Development of Sheet-Like Anthraquinone Porous Organic Polymer Prepared by Nano-Interfacial Azo Coupling Polymerization for Energy Storage Materials

Kanphitcha Opas and Natthawat Semakul*

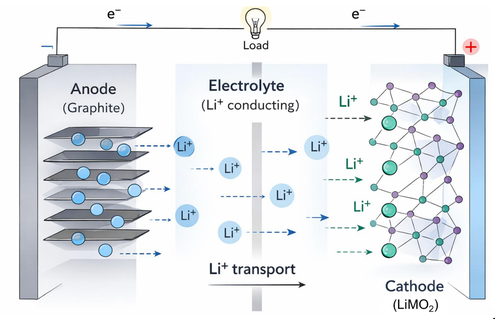
Department of Chemistry, Faculty of Science, Chiang Mai University, Thailand

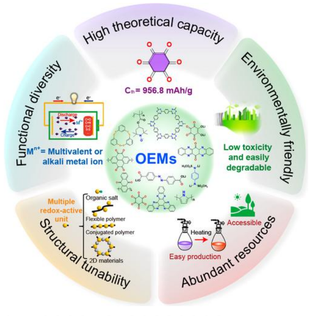
E-mail: kanphitcha_op@cmu.ac.th and natthawat.semakul@cmu.ac.th

Abstract

A nano-interfacial azo coupling polymerization is envisioned to synthesize an AQ-POP with a sheet-like morphology (AQ-POP-NI), as confirmed by scanning electron microscopy and Fourier Transform Infrared (FT-IR) spectroscopy. Nitrogen adsorption–desorption analysis revealed an improved specific surface area (22 m^2 g^{-1}) compared to the conventional AQ-POP (18 m^2 g^{-1}), along with a well-defined pore size distribution. Electrochemical evaluation in CR2016 coin cells demonstrated that AQ-POP-NI exhibits comparable rate capability relative to AQ-POP. Furthermore, the nano-interfacial synthesis approach was extended to fabricate AQ-POP-NI@TiO_2(B) composites that enhanced electrochemical properties of TiO_2(B). The effects of morphology control and composite formation on electrochemical performance will be discussed. Overall, this work presents a practical strategy for morphology control of AQ-POP electrodes and their TiO_2(B) composites, providing new insights into morphology-driven battery performance.

Introduction





Exploration **2022**, *2*, 20220066

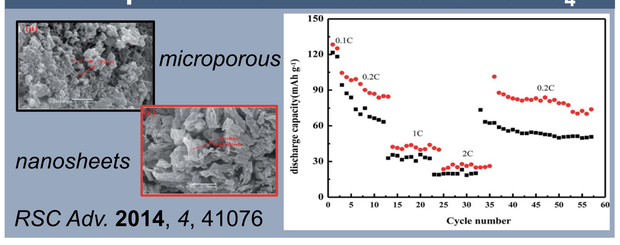
Advantages

- High sustainable
- Tunable redox
- Lightweight

Challenges

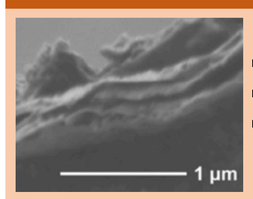
- Dissolution
- Low ionic conductivity
- Capacity fading

Microporous *vs.* Nanosheet $LiVOPO_4$



RSC Adv. **2014**, *4*, 41076

Nano-interfacial azo coupling



- 2D porous nanosheets
- Enhanced proton conductivity
- Application in high-temperature fuel cells

J. Membr. Sci. **2024**, *693*, 122344

Research Objectives

- To synthesize and characterize sheet-like anthraquinone-based porous organic polymer *via* nano-interfacial azo coupling polymerization.
- To investigate the structure-electrochemical performance relationship of AQ-POP-NI as an organic electrode material in lithium-ion batteries.
- To investigate the feasibility of AQ-POP-NI@TiO_2(B) composites for improved electrochemical performance.

