



Facile Fabrication of Triphenylamine-Based Redox-Active Nanocomposites by a Sol-Gel Method: Enhanced Electrochromic Response Capability and Stability Performance

Yang-Ze Fan, Chia-Hui Chen, and Guey-Sheng Liou*

In this research, a new design of organic-inorganic hybrid networks involving covalently bonding, novel, electron-donating triphenylamine (TPA)-containing electroactive molecules to inorganic metal oxides is successfully developed by using a facile sol-gel process. These anodically electrochromic TPA-containing materials exhibit multicolor electrochromic behaviors at various oxidation states. By introducing zirconium oxide into electrochromic materials, not only can an excellent optical transparency in the visible light region at a neutral state be achieved given the nature of the large energy bandgap, but the electrochromic switching can also be driven by a lower oxidation potential with an enhanced response capability (shorter coloring times and bleaching times). Moreover, the hybrid films show outstanding electrochemical stability and high reversibility under long-term operations owing to their good adhesion to the electrode. Consequently, the electrochromic devices derived from these novel hybrid electroactive materials reveal a huge potential for electrochromic applications.

Electrochromism is the phenomenon where materials undergo color changes when there is an applied electric current or field.^[1] Basically, the term “chromism” describes material color changes that could be induced by an external stimulus such as temperature, light, and electric current. The theory of electrochromism was first proposed and termed by Platt in 1961.^[2] After that, electrochromic (EC) materials have rapidly mushroomed for more than fifty years. Overall speaking, EC materials typically possess the characteristics of a high transmittance in their neutral state, low power operations, and bistable color changes. To date, various EC materials have been developed which can be classified into five major

categories, including metal oxides,^[3] coordination complexes,^[4] small organic molecules,^[5] side-chain-substituted polymers or main-chain fully conjugated polymers,^[6,7] and arylamine-based polymers.^[8,9] Compared with inorganic EC materials such as iridium(IV) oxide (IrO₂) or tungsten(VI) oxide (WO₃), the organic materials, including small molecules such as viologens and polymers, possess the merits of good coloration performance, ease of processing, and low cost. Notably, since 2005, our group has reported on some solution-processable, high-performance polymers that utilized triphenylamine (TPA) derivatives as EC moieties.^[10] During the oxidation process, TPA units transform to radical cations and simultaneously make the observed coloration change. In addition, TPA and its derivative-based polymers

are promising EC materials that could provide multicolor changes, high contrast, and rapid responses. Recently, hybrid EC materials incorporating inorganic solids into electroactive polymers have been rapidly developed, especially for metal oxides such as titanium(IV) oxide (TiO₂), zirconium(IV) oxide (ZrO₂), and WO₃.^[11–13] Additionally, conductive nanomaterials such as carbon nanotubes,^[14] graphene,^[15] gold,^[16] and silver nanowires are good candidates for EC hybrid materials.^[17,18]

For most EC hybrid designing concepts, polymers are mainly used as a matrix to blend with inorganic materials. However, there are a few studies about small molecules/inorganic composites in EC applications. Recently, an electrochromic device (ECD) assembled with a TiO₂-supported TPA derivative and viologen could achieve panchromatic absorptions by Xu et al., which demonstrated that the TiO₂-supported structure effectively facilitates electron transfers between the fluorine-doped tin oxide (FTO) glass-TiO₂ layer and the EC materials.^[19]

Organic/inorganic hybrids have attracted much attention as promising materials. Therefore, hybrid strategies have been well-developed, especially by the sol-gel process, which can precisely couple organic components containing hydroxy groups with metal alkoxides at a mild temperature through a condensation reaction.^[20] Consequently, the chemical links between organic and inorganic units could be established by covalent bonds, which not only solves the main problem of phase

Y.-Z. Fan, C.-H. Chen, Prof. G.-S. Liou
Institute of Polymer Science and Engineering
National Taiwan University
1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan
E-mail: gslou@ntu.edu.tw

Prof. G.-S. Liou
Advanced Research Center for Green Materials Science and Technology
National Taiwan University
Taipei 10617, Taiwan

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/marc.201900118>.

