

Supporting Information For

Rational Decoration of Porous Organic Polymers with Silver Nanoparticles for Strategic Reduction of Hazardous Nitroaryl Compounds

Mohammed G. Kotp,^a Ahmed F. M. El-Mahdy,^a and Shiao-Wei Kuo^{*a,b}

^aDepartment of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung, 80424, Taiwan

^bDepartment of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan

Corresponding Author:

E-mail: kuosw@faculty.nsysu.edu.tw (S. W. Kuo)

Instrumentation

PerkinElmer spectrums in the range between 4000 and 400 cm^{-1} were employed for detecting FTIR spectrums *via* KBr pellets. Bruker DPX-400 spectrometer was employed for measuring the ^{13}C solid state NMR of CH-POPs. Thermogravimetric analyzer (TA SDT-600) detected thermal gravimetric analysis (TGA) at heating rate of 20 $^{\circ}\text{C min}^{-1}$ under nitrogen flow (10 mL min^{-1}). Micrometrics ASAP 2020 surface area and porosity analyzer was applied for surface areas and porosities estimations of POPs and nanocomposites under progressive N_2 flow (up to ca. 1 atm) in a liquefied N_2 path (77 K) for a achieving the nitrogen isotherm. Scanning electron microscope (JEOL JSM-6700F) was used for imaging of the surface of our POPs. Transmission electron microscopy (JEOL-2010 FEI Tecnai G20) with field-emission microscope (JEOL, Tokyo, Japan) employed for TEM visualizing at 200 KV. Elemental analyzer (CE-440) employed for detecting of (C, N, O, and Ag). UV-2600 spectrophotometer (SHIMADZU) was employed for following up UV-visible spectrums.

Environmental concerns of some utilized chemicals in this research

1. Use of 1,2-Dichloroethane as a Solvent:

The 1,2-dichloroethane is a chlorinated solvent with environmental implications. However, we chose this solvent due to its effectiveness in facilitating the Friedel-Crafts alkylation reaction, which is crucial for achieving the desired polymer structures. Future work will explore alternative solvents that are less harmful while maintaining reaction efficiency.

2. Toxicity of Chloranil:

Regarding the toxicity of chloranil as a starting material in our synthesis of POPs. We would like to clarify our approach and the steps taken to mitigate these concerns:

While chloranil is indeed classified as a toxic compound, we believe that its toxicity is significantly reduced upon polymerization. During the synthesis process, chloranil undergoes chemical transformation, which alters its properties. Furthermore, after polymerization, we implement a

thorough rinsing protocol using water and various solvents to effectively remove any unreacted chloranil residues. This step is crucial in ensuring that the final POPs exhibit minimal toxicity. The extensive rinsing process not only helps eliminate residual chloranil but also contributes to reducing potential environmental impacts. Moreover, we recognize the importance of minimizing the use of toxic starting materials in our research. As part of our ongoing efforts, we are exploring alternative monomers that could replace chloranil while still achieving similar polymer characteristics. This will further enhance the sustainability profile of our synthesis process.

3. *Sustainability of Py and TPA:*

Indeed, both pyrene and TPA are derived from petrochemical sources, which raises questions about their sustainability. However, they were selected for their unique chemical properties that are critical for achieving the desired structural and functional characteristics of our POPs. Their ability to facilitate effective polymerization and enhance the performance of the resulting materials is a key consideration in our research.

While it is true that Py and TPA may not be the most economical options available, we believe that their benefits in terms of performance and functionality justify their use in this context. The resulting CH-POPs exhibit significant advantages, such as high surface area and catalytic activity, which can lead to cost-effective applications in environmental remediation.

Further, we are actively exploring alternative, more sustainable monomers that could replace Py and TPA in future studies. Our goal is to develop methods that not only maintain or enhance the performance of the POPs but also improve their sustainability profile. This includes investigating renewable materials that could serve as viable substitutes.

Furthermore, we revised our script to provide a more balanced discussion regarding the choice of starting materials, emphasizing both their advantages in terms of performance and the ongoing efforts to seek more sustainable alternatives.

