Electronic Supplementary Material (ESI) for Nanoscale.

Cu_2O Nanoparticle-Catalyzed Tandem Reactions for the Synthesis of Robust Polybenzoxazole

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SUPPLEMENTARY FIGURES

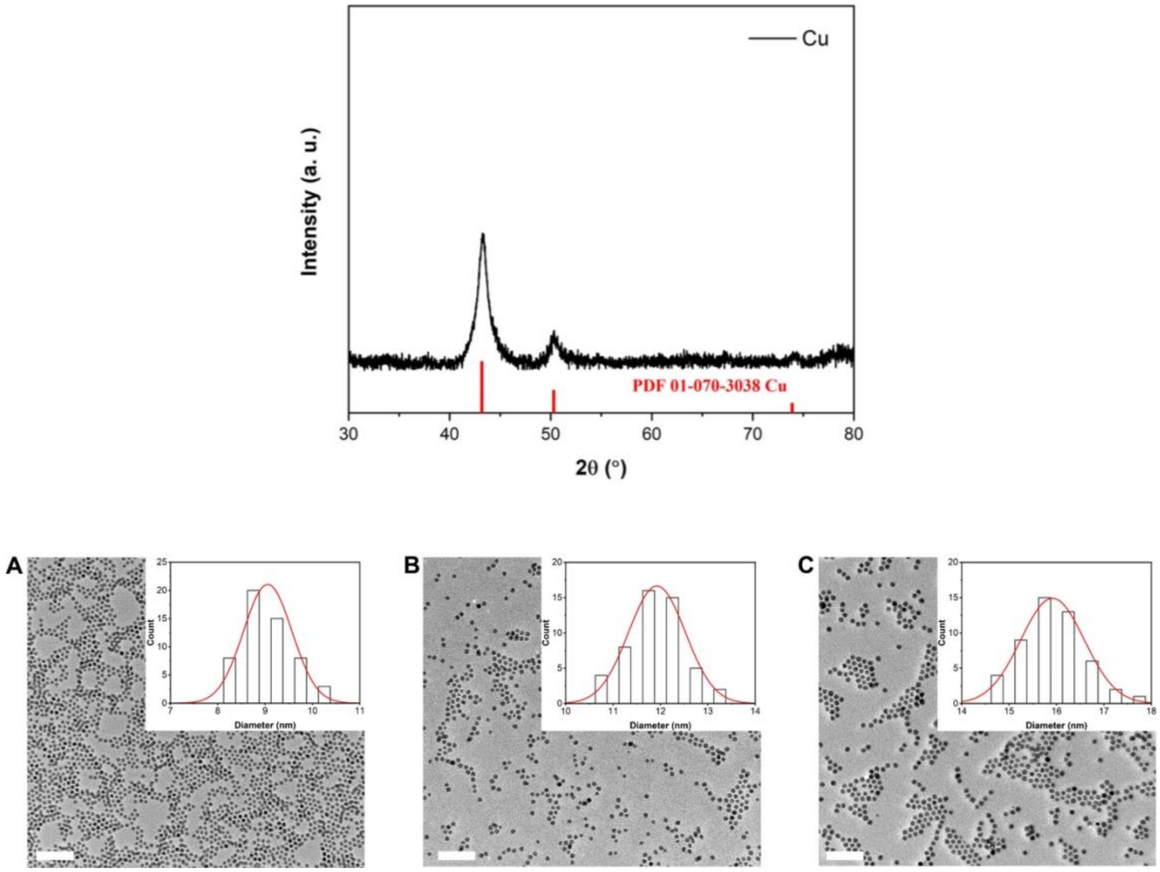

Figure S1. (Top) XRD patterns of 7 nm Cu NPs with standard PDF card (01-070-3038). (Bottom) TEM images and size distribution curves of (A) 9 nm (9.1 ± 0.5) Cu NPs, (B) 12 nm (11.9 ± 0.6) Cu NPs, and (C) 16 nm (15.9 ± 0.7) Cu NPs. Scale bar: 100 nm.