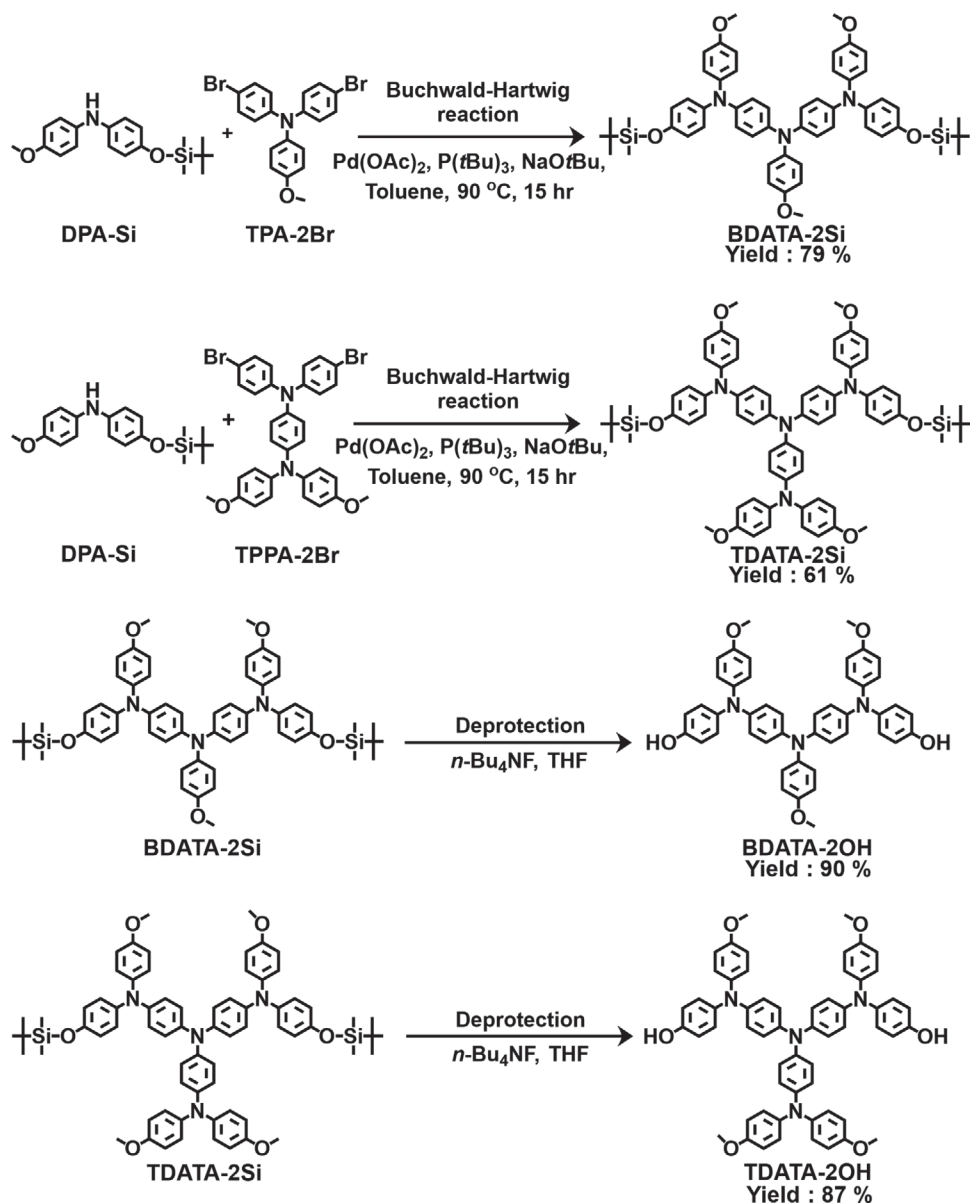
DOI: 10.1002/marc.201900118

separations but also enhances the optical transparency due to the formation of nanodomain size inorganic particles.^[21]

In this work, we report a novel design to covalently combine hydroxyl-containing electroactive compounds with the inorganic component zirconia (ZrO_2) via a sol-gel process. By this approach, the poor film-forming nature of small molecules could effectively be solved without the additional process of polymerization, and at the same time, we also combine the merits of the enhanced electrochromic performance. Herein, we successfully prepared two kinds of novel diphenol compounds with multi-triarylamine units, *N,N'*-bis(4-hydroxyphenyl)-*N,N'*-bis(4-methoxyphenyl)-4-methoxytriphenylamine (BDATA-2OH), and *N,N'*-bis(4-hydroxyphenyl)-*N,N'*-bis(4-methoxyphenyl)-*N'',N''*-di(4-methoxyphenyl)triphenylamine (TDATA-2OH), exhibiting improved EC behavior with multistage coloring changes. By introducing ZrO_2 as the electron acceptor in the hybrid

electrochromic system, the oxidation potential could be reduced,^[21] and the response time shortened.^[22,23] Furthermore, ZrO_2 polymer hybrid films have excellent optical transparency in the visible region due to their large bandgap, as reported in our previous study.^[24] Consequently, such an economical, mild, and simple method could be applied to fabricate compound-based hybrid EC films, providing a strategy and opportunity for ECD applications.