4. *Choice of sodium borohydride (NaBH₄):*

We acknowledge that while NaBH₄ is a commonly used reducing agent, it may not be the most environmentally friendly option available. Our choice of NaBH₄ based on the following considerations: the NaBH₄ is favoured in many chemical reduction processes due to its effectiveness and selectivity in reducing nitrophenol to aminophenol. Its ability to operate under mild conditions makes it a practical choice for our reactions. However, we recognize that its use does raise concerns regarding sustainability.

Our future research will focus on optimizing our reduction methodology by incorporating these greener alternatives. We aim to evaluate their performance in comparison to NaBH₄, ensuring that we achieve effective reduction while minimizing environmental concerns.

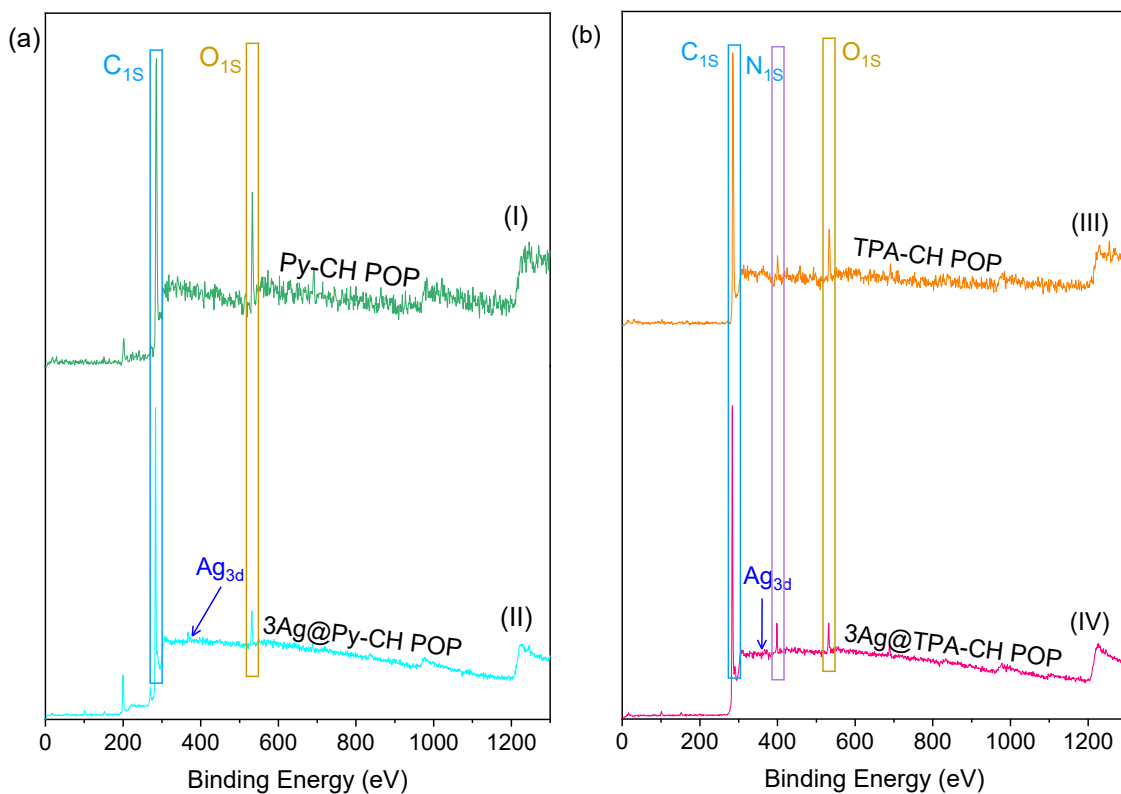


Fig. S1 Wide scan XPS of pristine Py-CH [(a), (I)], and TPA-CH [(b), (III)] POPs as well as 3Ag@Py-CH [(a), (II)], and 3Ag@TPA-CH [(b), (IV)] POPs nanocomposites.