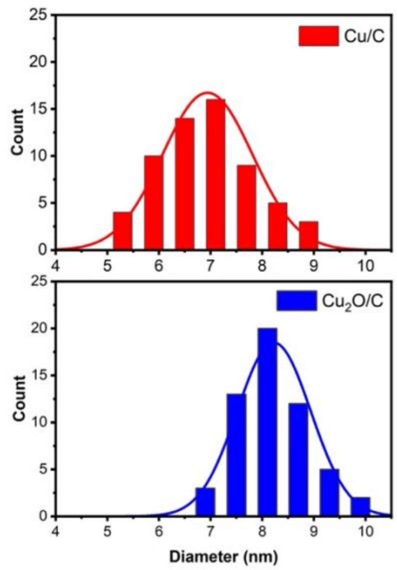

Figure S2. Particle size distribution of Cu and Cu_2O NPs.

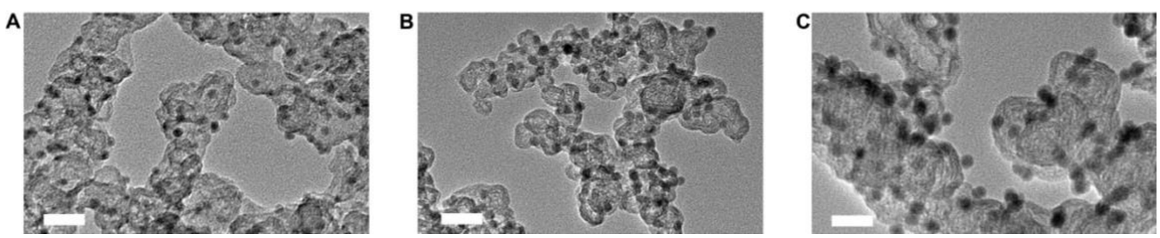

Figure S3. TEM images of various Cu_2O NPs. (A) 10 nm Cu_2O, (B) 13 nm Cu_2O, (C) 18 nm Cu_2O NPs. Scale bar: 50 nm.

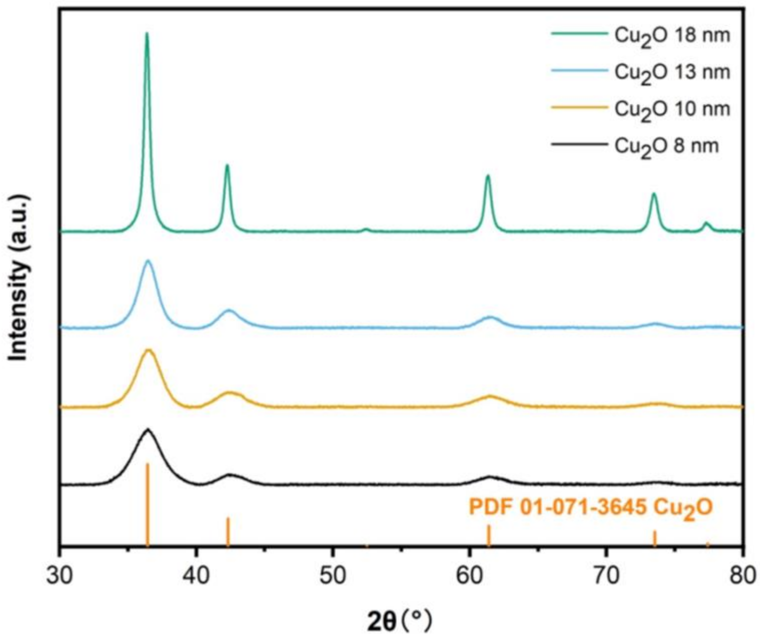

Figure S4. XRD patterns of various Cu_2O NPs and Cu_2O standard PDF card (01-071-3645).