The synthetic procedures of producing BDATA-2OH and TDATA-2OH are shown in Scheme S1, Supporting Information. To prepare these two new diphenol compounds, BDATA-2OH and TDATA-2OH, protecting groups are necessary. Silyl ethers, such as trimethylsilyl (TMS), *tert*-butyldiphenylsilyl (TBDPS), *tert*-butyldimethylsilyl (TBDMS), and triisopropylsilyl (TIPS), are widely used as protecting groups for preparing alcohols in organic synthesis and could be removed



Scheme 1. Synthesis of hybrids by using the sol-gel process.

selectively under mild conditions. The two desired target compounds, BDATA-2OH and TDATA-2OH, were successfully synthesized by removing TBDMS via a deprotection reaction from the precursors of *N,N'*-bis(4-*tert*-butyldimethylsilylphenoxy)-*N,N'*-bis(4-methoxyphenyl)-4-methoxytriphenylamine (BDATA-2Si), and *N,N'*-bis(4-*tert*-butyldimethylsilylphenoxy)-*N,N'*-bis(4-methoxyphenyl)-*N,N'*-di(4-methoxyphenyl)triphenylamine (TDATA-2Si), respectively, which were prepared through an Ullmann reaction, bromination, and a Buchwald–Hartwig amination. The key intermediate of 4-(*tert*-butyldimethylsilyloxy)-*N*-(4-methoxyphenyl)aniline (DPA-Si) was synthesized in two steps from 4-(bromophenoxy)-*tert*-butyldimethylsilane (Br-Si), which is synthesized from *tert*-butyldimethylsilyl chloride and 4-bromophenol, and then followed by a Buchwald–Hartwig amination. The obtained intermediates and target compounds mentioned above were characterized by 1D (^1H NMR, ^{13}C NMR) and 2D (^1H - ^1H -correlation and ^{13}C - ^1H heteronuclear multiple-quantum correlation (HMQC)) NMR spectroscopy, summarized in Figures S1–S9, Supporting Information.

Two kinds of hybrid films were prepared via a sol-gel process, as shown in Scheme 1. The monomers (BDATA-2OH and TDATA-2OH) with hydroxyl groups could react with the zirconium oxide precursors containing alkoxy or hydroxyl groups through the sol-gel process to form hybrid networks. Herein, we can divide the sol-gel system into three parts. One is the anodic EC materials, the TPA derivatives, which provide the electrochromic performance. Another is the inorganic metal oxide. Among them, the bandgap of ZrO_2 is so large there is no absorbance in the visible region, resulting in the high transparency and colorlessness of the hybrid films. Additionally, the introduction of ZrO_2 could improve the adhesion to the electrode leading to a higher electrochemical stability, as well as playing a role for good electron storage to shorten the response time.^[25–27] In addition, diphenyl silane diol oligomer provided by the Industrial Technology Research Institute (ITRI, Taiwan) was used to improve the film formability and uniformity. The nominal weight percentage composition of the hybrids in this work is 69% for the EC material, 17.3% for the ZrO_2 and 13.7% for the diphenyl silane diol oligomer. The hybrid films were

fabricated by drop coating on indium tin oxide (ITO)-coated glass substrate after being filtered through 0.45 mm filters. Moreover, the corresponding polyethersulfone (PES), BDATA-PES, was also synthesized via the silyl method polycondensation, as shown in Scheme S2, Supporting Information, to compare the EC behavior with the hybrid system.^[28,29]

