Supporting Information

Putting Forward Ni-Metallosalphen-Based Porous Organic Polymer for Detoxification of Sulfur Mustard Gas Simulant

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Experimental Section:

<u>Materials</u>:

o-Phenylenediammine, 2-hydroxy-5-methoxy-benzaldehyde, nickel (II) chloride hexahydrate, Iron (III) chloride, triphenylamine were purchased from Sigma Aldrich. Acetonitrile, ethyl acetate, dichloroethane (DCE), dichloromethane (DCM), acetone and methanol (MeOH) were purchased from Finar Chemicals and were used without further purification.

Characterization Techniques:

Wide angle Powder X-ray diffraction (PXRD) analysis of the synthesized materials were performed on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu K α radiation ($\lambda = 1.5406$ Å) with a scan speed of 2° min⁻¹ and a scan range of 2-60° at 30 kV and 15 mA.

The scanning electron microscopy (SEM) technique is used to study the morphology of the materials. The SEM equipment was FEI Verios 460L field-emission SEM (FE-SEM) which is an ultra-high resolution Schott key emitter SEM equipped with an electron diffraction spectroscopy (EDS) detector.

Transmission electron microscopy (TEM) images of the catalysts were captured at 100 kV on a JEOL 1010 TEM.

Brunauer-Emmett-Teller (BET) method is used to determine the surface area of the synthesized materials. The average pore volume and pore size were measured by Barrett-Joyner-Halenda (BJH) method. The BET surface area, pore volume and pore sizes were determined by using the N_2 adsorption-desorption method using BEL Sorb II Instruments, Japan at liquid nitrogen temperature. Before the measurement the samples were degassed at 130 °C for 2 h.

FT-IR spectra of materials were investigated on a DIGILAB (USA) IR spectrometer using the KBr disc method.

Solid-state ¹³C CP MAS NMR studies were performed by using a Bruker Advance III HD 400 MHz NMR spectrometer.

X-ray photoelectron spectroscopy (XPS) were investigated on a Thermo Scientific K-Alpha instrument (monochromatic Al K α radiation, Ephoton = 1486.6 eV). The binding energy (B.E) in each case, that is, core levels and valence band maxima were corrected using an internal reference peak of C 1 s peak centred at 284.8 eV. The Ni k-edge XAS spectra were measured using beamline 44A at Taiwan Photon Source (TPS) of the National Synchrotron Radiation Research Centre (NSRRC, S3 Hsinchu, Taiwan). All spectra were recorded in Transmission mode at room temperature. We have used Athena for raw data treatment (energy calibration, normalization, extraction) and Artemis for the fitting of the EXAFS spectra.

Synthesis of Ni-Salphen Complex from biomass derived isomer of vanillin (Ni@Com):



o-phenylenediamine

Scheme S1. Synthesis procedure of Ni@Com

For the synthesis of Ni-Salphen Complex, o-phenylenediamine (1 mmol), 2-hydroxy-5methoxy benzaldehyde (2 mmol) and NiCl₂.6H₂O (1 mmol) was taken in a 100 ml two necked round bottomed flask to which 30 ml of ethanol was added and refluxed at 80 °C under N₂ atmosphere. After 6h, the resultant mixture was cooled to room temperature and then filtered, washed with ethanol and finally dried under vacuum oven to afford reddish brown color powder product. Further the formation of **Ni@Com** was confirmed by ¹H and ¹³C NMR spectrum.



¹H NMR (500 MHz, CDCl₃): δ 8.15 (s, 2H), 7.67-7.64 (m, 2H), 7.16-7.14 (m, 2H), 7.06 (s, 1H), 7.04 (s, 1H), 6.98-6.95 (m, 2H), 6.61 (d, *J*= 3.1 Hz, 2H), 3.71 (s, 6H).

Figure S1: ¹H NMR spectrum of Ni@Com.



¹³C NMR (125 MHz, CDCl₃): δ 162.6, 153.2, 149.8, 142.8, 127.2, 126.9, 123.2, 118.4, 114.7, 111.0, 55.8.