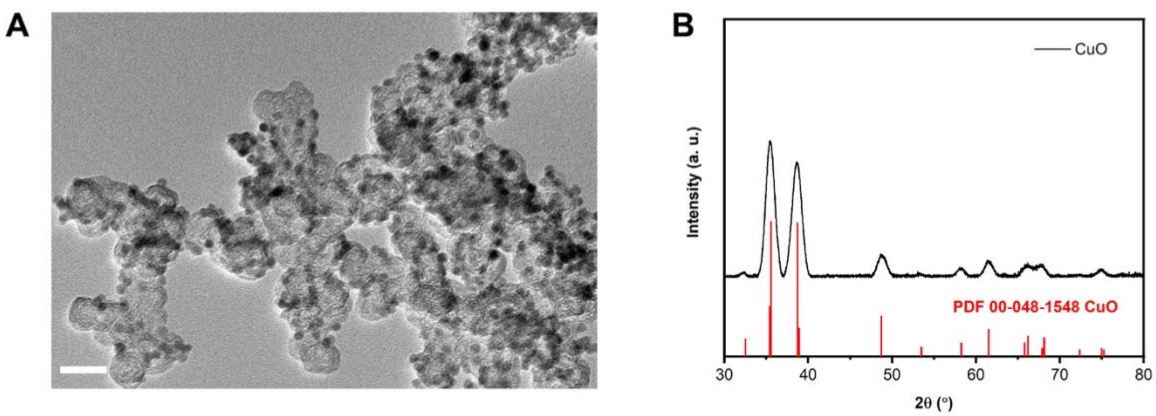

Figure S5. (A) TEM image and (B) XRD pattern of CuO NPs. Scale bar 50 nm. Standard PDF card (00-048-1548).

Table S1. TOF values normalized to the overall metal content for non-noble metal-based catalysts in AB dehydrogenation reaction.

Catalyst	**TOF (mol H_2 mol catalyst^{-1} min^{-1})**	**Reference**
Cu_2O/C	10.0	This study
$Cu/WO_{2.72}$	3.75	1
Cu_2O	0.2	2
Cu_2O/Co_3O_4	2.63	3
Cu/rGO	3.61	4
CuCo/graphene	9.81	5
3.2 nm Ni/C	8.8	6
PVP stabilized Ni	4.5	7
Co@N-C-700	5.6	8
CoNi/graphene	16.4	9

Table S2. Reaction condition screening for tandem nitro hydrogenation reaction (yield was normalized to the original 1,5-diisopropoxy-2,4-dinitrobenzene amount).

Entry	AB (mmol)	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%)
1	6	1	20	2	67
2	6	1	20	4	91
3	**6**	**1**	**20**	**6**	**>99**
4	6	1	20	8	>99
5	4	1	20	6	62
6	8	1	20	6	>99
7	6	0.5	20	12	73
8	6	0.1	20	12	51

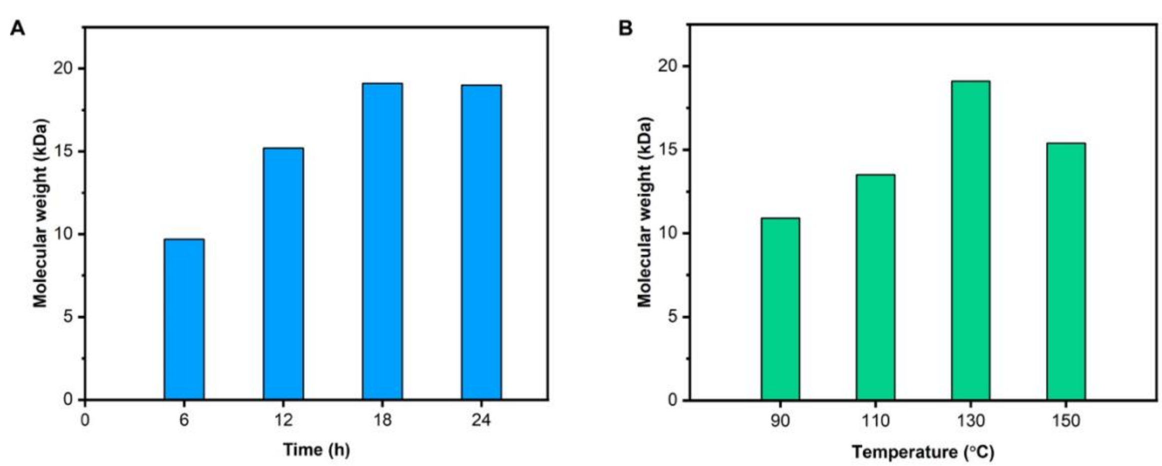

Figure S6. Cu_2O/C catalyzed pre-PBO formation. (A) time-dependent and (B) temperature-dependent polymerization.

