Electronic Supplementary Material (ESI) for Materials Advances.
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Cu-containing polyoxometalate-based melamine in environmental remediation of toxic organic pollutants

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Supporting Information

1. Materials and characterizations

All materials such as chemicals, reagents, and solvents including metal salts, melamine (2,4,6-triamino-1,3,5-triazine), sodium borohydride ($NaBH_4$), nitro aromatic compounds, and organic dyes were commercially accessible and purchased from authentic chemical companies. They were used with no more purification. Various techniques were applied for characterization of synthesized compounds. Fourier transform infrared (FT-IR) spectra were performed with a JASCO 6300 FTIR spectrometer (400–4000 cm^{-1}). A thermogravimetric analyzer TG50 was used for thermogravimetric analysis/differential thermal analysis (TGA/DTA) under air atmosphere with heating rate of 10 °C min^{-1} (25-800 °C). The X-ray diffraction (XRD) patterns were recorded on a Bruker diffractometer instrument (D8 advance) with Ni-filtered Cu Kα radiation (λ = 1.54178Å). The UV-vis spectra of nitro aromatic compounds and organic dyes during the reduction reactions were recorded by a Varian 5A spectrophotometer. The elemental mapping and field-emission scanning electron microscopic (FE-SEM) analyses were obtained by a Mira3 TESCAN. Inductively coupled plasma (ICP) was performed on PerkinElmer Optima 7300 DV ICP-OES spectrometer.

2. Preparation of transition metal substituted Keggin-type MPOMs@melamine compounds

At first, an aqueous solution of $[PW_{11}MO_{39}]^{n-}$ was prepared. For this purpose, to a solution of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$, 100 mmol) and disodium hydrogen phosphate (Na_2HPO_4, 9.1 mmol) in deionized water (200 mL) were added metal nitrate (MNO_3 where M = Cr, Mn, Fe, Co, Ni, Cu, and Zn, 12 mmol) under stirring. The pH of solution was adjusted at 4.8

in order to prepare the $[PW_{11}MO_{39}]^{n-}$ aqueous solution [1]. After that, melamine (15 g) was added slowly to the above solution and stirred for 12 h to complete the reaction. Finally, the obtained solids as MPOM@melamine (where M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) compounds were filtered and washed 2-3 times with deionized water and dried in air.

3. Catalytic reduction of toxic nitro aromatic compounds and organic dyes by MPOMs@melamine

A quartz cuvette (3 mL) was charged by aqueous solution of organic dye or nitro aromatic compound (0.1 mM, 2 mL) and aqueous solution of $NaBH_4$ (15 mM, 100 μL) at room temperature. After that, the MPOMs@melamine (where M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) catalyst in solution (1 mM, 40 μL) was added to the reaction mixture and the reduction reaction was initiated. The reaction progress was monitored by UV-vis spectrophotometer. The color of solution was gradually changed from yellow to colorless by the progress of reaction. Furthermore, simultaneous catalytic reduction of some dyes mixture was performed in the same procedure.

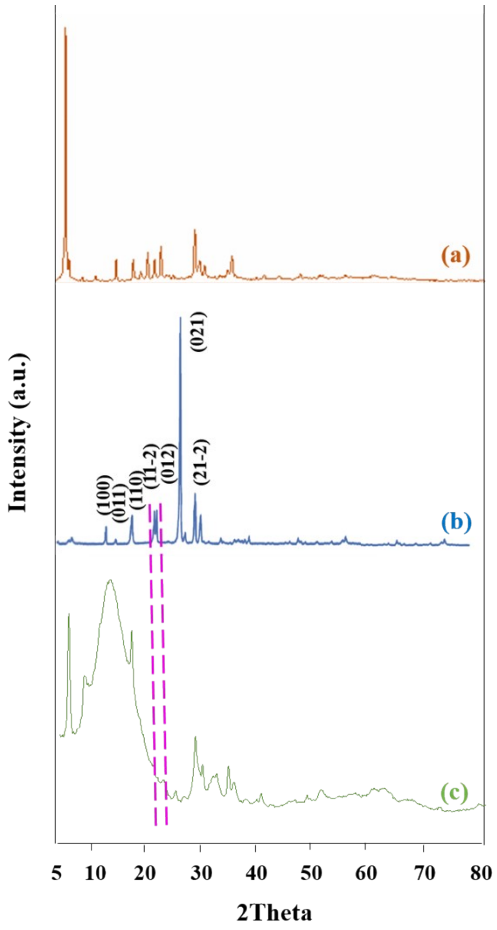


Figure S1. XRD patterns of (a) CuPOM, (b) melamine, and (c) CuPOM@melamine.