Research Methodology

1. Synthesis and characterizations

- Synthesis of AQ-POPs
- composite with TiO_2(B)
- FT-IR spectroscopy
- PXRD
- N_2 sorption study
- SEM

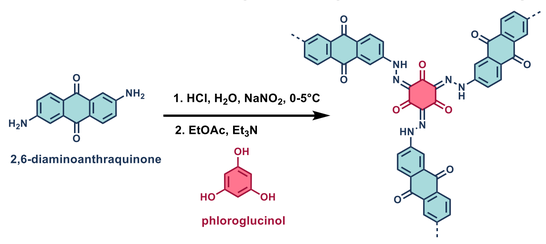
2. Electrochemical study

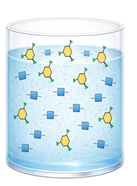
- Assembly of CR2016 coin cells
- rate performance

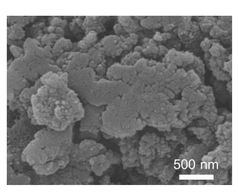
Results and Discussion

Synthesis

Previous work: Aqueous-phase azo coupling polymerization





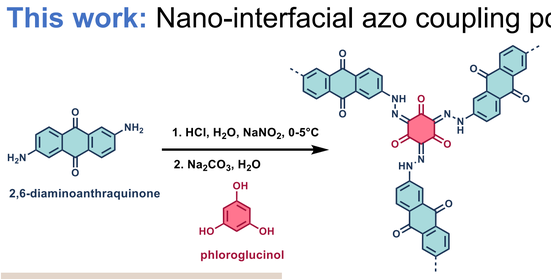


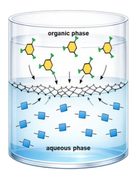
AQ-POP-1
75% yield

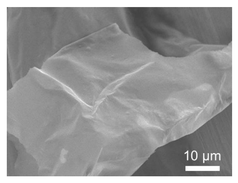
Irregular morphology and aggregation

Semakul et. al. *J. Mater. Chem. A* **2025**, *13*, 35622

This work: Nano-interfacial azo coupling polymerization







AQ-POP-NI
86% yield

Sheet-like morphology

Characterizations

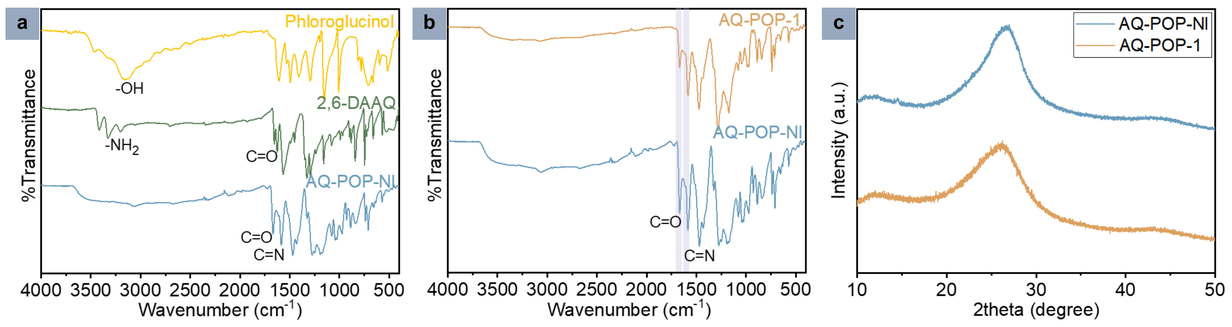
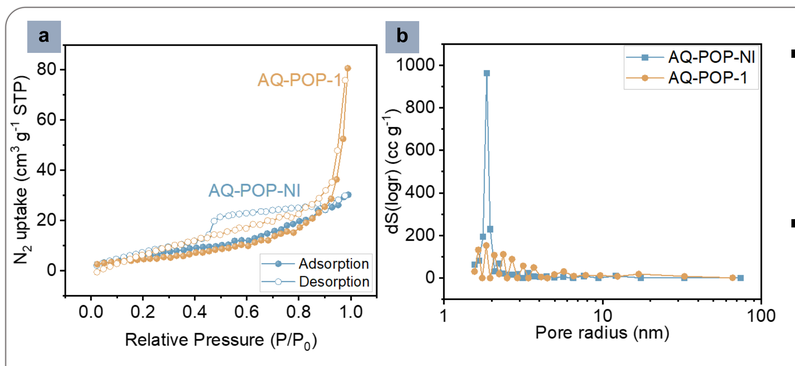