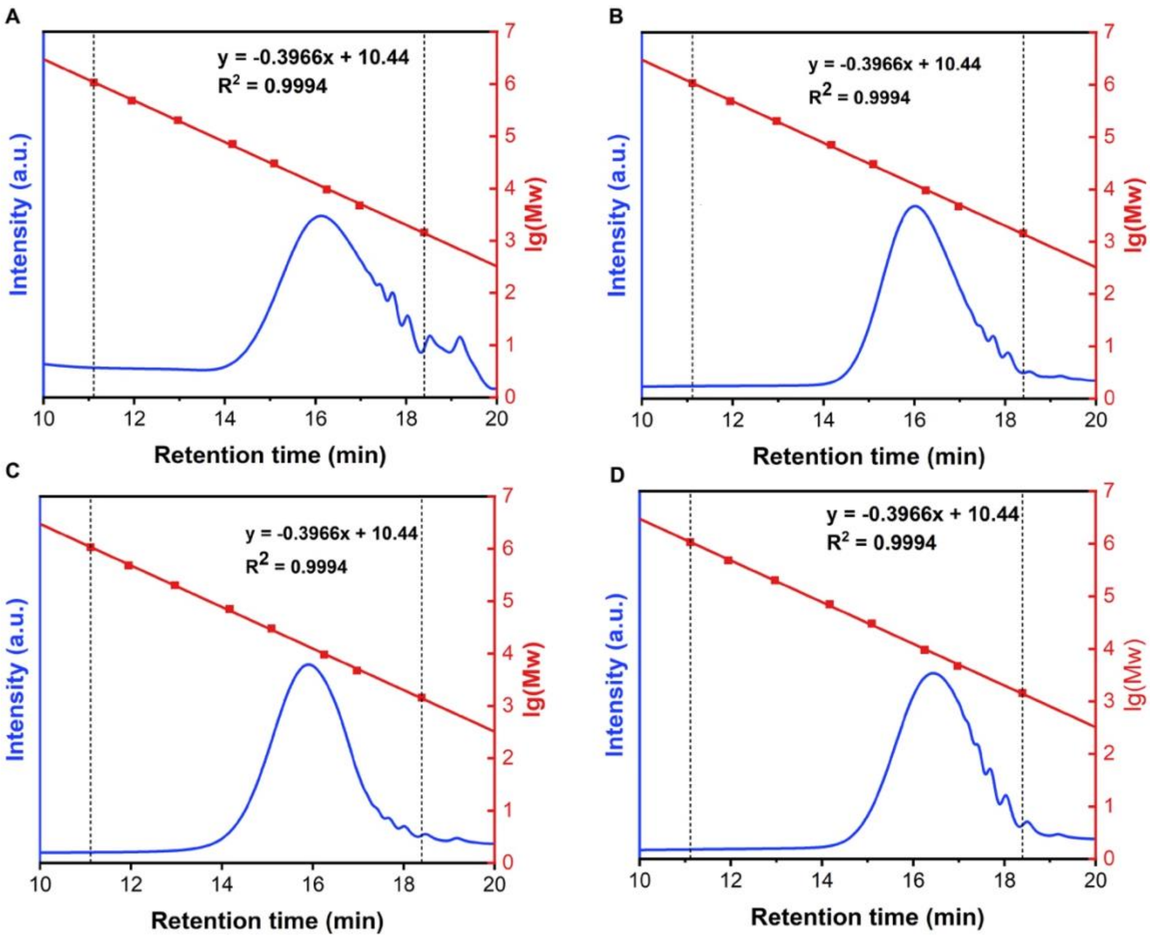

Figure S7. GPC of pre-PBO (blue) (and calibration curve (red)) made from tandem reactions catalyzed by different Cu_2O/C NPs of (A) 8 nm, (B) 10 nm, (C) 13 nm, and (D) 18 nm.