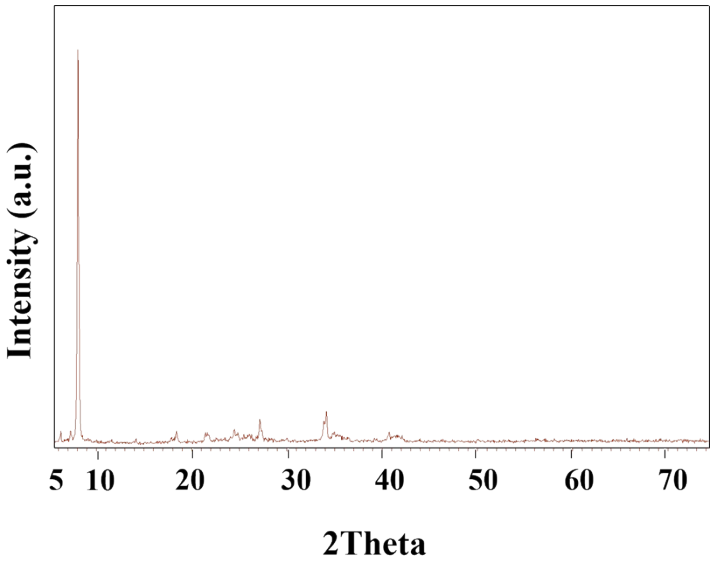
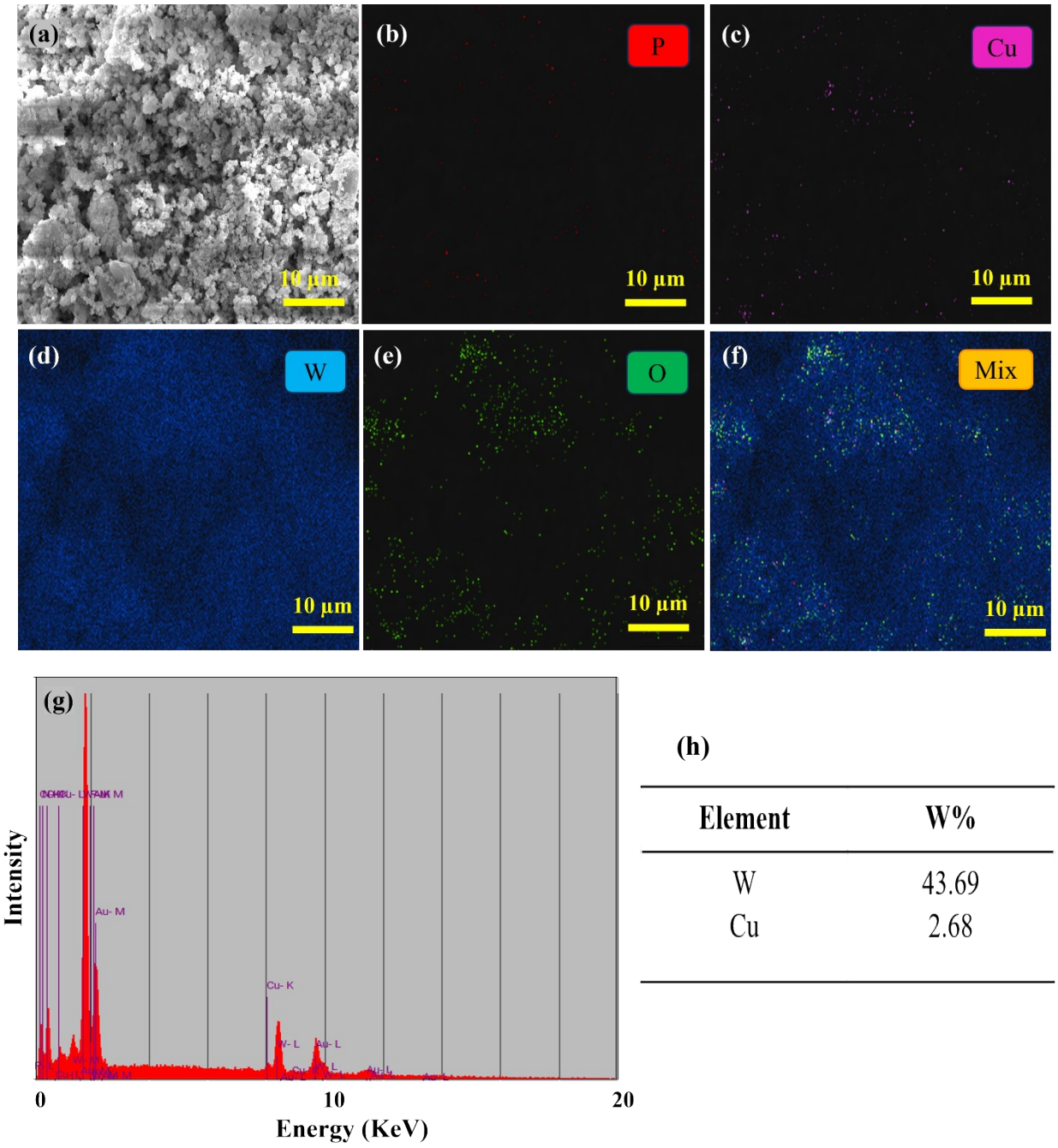