Synthesis of Ni@T-POP:

In a 100 ml two necked round bottomed flask, Ni-Salphen complex (463.15 mg, 1 mmol), triphenylamine (164 mg, 0.67 mmol) was taken in 30 ml dichloroethane (DCE) to which 650 mg FeCl₃ in DCE solvent was added dropwise and then refluxed at 130 °C for 72 h under N₂ atmosphere. After cooling to room temperature, the resultant mixture was added dropwise to acetone under constant stirring at room temperature and then filtered, washed with methanol, acetone and dichloromethane (DCM). The resulting reddish-brown solid was dried, and then subjected to Soxhlet extraction using methanol as solvent for two days and dried under vacuum at 80 °C for 12 h which afforded 90% yield (with respect to the amount of monomer) of a reddish-brown powder product (Ni@T-POP).



Scheme S2. Synthesis procedure of Ni@T-POP

Liquid-phase Selective Oxidation of Sulfides to Sulfoxides:

Liquid phase selective oxidation of sulfides to sulfoxides was carried out utilizing thioanisole (TA) as a model sulfide compound. In the commencement, a well-dispersed mixture comprising of 20 mg Ni@T-POP catalyst, 0.058 ml of TA (0.5 mmol), and 0.144 ml of TBHP (1.5 mmol) in 10 ml CH₃CN+H₂O solvent (2:1) was heated at 80°C for the specified duration of time. After the completion of the reaction, the catalyst was removed from the reaction mixture through filtration. Further, the product samples are collected at regular interval of time and was analysed by a gas chromatography (Shimadzu 2010) equipped with a flame ionization detector using an INNOWax capillary column (diameter: 0.25 mm, length: 30 m). The products were also identified by GC-MS (Shimadzu, GCMS-QP2010S). Following the validation of the sulfnite to sulfoxide conversion, catalytic oxidation reaction of other sulfur mustard (HD)

compounds was performed under similar reaction condition to transform HDs to less hazardous sulfoxide derivatives.



Scheme S3. Oxidation of thioanisole using Ni@T-POP

Synthesis of pristine ligand (SL):

For the synthesis of pristine ligand (SL), o-phenylenediamine (1 mmol) and 2-hydroxy-5methoxy benzaldehyde (2 mmol) was taken in a 100 ml two necked round bottomed flask to which 30 ml of ethanol was added and refluxed at 80 °C under N₂ atmosphere. After 6h, the resultant mixture was cooled to room temperature and then filtered, washed with ethanol and finally dried under vacuum oven to afford reddish brown colour powder product.



Scheme S4. Synthesis procedure of pristine ligand SL.

Synthesis of Ni_{4.5}@T-POP:

For the synthesis of $Ni_{4.5}$ @T-POP, we have taken a mixture of Ni@Com (347.4 mg, 0.75 mmol and SL (94 mg, 0.25 mmol) along with triphenylamine (164 mg, 0.67 mmol) in the reaction mixture. The remaining synthesis procedure follows the same method as that of our as-synthesized Ni@T-POP.

Synthesis of Ni_{2.9}@T-POP:

For the synthesis of Ni_{2.9}@T-POP, we have taken a mixture of Ni@Com (231.6 mg, 0.5 mmol and SL (188.07 mg, 0.5 mmol) along with triphenylamine (164 mg, 0.67 mmol) in the reaction

mixture. The remaining synthesis procedure follows the same method as that of our assynthesized Ni@T-POP.

Synthesis of Ni_{1.4}@T-POP:

For the synthesis of $Ni_{1.4}$ @T-POP, we have taken a mixture of Ni@Com (115.8 mg, 0.25 mmol and SL (397.9 mg, 0.75 mmol) along with triphenylamine (164 mg, 0.67 mmol) in the reaction mixture. The remaining synthesis procedure follows the same method as that of our as-synthesized Ni@T-POP.

After synthesis of all the materials we have performed inductively coupled plasma-mass spectrometric (ICP-MS) analysis for all the samples which determines the amount of Ni in the porous framework.

Table S1: Elemental C, H, N analysis of Ni@T-POP.

Catalyst	Nitrogen (wt%)	Carbon (wt%)	Hydrogen (wt%)
Ni@T-POP	8.95	89.26	1.56



Figure S3: Wide Angle Powder X-ray Diffraction (PXRD) pattern of Ni@T-POP.



Figure S4: Thermogravimetric (TGA) analysis of Ni@T-POP.