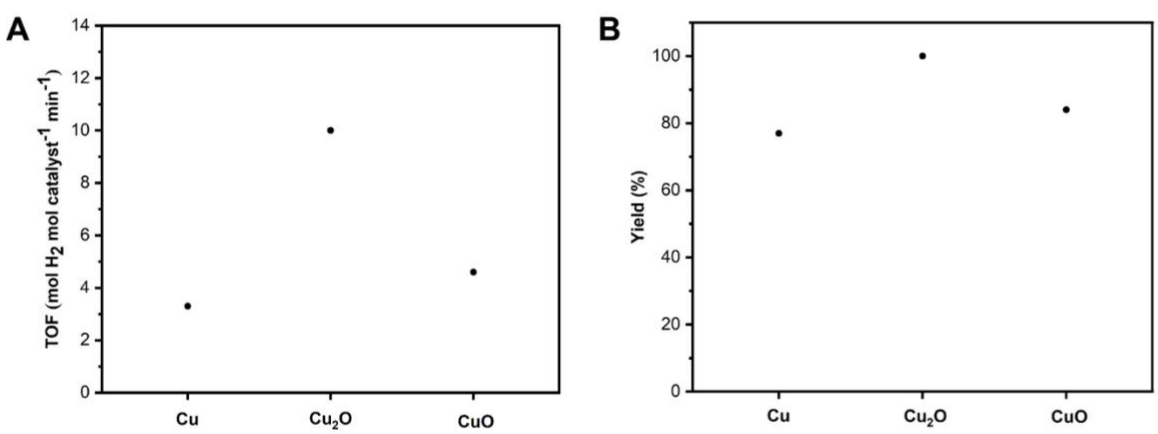

Figure S8. (A) TOF values of NP-catalyzed AB dehydrogenation reaction, and (B) yields of the amine product obtained from nitro-hydrogenation in the presence of different NP catalysts.

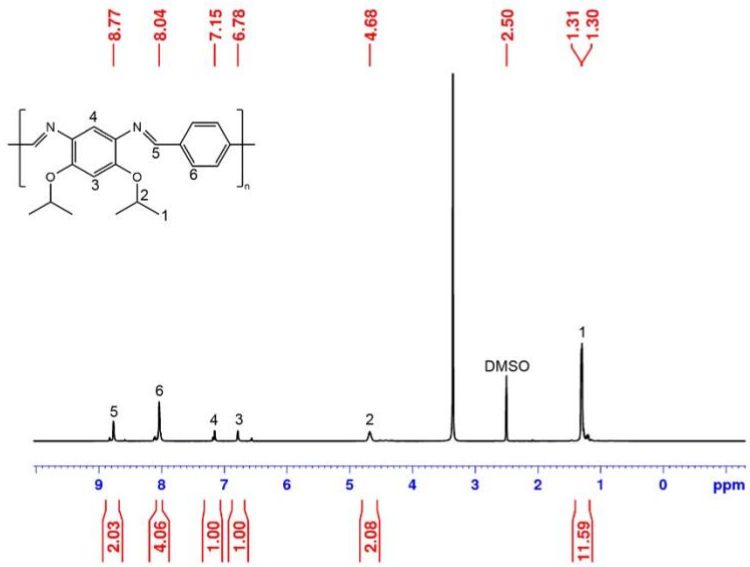

Figure S9. ^{1}H NMR of pre-PBO. Inset: assignment of the proton signals in the pre-PBO chemical structure (400 MHz, d_6-dimethyl sulfoxide).

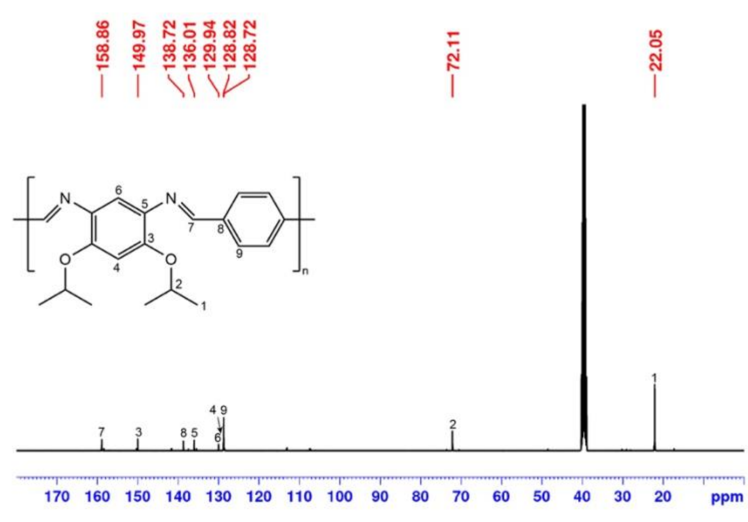

Figure S10. ^{13}C NMR of pre-PBO. Inset: assignment of the carbon signals in the pre-PBO chemical structure (101 MHz, d_6-dimethyl sulfoxide).