The electrochemical properties of BDATA-hybrid, TDATA-hybrid, and BDATA-PES films were evaluated by differential pulse voltammetry (DPV) in quartz cells with three electrodes with Ag/AgCl as the reference electrode, platinum wire as the counter electrode, and an ITO-coated glass substrate as the working electrode in a acetonitrile (CH_3CN) solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF_4) as the supporting electrolyte under a nitrogen atmosphere, as shown in Figure 1. BDATA-hybrid film exhibits three oxidation peaks at 0.41, 0.63, and 0.93 V, as depicted in Figure 1a. TDATA-hybrid film displays four oxidation peaks at 0.43, 0.67, 0.86, and 1.02 V, as shown in Figure 1b. BDATA-PES film also reveals three oxidation peaks at 0.52, 0.73, and 1.20 V, as presented in Figure 1c. However, the oxidation potentials of BDATA-PES film are much higher than those of BDATA-hybrid film. The interactions between the organic parts (electron donors) and the inorganic metal oxides (electron acceptors) could effectively lower the oxidation potential and enhance the redox response capability of the EC parts.^[22,30] Regarding other polymer type electrochromic materials with BDATA moiety in previous studies,^[29] such as poly(ether oxadiazole), the oxidation peaks at 0.68, 0.91, and 1.41 V are also much higher than BDATA-hybrid.

The spectroelectrochemical properties were measured by cyclic voltammetry coupled with UV–vis spectroscopy to investigate the optical behavior at different applied potentials. The absorption curves of BDATA-hybrid, TDATA-hybrid, and BDATA-PES films correlated to different applied potentials are presented in Figure 2. These films were transparent and colorless in the neutral form (0 V) due to no apparent absorption appearing in the visible region. The absorption peaks could be observed at 324 nm (BDATA-hybrid, Figure 2a), 320 nm (TDATA-hybrid, Figure 2b), and 317 nm (BDATA-PES, Figure 2c). As the applied potential (0–0.55 V) increases, the intensity of the characteristic absorption peaks of BDATA-hybrid

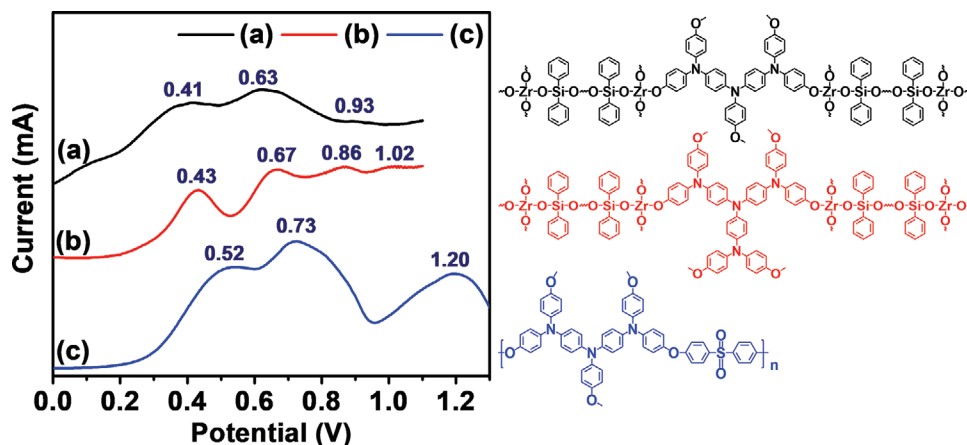


Figure 1. Differential pulse voltammetry diagrams of a) BDATA-hybrid, b) TDATA-hybrid and c) BDATA-PES films onto an ITO-coated glass substrate in CH_3CN containing 0.1 M TBABF_4 . Scan rate: 2 mV s^{-1} ; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s.