Thermogravimetric analysis (TGA) (**Fig. S5**) of **Ni@T-POP** exhibits no significant weight loss up to 230 °C except for a small loss (~2-3%) around 100 °C due to the loss of solvent molecules inside the pores.



Figure S5: Pore Size Distribution analysis of Ni@T-POP by Non-Local Density Functional Theory (NLDFT) method.



Figure S6: Field emission scanning electron microscopy (FE-SEM) images of Ni@T-POP.



Figure S7: Transmission Electron Microscopy (TEM) images of Ni@T-POP.



Figure S8: XP Survey Spectrum of Ni@T-POP



Figure S9: Core-level XP spectra of (a) C-1s, (b) N-1s, and (c) O-1s of Ni@T-POP, respectively.



Figure S10: The corresponding Ni–N/O first-shell EXAFS fitting curves at K space for Ni@T-POP.

Table S2. Parameters obtained after fitting the XAS data of Ni@T-POP.

First	Coordination	So ²	Fitting range	Fitting range	σ ² (10 ⁻² Å ²)	Bond
Shell	number (N)		in k (Å-1)	in R (Å)		Length
						R(Å)
01.1	2	1.069	2-14.1	1-4	0.721	1.79
N1.1	2	1.069	2-14.1	1-4	0	1.85



Figure S11: Cyclic voltammetry (CV) plot of **Ni@Com** and **Ni@T-POP** referenced to saturated calomel (SCE) at a scan rate of 0.05 V S⁻¹.

The redox property of the Ni-salphen complex and Ni@T-POP were studied in the potential range of +1.5 to -1.5V. The Ni@T-POP demonstrates two quasi reversible peaks. The first reduction peak at -0.04 V is associated with oxidation peak at 0.4 V. Second reduction peak at 0.3 V is associated with an oxidation peak at 0.52 V at a scan rate of 0.05 V S⁻¹. The difference between first and second redox couples was 0.36 and 0.22 V, respectively which confirms the quasi-reversible nature associated with one electron reduction process. Moreover, the higher current density of 5.91 mA cm⁻² for Ni@T-POP clearly indicates the higher conductivity in the polymeric system compared to its Ni@Com precursor with lower current density of 1.18 mA cm⁻².



Figure S12: Oxidation of thioanisole (TA) using different catalytic systems under optimized reaction conditions.

We have accomplished oxidation of thioanisole employing Ni@Com, NiCl₂.6H₂O, Ni@T-POP and without using any catalyst under optimized reaction condition. The performance of the reaction without using any catalyst demonstrated only 17% conversion of thioanisole with 98% selectivity towards sulfoxide. Compared to Ni@Com and NiCl₂.6H₂O, Ni@T-POP displayed enhanced catalytic efficiency for the oxidation of thioanisole with 95% conversion and 98% selectivity for sulfoxide. Ni@Com and NiCl₂.6H₂O achieved 43%, 37% conversion of thioanisole with 98% and 93% selectivity towards sulfoxide respectively.



Figure S13: Oxidation of thioanisole (TA) in different solvent systems under optimized reaction conditions.

We have performed oxidation of TA with various solvent systems such as polar protic solvent, polar aprotic solvent, non-polar solvent etc. Considering both miscibility and proton donation ability, methanol resulted in better catalytic activity in comparison to acetonitrile, methanol, toluene and water. Though water has high protonation ability, but the miscibility and dispersibility is very low. On the other hand, the low catalytic activity in case of acetonitrile in contrast to methanol is due to the higher protonation ability of methanol compared to acetonitrile. Moreover, the higher proton donation ability of water enhances the catalytic activity of acetonitrile towards oxidation of TA. Water plays an essential role on the oxidation of TA which act both as proton donating solvent and as catalyst poison which suppresses the overoxidation of thioanisole and we selectively obtain single oxygen product.



Figure S14: Oxidation of thioanisole (TA) using various oxidants under optimized reaction conditions.

