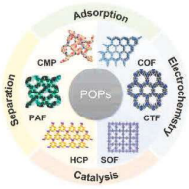
Gaurav Kumar Silori, Kuo-Chuan Ho*
Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan
kcho@ntu.edu.tw

Read full paper

Background

Electrochromic materials (ECMs) refers to a special class of materials whose optical properties can be reversibly altered by applied external potential. Any indoor or outdoor device that harnesses ECMs can be regarded as an electrochromic device (ECD).





Why E-CMPs?
Micropores
π-conjugation
Synthetic tunability
Optical memory

Conjugated microporous polymers (CMPs) are a new class of amorphous organic polymers with π-conjugated skeletons and persistent micropores.

The first conjugated microporous polymers with electrochromic feature (E-CMPs) was displayed in 2015.

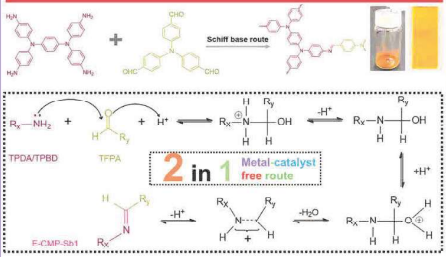
Problem statement

I. Current practices involves the *use of metal catalyst during the synthesis of E-CMPs*. Metal traces greatly hinders E-CMPs end use in electronics, and microelectronics.

II. *Arduousness of the currents methods to produce powder analogs* significantly limits E-CMPs characterization (to illuminate their microporous nature) through adsorption analyzers (or BET), powder X-ray diffractometer (PXRD) and transmission electron microscope (TEM).

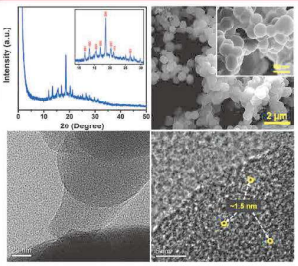
Hmm..is it possible to parallelly produce E-CMP film and powder without metal catalyst pathway?

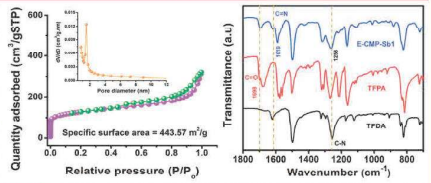
Our *two-in-one* solution



TPDA was selected as the donor (D) due to its tunability, strong redox activity, and previous utilization in the synthesis of electrochromic conductive polymers.
TFPA was opted as an acceptor (A) owing to its versatility to offer stable conjugated linkage, which is hypothesized to enhance conductivity and boost charge transfer in the synthesized framework.

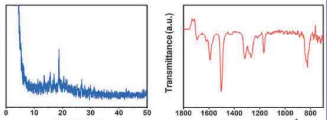
Powder bulk & film characterization

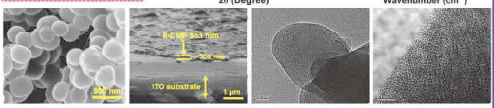




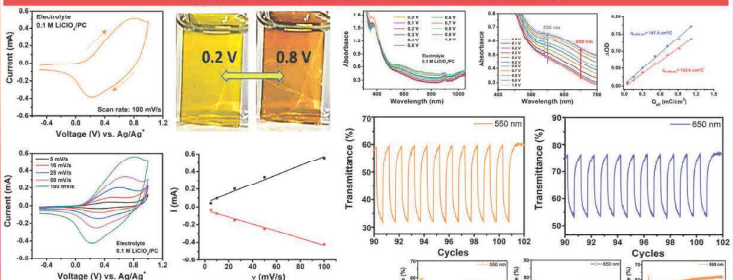
Powder: The XRD patterns showed a broad hump from 10 to 50°, revealing the amorphous nature of the synthesized polymer. The strong peak at ~18.5° suggested the relatively higher availability of (200) planes in E-CMP-Sb1. The HR-TEM evidenced the presence of micropores in the polymer structure. The PSD endowed the pore size of ~1.5 nm, thus ensuring the microporous feature of the synthesized E-CMP-Sb1. The specific surface area (BET model) was determined to be ~443 m^2/g. The vibration modes at 1621 cm^{-1} in the FTIR spectra, corresponding to C=N confirmed the occurrence of Schiff-base reaction.