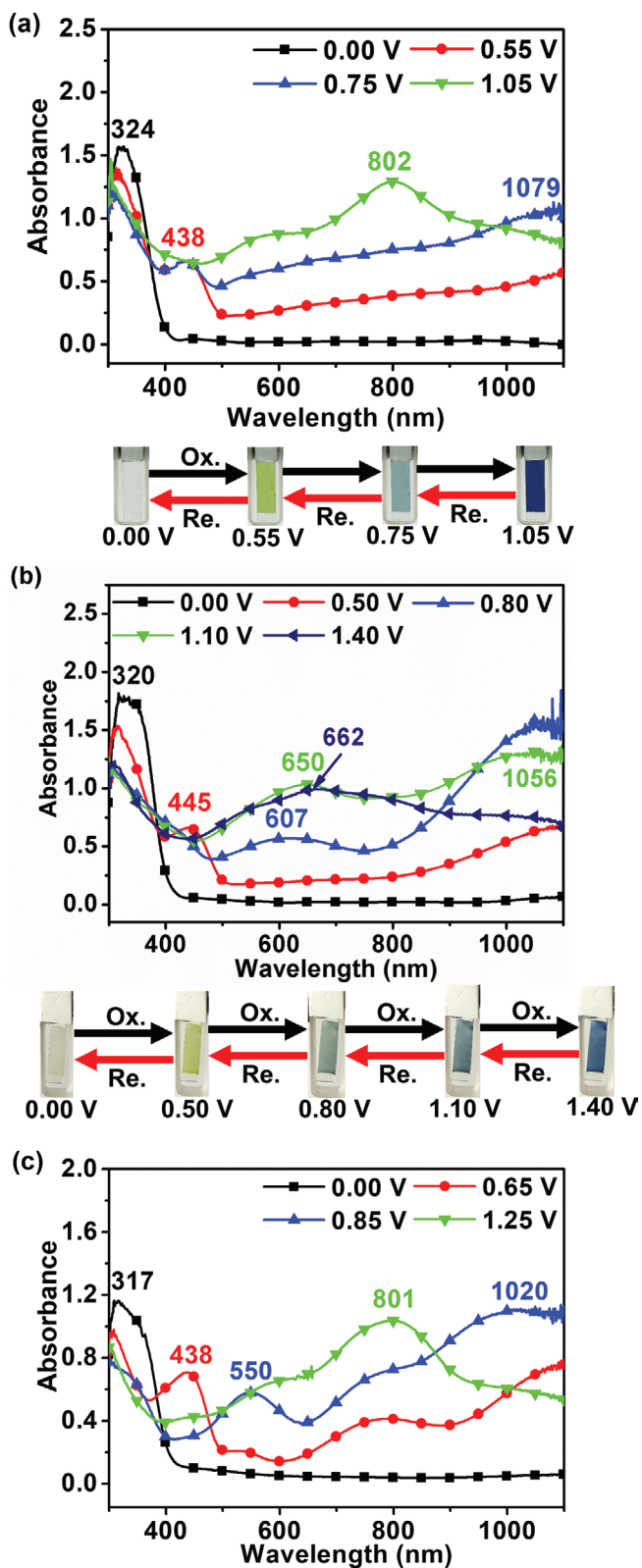


Figure 2. Absorbance spectra and multicolored electrochromic behaviors for a) BDATA-hybrid (850 ± 80 nm), b) TDATA-hybrid (800 ± 60 nm) and c) BDATA-PES (500 ± 60 nm) film onto an ITO-coated glass substrate in CH_3CN containing 0.1 M TBABF₄ at various applied potentials (V versus Ag/AgCl).

film at 438 nm gradually increased, and a color change could also be observed from colorless ($L^* = 94.82$, $a^* = -0.25$, $b^* = 4.08$) to light green ($L^* = 83.48$, $a^* = -10.57$, $b^* = 15.36$), as shown in Figure 2a and Figure S10a, Supporting Information, owing to the formation of mono-cation radical TPA moieties. The absorption peak at 438 nm remained as the potential increased to 0.75 V but with an intensified broad absorption in the near IR region due to intervalence charge transfer (IV-CT) excitations between different electroactive nitrogen centers within TPA moieties.^[31] Meanwhile, the color changed to blue-green ($L^* = 73.23$, $a^* = -1.61$, $b^* = -5.82$). By further increasing the potential to 1.05 V a characteristic absorption appeared at 802 nm and the color became deep blue ($L^* = 69.51$, $a^* = 1.86$, $b^* = -11.41$). For TDATA-hybrid film the characteristic absorption peak at 445 nm increased obviously from the neutral state to 0.5 V with a color change to yellow-green ($L^* = 80.21$, $a^* = -17.5$, $b^* = 55.45$). In the second and the third oxidation states, the characteristic peaks of 607 and 650 nm at 0.8 and 1.1 V appeared, respectively, and the intensity of the IV-CT broad absorption peak in the near IR region also enhanced simultaneously. The applied potential was then adjusted to 1.4 V, related to the fourth oxidation state, and the absorption peak in the near IR region decreased while the characteristic peak in the visible light region slightly redshifted to 662 nm with a navy blue ($L^* = 36.26$, $a^* = -0.51$, $b^* = -20.69$) color, as shown in Figure 2b and Figure S10b, Supporting Information. In comparison with BDATA-hybrid, the EC characteristic absorption peaks from the first to the third oxidation states for BDATA-PES film at 438, 550, and 801 nm, respectively, were similar to those of BDATA-hybrid, as shown in Figure 2c. However, the oxidation potentials of BDATA-PES are much higher than BDATA-hybrid. These results compared well with the oxidation potentials of polyamide containing BDATA segments in our previous report, which need higher potentials of 0.55, 0.80, and 1.25 V to reach saturation.^[32] For TDATA related polyimide type electrochromic materials the oxidation potentials required to reach saturation are 0.60, 0.90, 1.25, and 1.50 V, which are also greater than the hybrid type.^[33,34] This is consistent with electrochemical behaviors measured by differential pulse voltammetry, confirming that the approach of hybrid systems could enhance redox response capabilities.