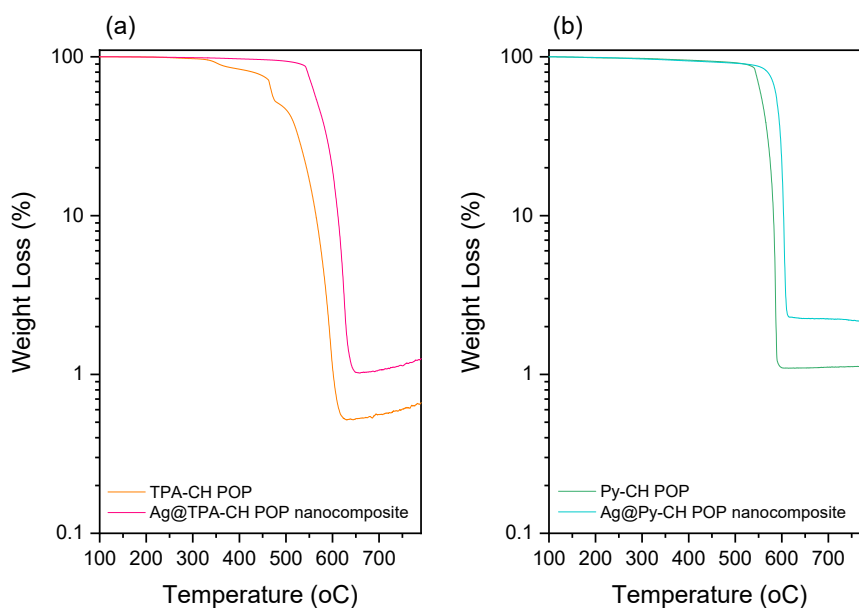


Fig. S2 TGA profiles of Py-CH, Ag@Py-CH, TPA-CH, and Ag@TPA-CH POPs under air.

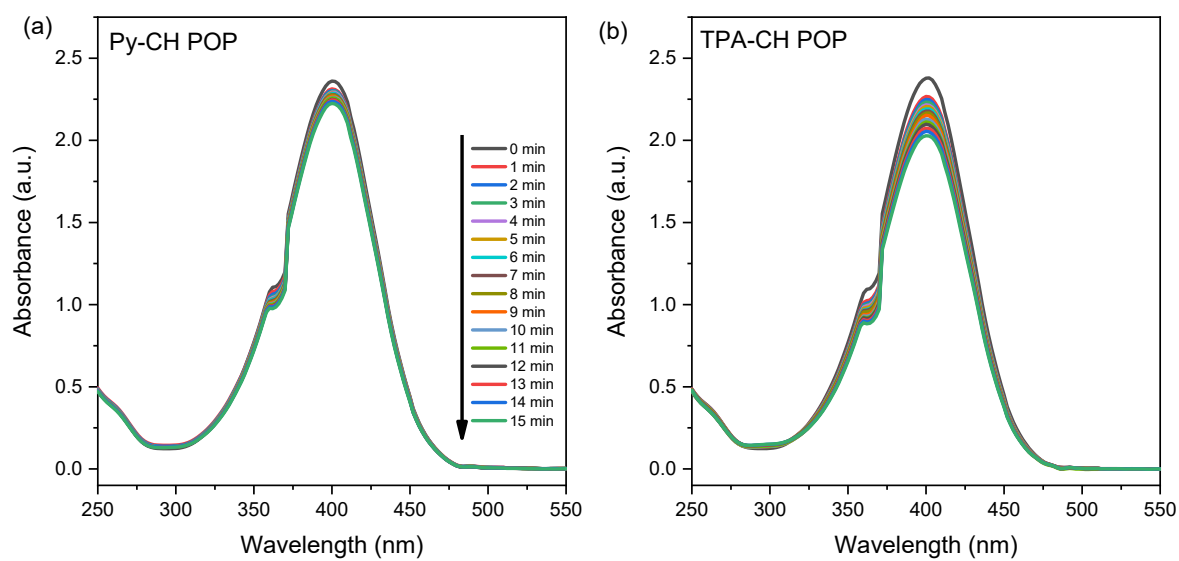


Fig. S3. Time-resolved UV-vis spectra of 4-NP reduction using pristine Py-CH (a), and TPA-CH (b) POPs