Film: The XRD spectra of E-CMP-Sb1 film, reflected a broad, amorphous hump in 10–30°, along with the presence of identical peaks previously witnessed for the amorphous powder analogs. Similarly, the FTIR spectra recorded for the E-CMP-Sb1 film registered identical bend stretching (particularly at 1258 and 1621 cm^{-1}) as witnessed earlier. Moreover, the FE-SEM side view of the film/substrate duo, revealed a film thickness of ~300 nm layered on the substrate surface. The film layer was found to be distributed uniformly over the conductive ITO substrate, though the topology varied at some locations. The TEM imaging confirmed the amorphous nature of the synthesized film, while the HR-TEM visual verified the presence of micropores in the framework.
The performed characterization for the film samples and their high resemblance with the powder analogs validates the formation of identical material during the synthesis.

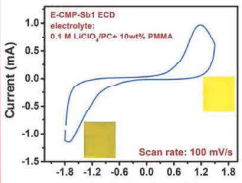


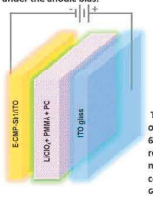


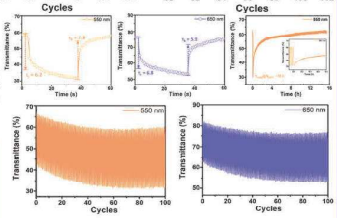
Electrochemical characterization



The cathodic and anodic peak potential of the scanned film was registered to be 0.2 and 0.8 V, thus showcasing a low driving voltage window of 0.6 V. . The synthesized E CMP Sb1 film initially held a yellow-green color, which, upon forward bias (~0.8 V), changed to brownish and reverted to the default yellow-green at ~0.2 V. the electrochromic mechanism for synthesized E-CMP-Sb1 can be attributed to the facile radical formation at the nitrogen centers due to their higher oxidizability under the anodic bias.







The maximum gain in optical density was marked around the wavelengths of ~550 and ~650 nm in the visible range. The E-CMP-Sb1 film at 550 and 650 nm unveiled high coloration efficiency of ~121 and ~147 cm^2/C, respectively. The optical contrast (ΔT) for fabricated ECD at ~550 and ~650 nm was noticed to be ~27 and ~24%, respectively. The retention of optical contrast for E-CMP-Sb1-ECD was noticed to be ~76 and ~91 % at 550 and 650 nm, respectively, after 1000 prolonged cycles.

References:

1. G. K. Silori, S.-C. Chien, L.-C. Lin and K.-C. Ho, *Chem. Eng. J.*, 2024, 484, 149417.
2. G. K. Silori, S. Thoka and K.-C. Ho, *ACS Appl. Mater. Interfaces*, 2024, 16, 4958–4974.
3. G. K. Silori, S. Thoka and K.-C. Ho, *ACS Appl. Mater. Interfaces*, 2023, 15, 25791–25805.
4. Y. Liao, H. Wang, M. Zhu and A. Thomas, *Adv. Mater.*, 2018, 30, 1705710.
5. H. Bildirir, I. Osken, T. Ozturk and A. Thomas, *Chem. – A Eur. J.*, 2015, 21, 9306–9311.
6. D. Bessinger, K. Muggli, M. Beetz, F. Auras and T. Bein, *J. Am. Chem. Soc.*, 2021, 143, 7351–7357.

Summary & future prospects:

I. The synthesis of a novel electrochromic CMP framework through a *two-in-one* approach has been demonstrated. Our utilized method avoids metal catalysts and parallelly generates powder and film analogs of E-CMP-Sb1, thus immensely relaxing their characterization. The characteristic porous nature of the synthesized E-CMP-Sb1 was revealed through BET and TEM analysis. The good coloration efficiency (650 nm) of ~147 cm^2/C fairly approved the E-CMP-Sb1's candidature for electrochromic gadgets.

II. The good tunability in the NIR region enables E-CMP-Sb1's use in military/defense applications. Further, the rich-memory retention feature broadens its scope in energy-saving devices. *Currently, we are working on the methods to achieve metal free E-CMPs with at least three-state electrochromism.*

Connect with me!
gksilori@ntu.edu.tw

Acknowledgements

ITRI Industrial Technology Research Institute
NSTC