Fig. 1. a) FT-IR spectra of phloroglucinol, 2,6-DAAQ and AQ-POP-NI **b)** FT-IR spectra of AQ-POP-NI and AQ-POP-1 **c)** XRD pattern of AQ-POP-NI and AQ-POP-1.

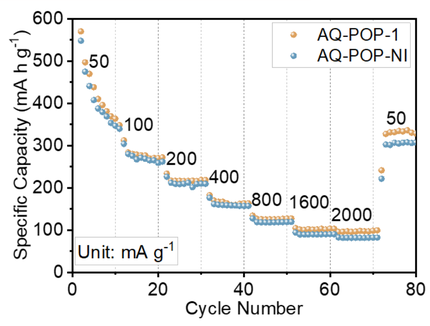
- FT-IR spectra confirm the disappearance of the N–H and O–H stretching bands from the precursors and the appearance of C=O and C=N bond at 1670 and 1581 cm^{-1}, respectively (Fig 1a), with similar features observed for AQ-POP-1 and AQ-POP-NI (Fig 1b).
- XRD patterns show a broad halo peak at 2θ ≈ 26-27°, indicating that the materials possess an amorphous structure (Fig 1c).



- AQ-POP-NI has a mesoporous structure with a specific surface area of 22 m^2 g^{-1}, which is slightly higher than that of AQ-POP-1 (18 m^2 g^{-1}) (Fig. 2a).
- AQ-POP-NI shows a better pore size distribution than AQ-POP-1, with an average pore radius of 3.6 nm (Fig. 2b).

Fig. 2. a) N_2 adsorption-desorption isotherms and **b)** pore size distribution of AQ-POP-NI and AQ-POP-1

Electrochemical study

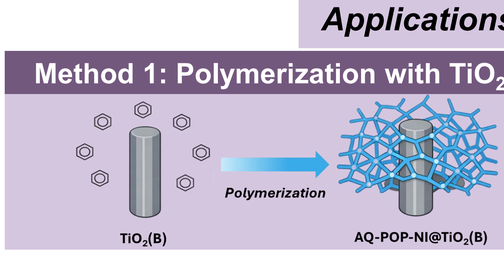


- AQ-POP-1 consistently delivers slightly higher capacities than AQ-POP-NI at each rate, but the two show very similar overall trends, demonstrating comparable rate performance.
- AQ-POP-NI delivers a specific capacity of 346.74 mA h g^{-1} at 50 mA g^{-1} with good capacity retention of 82.01 mA h g^{-1} at 2000 mA g^{-1} and a reversible capacity when the current density returns to 50 mA g^{-1}.

Fig. 3. rate performance of AQ-POP-NI and AQ-POP-1

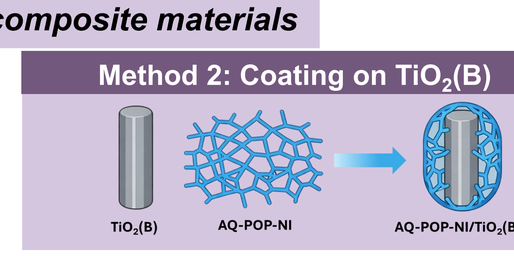
Applications for composite materials

Method 1: Polymerization with TiO_2(B)