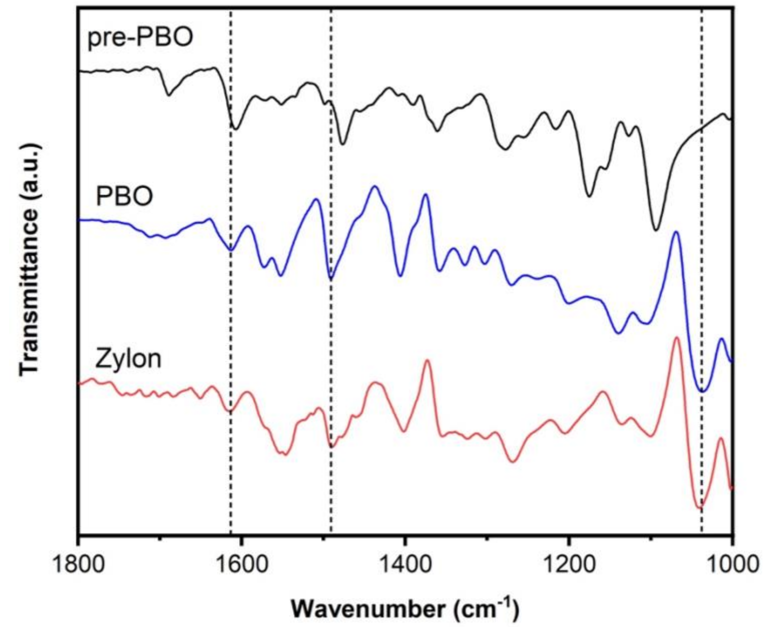

Figure S11. ATR-FTIR spectra of pre-PBO, PBO and Zylon with the assignment of benzoxazole ring (dashed lines).

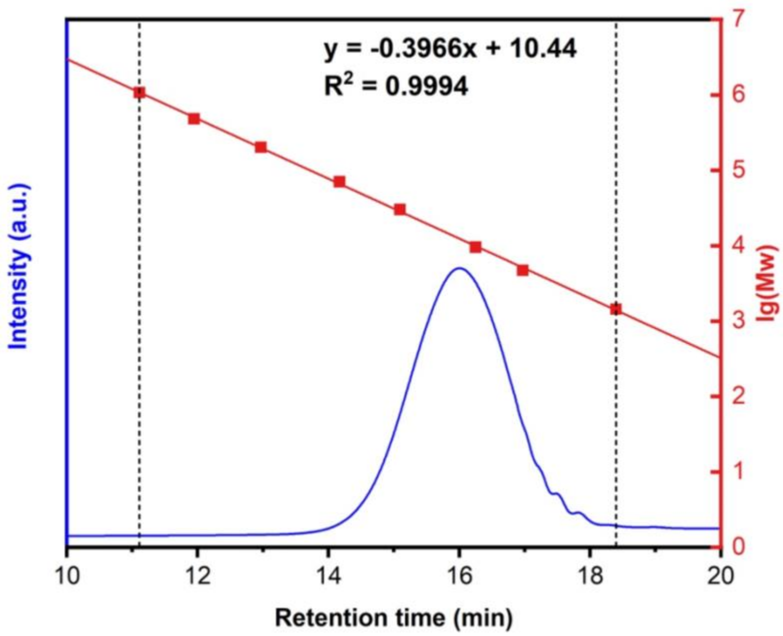

Figure S12. GPC of pre-PBO synthesized by one pot method.