We have also performed the thioanisole oxidation reaction employing different reaction conditions such as under innert (N₂) atmosphere, without any oxidant, and using different oxidants like TBHP, DMSO, H₂O₂, NaOCl and atmospheric O₂ under optimized reaction condition (**Fig. S14, ESI**). Using TBHP as oxidant, the catalytic conversion reaches to 95% with 98% selectivity for sulfoxide whereas, only a 2% conversion was achieved without using any oxidant in the reaction. The performance of the reaction using DMSO, H₂O₂, NaOCl and atmospheric O₂ demonstrated 21%, 68%, 37%, 17% conversion of thioanisole with 100% selectivity towards sulfoxide respectively. Again, recation carried out under N₂ atmosphere resulted only 8% conversion of thioanisole with 100% selectivity for sulfoxide.



Figure S15: Oxidation of thioanisole (TA) using different Ni@T-POP catalyst having different Ni-content under optimized reaction conditions.

Employing different Ni@T-POP materials with various Ni wt%, we have accomplished oxidation of thioanisole under optimized reaction conditions. The Ni@T-POP material with 6 wt% of Ni resulted better catalytic efficiency achieving 95% conversion for thioanisole and 98% selectivity for sulfoxide. The performance of the reaction using Ni@T-POP materials with Ni wt% 4.5%, 2.9% and 1.4% demonstrated 41%, 38%, 22% conversion of thioanisole with 99% selectivity towards sulfoxide repectively. From the performances, it is evident that with increasing Ni wt% in the Ni@T-POP materials, the conversion of thioanisole increases accordingly.

Hot-filtration Test:

To confirm the heterogeneous nature of the Ni@T-POP catalyst, we have carried out hot filtration test. The reaction was carried out by dispersing 20 mg catalyst, thioanisole (0.5 mmol), TBHP (1.5mmol) in 10 ml acetonitrile and water mixture (2:1) in a round bottom flask at 80°C and the reaction was continued for 6h. After that, the catalyst was separated from the resulting solution and the obtained hot reaction mixture was subjected to GC analysis, which exhibited only ~24% conversion of thioanisole for Ni@T-POP. After removing the catalyst, the reaction was again carried out using the remaining supernatant solution up to 12h under similar reaction conditions. The product samples were withdrawn at 8h, 10h and 12h and analysed in gas chromatography which showed no obvious increase in conversion of thioanisole. Atomic absorption (AAS) spectroscopic analysis was carried out to evidence the absence of metal leaching from the catalyst in the filtered reaction mixture.



Figure S16: Schematic diagram for hot-filtration test (a); TA conversion before and after the hot-filtration experiment with respect to time (b), respectively.



Figure S17: Reusability analysis of Ni@T-POP for oxidation of thioanisole.

Reusability study

To confirm the heterogeneous nature of the as-synthesized catalyst, we have performed reusability test for Ni@T-POP up to 6th catalytic cycle under optimized reaction condition. After completion of each catalytic cycle, the catalyst was filtered off and washed with methanol for several times and then dried at 80 °C in vacuum oven for used in the next catalytic run. Up to 6th catalytic cycle the catalyst showed no remarkable change in catalytic activity towards oxidation of thioanisole. After the 6th cycle the reused catalyst (Ni@T-POP-R) was separated through filtration and subjected to Soxhlet extraction with MeOH and DCM for 36 h to remove some oligomers formed during catalysis. Finally, after extraction the Ni@T-POP-R was dried in vacuum oven. Further, in order to better comprehend the change in crystallinity and morphology of the reused Ni@T-POP-R material from the fresh catalyst after 6th consecutive catalytic cycles, we have performed PXRD, N2-adsorption/desorption analysis, FE-SEM and TEM analysis of the material. The PXRD pattern of the reused Ni@T-POP-R demonstrate the same pattern as that of fresh materials thereby confirming the intactness of amorphous nature of the polymer (Fig. S18a, ESI). N₂-adsorption/desorption analysis (Fig. S18b, ESI) of Ni@T-**POP-R** material showed lowered BET surface area (166 m²/g) due to the carbon deposition and blocking of pores during catalysis. FE-SEM & TEM analysis of the reused material reveals

almost the same morphology as that of the fresh material but some random agglomerations have been seen possibly due to the acquaintance of reactive environment up to 6th catalytic cycle which causes slight destruction of the polymeric framework (**Fig. S18c & d, ESI**).



Figure S18: Wide angle PXRD (a), N₂-adsorption/desorption (b), FE-SEM (c) and TEM (d) analysis of reused Ni@T-POP-R after 6th catalytic cycle.