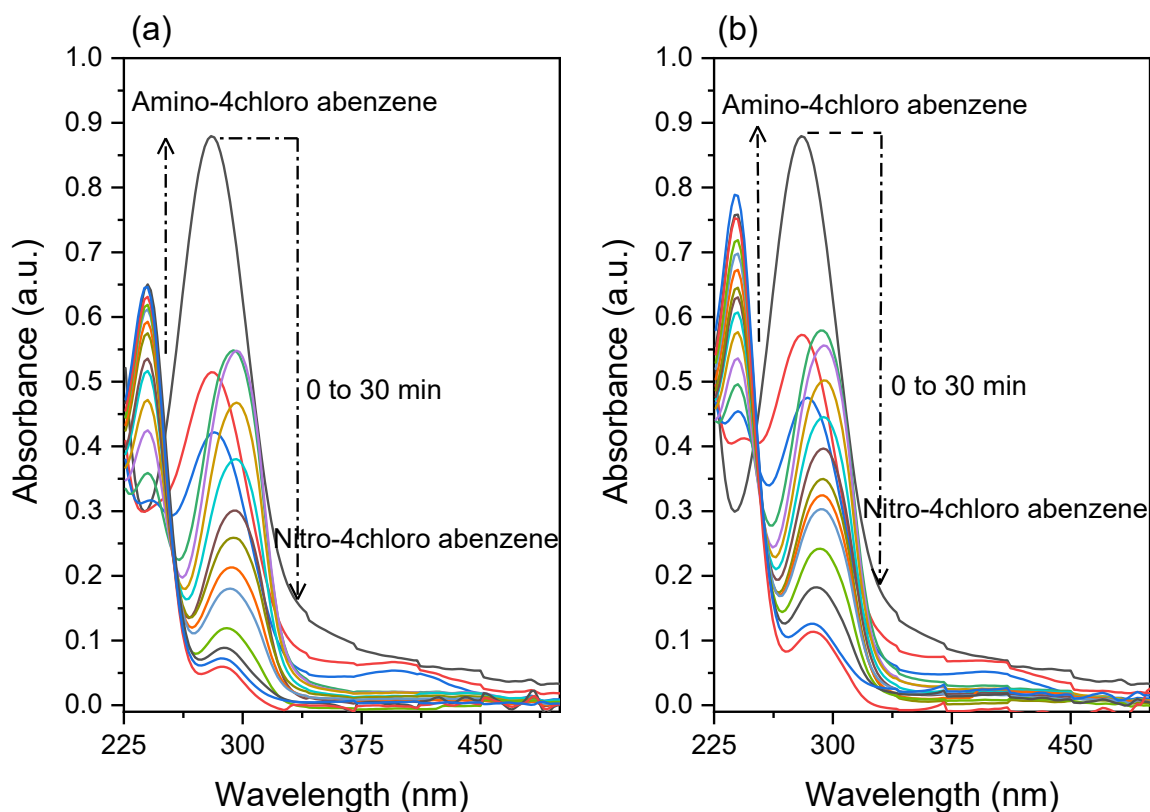


Fig. S4. Time-resolved UV-vis spectra of p-chloro nitrobenzene reduction catalyzed 1Ag@Py-CH (a), and 1Ag@TPA-CH (b) POPs toward the reduction of p-NP