Figure S2. XRD pattern of FePOM.



(h)

Element	W%
W	43.69
Cu	2.68

Figure S3. (a) SEM, (b-f) elemental mapping (obtain from SEM analysis), (g) EDAX analysis (obtain from SEM analysis) of CuPOM and (h) the related quantitative results obtain from EDAX analysis.

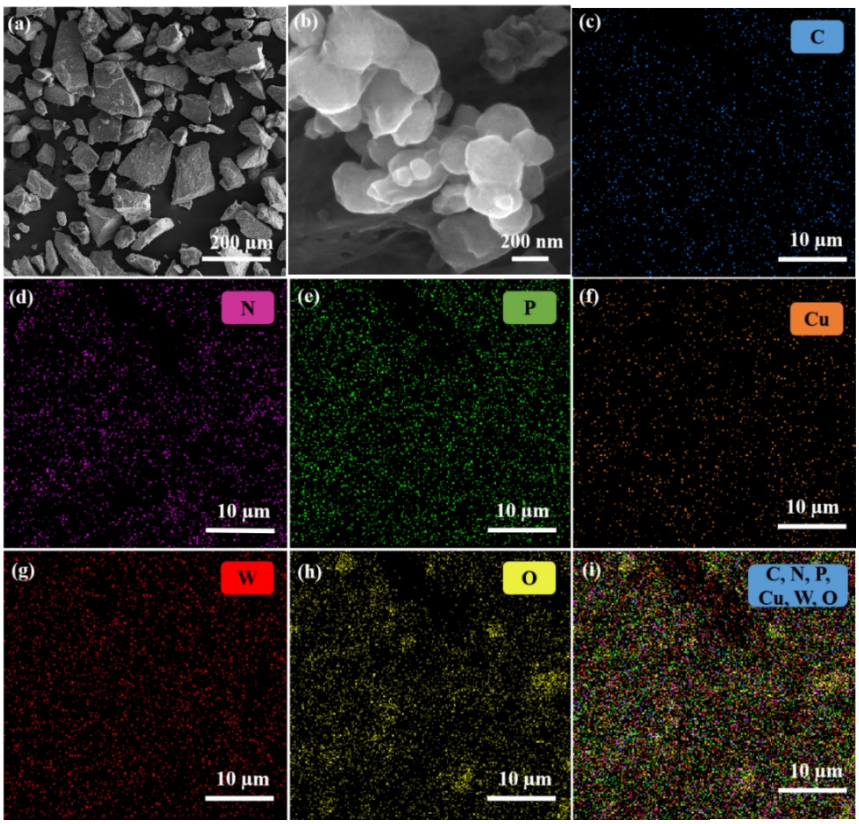


Figure S4. (a, b) FE-SEM images and (c-i) elemental mapping of CuPOM@melamine.