EC response time was investigated by cyclic voltammetry coupled with UV-vis spectroscopy, which could be used to evaluate the EC efficiency of the hybrid films. The results are depicted in Figure 3. The response time is defined as the time encompassing 90% of the full switching, including the coloration and bleaching processes, because the naked eye cannot distinguish further color changes after the point. When the potential was applied between 0.55 and -0.55 V for BDATA-hybrid film, the response times needed for the coloration and bleaching processes were 2.8 and 0.9 s, respectively (Figure 3a). To compare the differences between BDATA-hybrid and BDATA-PES, the thickness of these two thin films was controlled to be almost the same (200 and 190 nm). As expected, the switching times of BDATA-PES film for the coloring and bleaching processes were 7.4 and 1.4 s, respectively (Figure 3c), which are obviously longer than those of the BDATA-hybrid film mentioned above. These results demonstrate that ZrO_2 as an electron acceptor exerts into organic anodic EC materials, leading to the

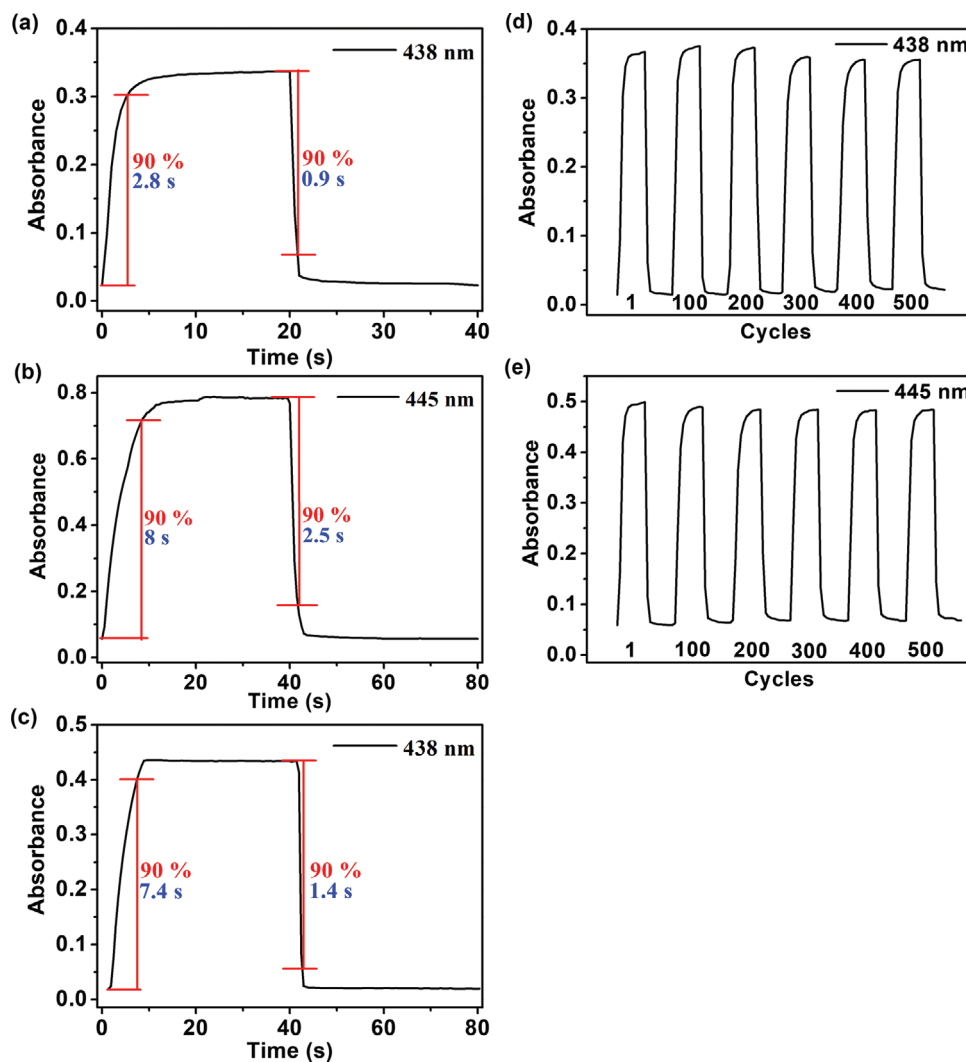


Figure 3. Response time of a) BDATA-hybrid (200 ± 70 nm), b) TDATA-hybrid (850 ± 80 nm), and c) BDATA-PES (190 ± 60 nm) and the cycle stability (80 s per cycle) of d) BDATA-hybrid (200 ± 50 nm) and e) TDATA-hybrid (400 ± 50 nm) films onto an ITO-coated glass substrate in CH_3CN containing 0.1 M TBABF₄ at an applied potential from a) d) 0.55 to -0.55 , b) e) 0.50 to -0.50 and c) 0.65 to -0.65 (V versus Ag/AgCl).

more effective electron transfer and shorter response times. The response times of TDATA-hybrid film with a thickness of 850 nm were 8 and 2.5 s for the coloration and bleaching processes (Figure 3b), respectively.

The stability of these EC hybrid films under long-term operations was also investigated, which is an important parameter to evaluate the feasibility of applications. The long-term stability measurements were conducted at a cycle time of 80 s for each scan. In other words, the applied potentials were maintained for 40 s at both the