A very small number of oligomers may form during catalysis, which was removed *via* Soxhlet extraction with MeOH and DCM (100 ml, 1:1) for 36 h. We have also performed PXRD analysis, which reveals the amorphous nature of the **Ni@T-POP-R** is maintained even after the 6th catalytic cycle Absence of the sharp peaks after the Soxhlet analyses clearly devoid the idea to the metallic phase related with the FeNi alloy. We have also performed the atomic adsorption spectroscopy (AAS) analysis of the reused **Ni@T-POP-R** to check the presence of any residual Fe in the porous framework. In this case, we didn't find presence of any Fe, even the amount of Fe is below the detection level which denies the formation of FeNi alloy in the framework.



Redox Cycle to activate TBHP Catalytic Oxidation of Thioanisole and role of H_2O

Figure S19: Proposed mechanism for thioanisole oxidation.

Entry	Previously reported catalysts	Conditions	Conv (%)	Ref.
1	Porous metallosalan- organic framework containing titanium-oxo clusters	Sulfide (0.25 mmol) CH ₂ Cl ₂ (1 mL), 1.2 equiv. 30% H ₂ O ₂ , 80 °C, 24 mol% catalyst	77%	1
2	TiO ₂ /AA/Fe nanohybrid	sulfide/TBHP/Cat=1000:2000:3 solvent free, 60 °C.	75%	2
3	VO–TAPT–2,3-DHTA	TBHP (1.5 mmol), Catalyst (20 mg), CH ₃ CN, 25 °C	99%	3
4	H ₅ PV ₂ Mo ₁₀ O ₄₀ @MOF- 808	25 °C; 4 μL of HD, 30 μL of petroleum ether, 5 μL H ₂ O 30 mg catalyst	92%	4
5	Chromium carboxylate MIL-101	5 mg catalyst, 1 mmol of sulfide, H ₂ O ₂ /benzyl phenyl sulfide = 2, CH ₃ CN, r. t, 12 h.	99%	5
6	Ti(salan) based metal– organic frameworks	1.12 mol% sulfide, 6 h, catalyst loading 4.5 mol%, 1.15 equiv. 30% H ₂ O ₂ , CH ₃ COCH ₃	94%	6
7	Ni@T-POP	Catalyst (20 mg), reactant (0.5 mmol), oxidant TBHP (3 equiv.), CH ₃ CN+H ₂ O (5ml, 2:1), 80 °C, time 12 h	95%	Our work

Table S3: Comparison study of decontamination of sulfur mustard with previously reported catalytic systems under different reaction conditions.

Cui and his co-workers developed a Porous metallosalan-organic framework containing titanium-oxo clusters and utilized for enantioselective catalytic sulfoxidation, which showed only 77% of sulfide conversion.¹ Similarly, TiO₂/AA/Fe nanohybrid developed by Feizpour *et al.* showed only 75% thioanisole conversion.² But, some other reports where various porous catalyst like VO-TAPT-2,3-DHTA,³ H₅PV₂Mo₁₀O₄₀@MOF-808,⁴ Chromium carboxylate MIL-101⁵ and Ti(salan)⁶ based MOFs developed by other groups more than 90% TA conversion with good selectivity of sulfoxide. But we found no such report on the use of M-POPs as a catalyst for TA oxidation with TBHP. In this regard, our as-synthesized **Ni@T-POP** one of its kind, which showed very good catalytic activity of ~95% TA conversion with high sulfoxide (~98%) selectivity. This work will surely open new avenue towards the development of such M-POP catalysts for detoxification of sulfur mustards.

¹H NMR Spectra:

Methylphenyl sulfoxide (1B): No purification needed, the crude mixture was collected *via* filtration and extracted with DCM. Finally, the solvent was evaporated with rotary evaporator; 96% yield; yellowish oil. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.48 - 7.41 (m, 3H), 2.68 (s, 3H).



The other products are also collected in a similar way and subjected to ¹H NMR for determination of the structure of the respective products.

Ethylphenyl sulfoxide (2B)









(4-Methoxyphenyl)methylsulfoxide (4B)



(4-Chlorophenyl)methylsulfoxide (6B)



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