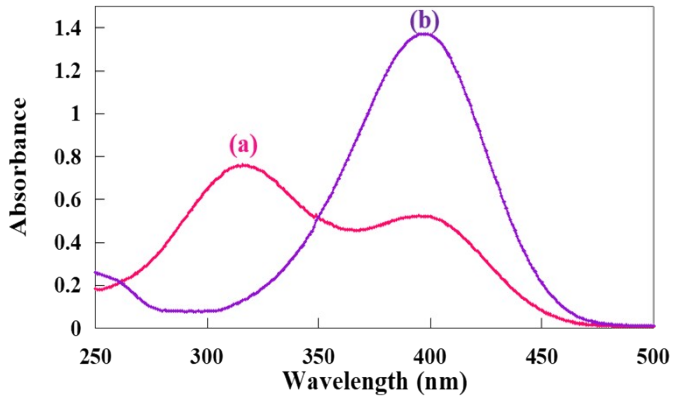


Figure S5. The UV-vis spectra of 4-NP solution in water (a) before and (b) after addition of $NaBH_4$.

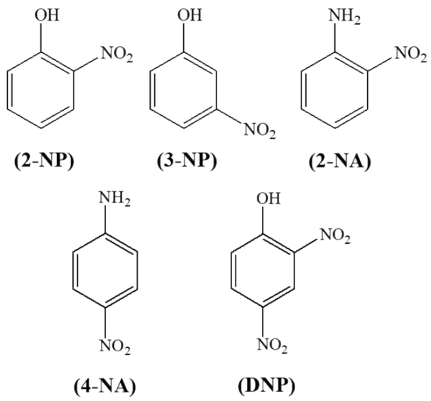


Figure S6. The structures of different nitrophenol derivatives.