coloration and the bleaching stage. The long-term stability performance for a continuous 500 cycles is shown in Figure 3. According to the results, both BDATA-hybrid and TDATA-hybrid films showed excellent electrochemical stability and EC reversibility even after 500 continuous oxidation redox cycles. The stable long-term performance could be attributed to the additive properties of enhanced adhesion,^[22,30,35,36] lower oxidation potential, and the fast switching response for the hybrid films.

The newly synthesized electroactive compounds with BDATA and TDATA moieties revealed multicolored EC behavior from a colorless neutral form to their different oxidation states. Afterward, the novel hybrid EC materials, BDATA-hybrid and TDATA-hybrid films with covalent bonds to ZrO₂, could be readily prepared by a sol-gel reaction, which could provide a simple method to broaden the applications for those electroactive compounds without utilizing polymerization. Introducing ZrO₂ as an electron acceptor into the electroactive matrixes not only could reduce the EC oxidation potential and switching time but could also enhance the adhesion to the ITO-coated glass. In addition, the resulting hybrid films exhibit excellent electrochemical stability for long-term operations, even after 500 cycles. Thus, these excellent EC characteristics demonstrate that these novel hybrid films derived from this facile sol-gel approach possess a high potential for the application of high-performance ECDs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Y.-Z.F. and C.-H.C. contributed equally to this work. This work was financially supported by the "Advanced Research Center for Green Materials Science and Technology" from The Featured Area Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (107L9006) and the Ministry of Science and Technology in Taiwan (MOST 107-3017-F-002-001 and 107-2113-M-002-002-MY3).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge storage, electrochromism, hybrid materials, sol-gel, triphenylamine

Received: March 8, 2019

Revised: April 18, 2019

Published online:

- [1] C. G. Granqvist, M. A. Arvizu, I. B. Pehlivan, H.-Y. Qu, R.-T. Wen, G. A. Niklasson, *Electrochim. Acta* **2018**, 259, 1170.
- [2] J. R. Platt, *J. Chem. Phys.* **1961**, 34, 862.
- [3] S. Heo, J. Kim, G. K. Ong, D. J. Milliron, *Nano Lett.* **2017**, 17, 5756.
- [4] Y. W. Zhong, *Electrochromic Materials and Devices*, Wiley-VCH Weinheim, Germany **2015**, p. 185.
- [5] K. C. Ho, C. W. Hu, T. S. Varley, *Electrochromic Materials and Devices*, Wiley-VCH Weinheim, Germany **2015**, p. 91.
- [6] L. Beverina, G. A. Pagani, M. Sassi, *Chem. Commun.* **2014**, 50, 5413.
- [7] P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* **2010**, 110, 268.
- [8] H.-J. Yen, G.-S. Liou, *Polym. Chem.* **2018**, 9, 3001.
- [9] H.-J. Yen, G.-S. Liou, *Prog. Polym. Sci.* **2019**, 89, 250.
- [10] S.-H. Cheng, S.-H. Hsiao, T.-H. Su, G.-S. Liou, *Macromolecules* **2005**, 38, 307.
- [11] J. M. C. Puguán, H. Kim, *Electrochim. Acta* **2017**, 230, 39.
- [12] V. K. Thakur, G. Ding, J. Ma, P. S. Lee, X. Lu, *Adv. Mater.* **2012**, 24, 4071.
- [13] S. Cong, F. Geng, Z. Zhao, *Adv. Mater.* **2016**, 28, 10518.
- [14] S. Bhandari, M. Deepa, A. K. Srivastava, C. Lal, R. Kant, *Macromol. Rapid Commun.* **2008**, 29, 1959.
- [15] M. P. Araújo, M. Nunes, J. Fonseca, C. Moura, R. Hillman, C. Freire, *J. Colloid Interface Sci.* **2017**, 504, 790.
- [16] S. Xiong, J. Lan, S. Yin, Y. Wang, Z. Kong, M. Gong, B. Wu, J. Chu, X. Wang, R. Zhang, *Sol. Energy Mater. Sol. Cells* **2018**, 177, 134.
- [17] G. Cai, J. Wang, P. S. Lee, *Acc. Chem. Res.* **2016**, 49, 1469.
- [18] H.-Y. Lu, C.-Y. Chou, J.-H. Wu, J.-J. Lin, G.-S. Liou, *J. Mater. Chem. C* **2015**, 3, 3629.
- [19] D. Weng, Y. Shi, J. Zheng, C. Xu, *Org. Electron.* **2016**, 34, 139.
- [20] S. Pandey, S. B. Mishra, *J. Sol-Gel Sci. Technol.* **2011**, 59, 73.
- [21] J. Wen, G. L. Wilkes, *Chem. Mater.* **1996**, 8, 1667.
- [22] S. Xiong, S. L. Phua, B. S. Dunn, J. Ma, X. Lu, *Chem. Mater.* **2010**, 22, 255.
- [23] J. Baek, Y. Kim, H. Oh, E. Kim, *Curr. Appl. Phys.* **2009**, 9, S110.
- [24] C.-L. Tsai, G.-S. Liou, *Chem. Commun.* **2015**, 51, 13523.
- [25] T.-T. Huang, S.-W. Cheng, C.-L. Tsai, G.-S. Liou, *Sci. Rep.* **2017**, 7, 7978.
- [26] C.-L. Tsai, H.-J. Yen, G.-S. Liou, *React. Funct. Polym.* **2016**, 108, 2.
- [27] S.-W. Cheng, T.-T. Huang, C.-L. Tsai, G.-S. Liou, *J. Mater. Chem. C* **2017**, 5, 8444.
- [28] H. R. Kricheldorf, G. Bier, *J. Polym. Sci. A* **1983**, 21, 2283.
- [29] J.-T. Wu, Y.-Z. Fan, G.-S. Liou, *Polym. Chem.* **2019**, 10, 345.
- [30] B.-C. Pan, W.-H. Chen, T.-M. Lee, G.-S. Liou, *J. Mater. Chem. C* **2018**, 6, 12422.
- [31] A. V. Szeghalmi, M. Erdmann, V. Engel, M. Schmitt, S. Amthor, V. Kriegisch, G. Nöll, R. Stahl, C. Lambert, D. Leusser, D. Stalke, M. Zabel, J. Popp, *J. Am. Chem. Soc.* **2004**, 126, 7834.
- [32] G.-S. Liou, H.-Y. Lin, *Macromolecules* **2009**, 42, 125.
- [33] C.-J. Chen, H.-J. Yen, Y.-C. Hu, G.-S. Liou, *J. Mater. Chem. C* **2013**, 1, 7623.
- [34] H. J. Yen, C. J. Chen, G. S. Liou, *Adv. Funct. Mater.* **2013**, 23, 5307.
- [35] Y.-H. Yu, C.-Y. Lai, C.-L. Chen, J.-M. Yeh, *J. Electron. Mater.* **2006**, 35, 1571.
- [36] D. Zhou, B. Che, X. Lu, *J. Mater. Chem. C* **2017**, 5, 1758.