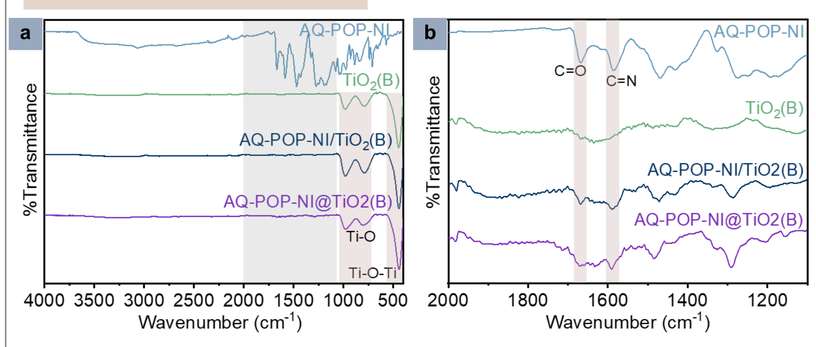
TiO_2(B): *ACS Omega* **2023**, *8* (17), 15360–15370

Method 2: Coating on TiO_2(B)



AQ-POP-NI : TiO_2(B) = 1 : 9

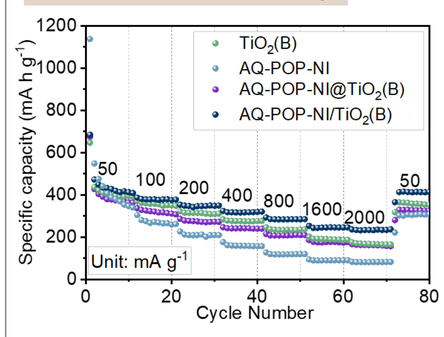
FT-IR Characterization



- TiO_2(B) shows strong low-wavenumber Ti–O and Ti–O–Ti lattice vibrations, which are retained in the composites, confirming the TiO_2(B) phase (Fig. 4a).
- The composites retain the C=O and C=N bands of AQ-POP-NI, confirming successful incorporation with TiO_2(B) while preserving key functional groups.

Fig. 4. a) FT-IR spectra of AQ-POP-NI, TiO_2(B) and AQ-POP-NI/TiO_2(B) composites **b)** enlarged view of the selected region.

Electrochemical study

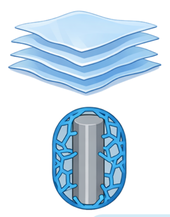


- TiO_2(B) delivers higher capacities and better retention than AQ-POP-NI.
- Compared with pristine AQ-POP-NI, AQ-POP-NI@TiO_2(B) delivers higher capacity and better rate retention, while, relative to TiO_2(B), it shows a slightly lower overall capacity suggesting polymerization onto TiO_2(B) gave composite with deteriorate performance than TiO_2(B).
- Interestingly, simply coating AQ-POP onto TiO_2(B), i.e., forming AQ-POP-NI/TiO_2(B), delivers the improved overall rate performance.

Fig. 5. rate performance of AQ-POP-NI, TiO_2(B) and AQ-POP-NI/TiO_2(B) composites

Conclusion and Outlooks

- Sheet-like porous AQ-POP-NI was successfully synthesized *via* nano-interfacial azo coupling polymerization, exhibiting a higher surface area than AQ-POP-1, while both materials showed comparable electrochemical performance.
- AQ-POP-NI and TiO_2(B) composites were preliminarily investigated by polymerization and coating methods, with the coated method showing better rate performance.



Sheet-like AQ-POPs
- *Mesoporous*
- *High surface area*
- *Comparable electrochemical performance*

AQ-POP-NI/TiO_2(B) coating
- *Improved rate capability*
- *Higher capacity than polymer and TiO_2(B)*

Future work
- *Optimization of composite ratio*
- *Study composites morphology*
- *Further electrochemical investigation*

Acknowledgement

Fundamental Fund 2569 and Department of Chemistry, Faculty of Science, Chiang Mai University are acknowledged for financial support and research facilities. We also extended our gratitude to Assoc. Prof. Dr. Thapanee Sarakornsri (battery testing facilities), Asst. Prof. Dr. Yothin Chimupala (TiO_2(B) material) and Laboratory of Organic Synthesis and Catalysis (Mr. Sirakorn Wiratchan and Mr. Wittawat Punyaarthansakun) for their support and guidance.