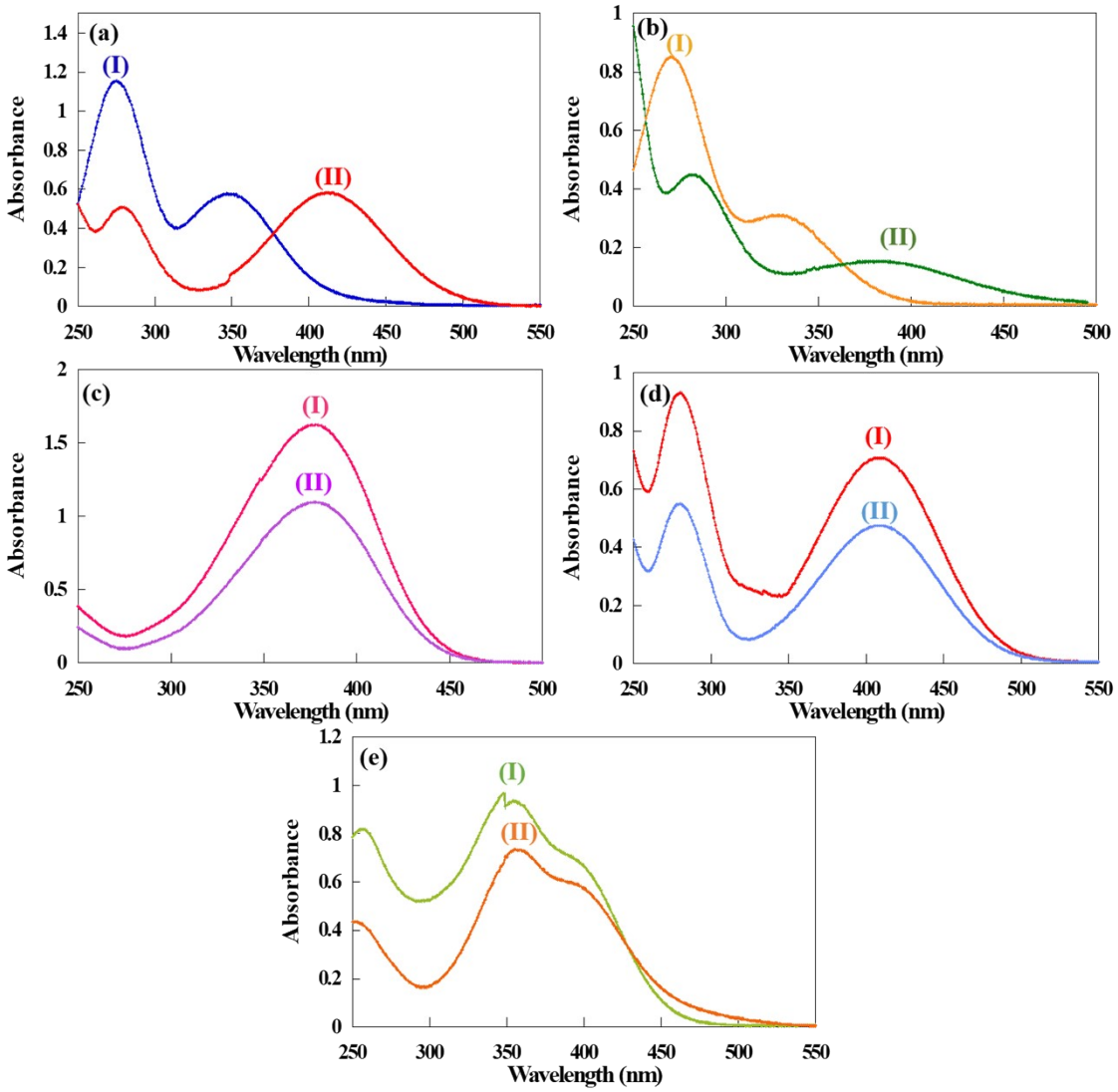


Figure S7. The UV-vis spectra of (a) 2-NP, (b) 3-NP, (c) 4-NA, (d) 2-NA, and (e) DNP solutions in the (I) absence and (II) presence of $NaBH_4$.

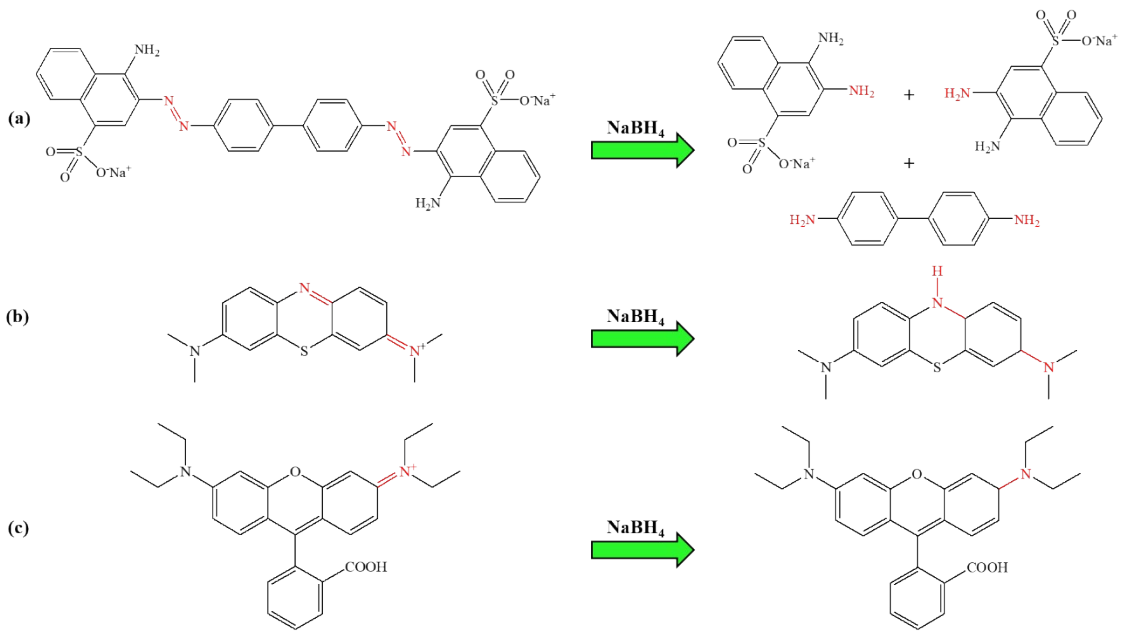


Figure S8. Possible suggested reaction routes and products in the reduction of (a) CR, (b) MB, and (c) RhB.

Table S1. Elemental analysis of MPOMs (weight percentages).

Entry	Compounds	Elemental analysis (wt. %)	
		%W	%M
1	CuPOM	40.771	2.178
2	FePOM	44.607	2.891

Reference

[1] S.Y. Lai, K.H. Ng, C.K. Cheng, H. Nur, M. Nurhadi, M. Arumugam, 2021. Photocatalytic remediation of organic waste over Keggin-based polyoxometalate materials: A review. Chemosphere. 263, 128244. https://doi.org/10.1016/j.chemosphere.2020.128244.