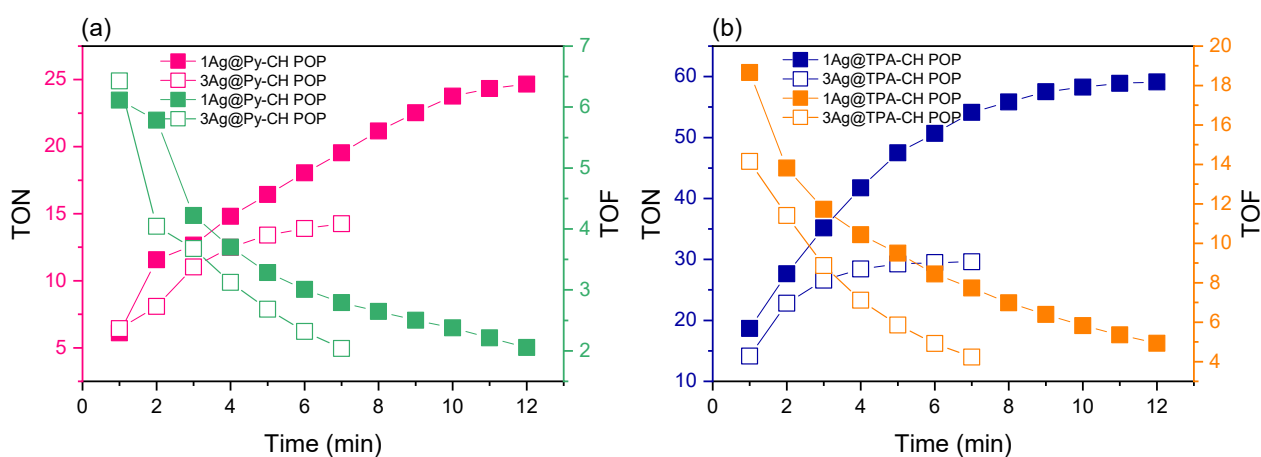


Fig. S5. Turnover number (TON) and turnover frequency (TOF) within the catalytic reduction of p-NP utilizing 1Ag@Py-CH POP (a), 3Ag@Py-CH POP (b), 1Ag@TPA-CH POP (c), 3Ag@TPA-CH POPs.

Table S1. Porous and thermal properties of CH POPs

CMP	S _{BET} (m ² /g)	Pore Sizes (nm)	Pore Volume (cm ³ g ⁻¹)	T _{d10} (°C)	Char Yield (wt%)
Py-CH POP	463	1.83, and 1.07	0.492	563	65.0
TPA-CH POP	822	1.73, and 1.34	0.547	602	79.5

Table S2. Comparative study of Ag@CH-POPs nanocomposites with other Ag decorated materials

Entry	Catalyst	Catalyst dose (mg)	k _{app} (s ⁻¹)	k _{nor} (mg s ⁻¹)	Reference	
1	Ag@ Pyridinyl-Phenanzine Conjugated Microporous Polymer (1Ag@TPPQP)	0.5	9.7×10 ⁻³	19.4	1	
2	Ag@CMP	7.4	1.33×10 ⁻³	1.84	2	
3	Silver nanoparticles-doped cellulose microgels (AgNPs@CMG nanohybrids)	10	3.4×10 ⁻³	0.3	3	
4	Ag anchored magnetic polyaniline-chitosan nanocomposite (Ag@PANI-CS-Fe ₃ O ₄)	1	2.0×10 ⁻³	2	4	
5	Ag@Gd-MOFs	1	21.33×10 ⁻³	21.3	5	
6	Ag-coated PVDF nanofiber mat	NA	5.5×10 ⁻⁴	NA	6	
7	Ag End Capped L-glutathione bridged amphiphilic Diblock Copolymer	0.02	3.22×10 ⁻³	0.161	7	
8	Ag decorated Spherical Covalent Organic Framework (AgNPs@SCOF)	25	1.77×10 ⁻²	7.08	8	
9	Ag@Sugar-based hypercross-linked (AgNPs/SugPOP-1)	micro/mesoporous polymers	1	5.14×10 ⁻³	5.14	9
10	meso-KIT-6-Ag	1	2.25×10 ⁻³	2.25	10	
11	1Ag@Py-CH POP nanocomposite	0.2	4.03×10 ⁻³	19.7	This study	
12	3Ag@Py-CH POP nanocomposite	0.2	9.7×10 ⁻³	48.5		
13	1Ag@TPA-CH POP nanocomposite	0.2	6.34×10 ⁻³	31.7		
14	3Ag@TPA-CH POP nanocomposite	0.2	13.06×10 ⁻³	65.3		

Table S3. Turnover Frequencies (TOF) and rate constant (k) values for different nanocomposite catalysts in the reduction of p-NP.

Nanocomposites	K ($\times 10^{-3}$)	TOF (h^{-1})	Reference
Hollow porous AuNPs	7.47	94	11
Ag/TiO ₂ NPs	32.00	4800.00	12
Pt-PDA/rGO NPs	3.34	72.00	13
CNTM/Au NPs	13.30	9.50	14
Ag-Au@RGO	3.47	152.00	15
Ni-P/NFM NPs	19.40	93.24	16
1Ag@Py-CH POP	4.03	366.76	Our Study
3Ag@Py-CH POP	9.7	385.73	
1Ag@TPA-CH POP	6.34	1119.66	
3Ag@TPA-CH POP	13.06	848.82	

References

- 1 M. G. Kotp, A. F. M. El-Mahdy, T.-L. Yang and S.-W. Kuo, *Microporous Mesoporous Mater.*, 2022, **331**, 111669.
- 2 H.-L. Cao, H.-B. Huang, Z. Chen, B. Karadeniz, J. Lü and R. Cao, *ACS Appl. Mater. Interfaces*, 2017, **9**, 5231-5236.
- 3 Y. Han, X. Wu, X. Zhang, Z. Zhou and C. Lu, *ACS Sustain. Chem. Eng. ACS*, 2016, **4**, 6322-6331.
- 4 M. M. Ayad, W. A. Amer, M. G. Kotp, I. M. Minisy, A. F. Rehab, D. Kopecký and P. Fitl, *RSC Adv.*, 2017, **7**, 18553-18560.
- 5 Y.-P. Wu, G.-W. Xu, W.-W. Dong, J. Zhao, D.-S. Li, J. Zhang and X. Bu, *Inorg. Chem.*, 2017, **56**, 1402-1411.
- 6 L. Miao, G. Liu and J. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 7397-7404.
- 7 M. Jeyapriya, B. Meenarathi and R. Anbarasan, *J. Appl. Polym. Sci.*, 2016, **133**.
- 8 N. Wang, F. Wang, F. Pan, S. Yu and D. Pan, *ACS Appl. Mater. Interfaces*, 2021, **13**, 3209-3220.
- 9 Q. Yin, Q. Chen, L.-C. Lu and B.-H. Han, *Beilstein J. Org. Chem.*, 2017, **13**, 1212-1221.
- 10 M. M. Ayad, N. L. Torad, A. A. El-Nasr and W. A. Amer, *J. Porous Mater.*, 2021, **28**, 65-79.
- 11 M. Guo, J. He, Y. Li, S. Ma and X. Sun, *J. Hazard. Mater.*, 2016, **310**, 89-97.
- 12 X. Wang, Z. Zhao, D. Ou, B. Tu, D. Cui, X. Wei and M. Cheng, *Appl. Surf. Sci.*, 2016, **385**, 445-452.
- 13 W. Ye, J. Yu, Y. Zhou, D. Gao, D. Wang, C. Wang and D. Xue, *Appl. Catal. B.*, 2016, **181**, 371-378.
- 14 H. Wang, Z. Dong and C. Na, *ACS Sustain. Chem. Eng. ACS*, 2013, **1**, 746-752.
- 15 K. Hareesh, R. Joshi, D. Sunitha, V. Bhoraskar and S. Dhole, *Appl. Surf. Sci.*, 2016, **389**, 1050-1055.
- 16 K. Liu, Y. Wang, P. Chen, W. Zhong, Q. Liu, M. Li, Y. Wang, W. Wang, Z. Lu and D. Wang, *Appl. Catal. B.*, 2016, **196**, 223-231.