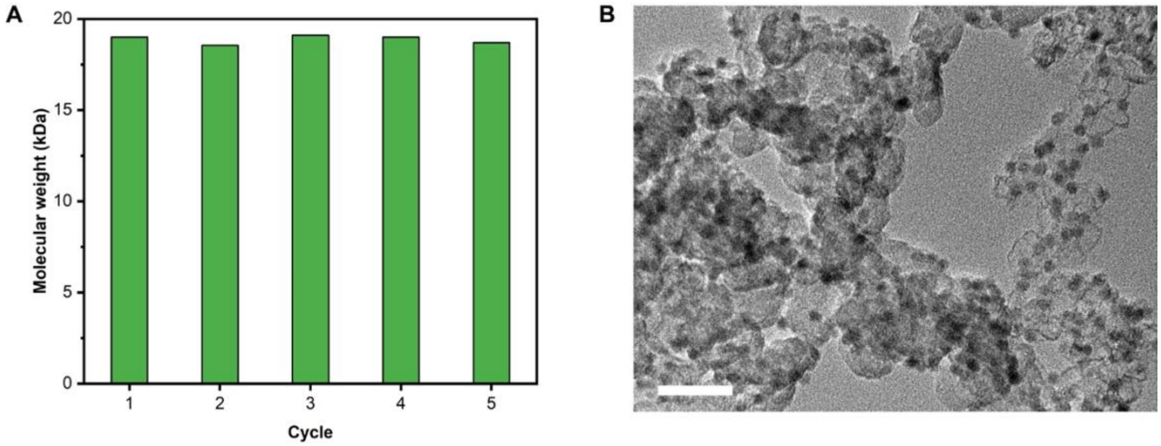

Figure S13. Recyclability tests of Cu_2O/C catalysts. (A) The polymerization degree (in the form of M_w) of pre-PBO obtained from each of the 5 reaction cycles. (B) TEM image of the Cu_2O/C catalyst after 5 reaction cycles. Scale bar: 50 nm.

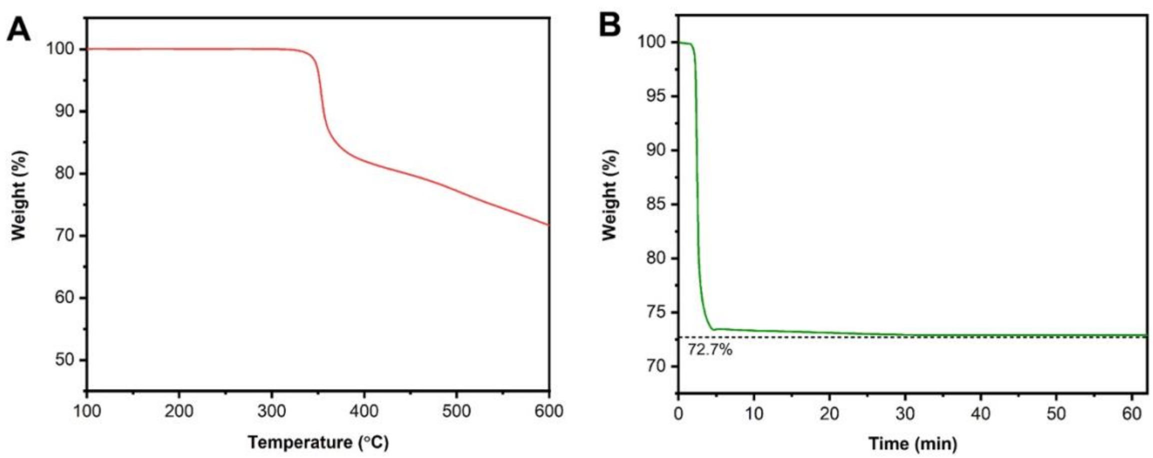

Figure S14. (A) Dynamic TGA curve of pre-PBO and (B) static TGA curve of pre-PBO at 350 °C.

Table S3. Mechanical properties of as-prepared PBO, Zylon and PBO from previous work.[10]

Sample	Initial tensile stress (MPa)	Final tensile stress after boiling water treatment (MPa)	Final tensile stress after boiling simulated seawater treatment (MPa)
As-prepared PBO (19 kDa)	55.2	52.4	49.2
Commercial Zylon (40 kDa)	60.2	42.7	32.7
PBO from AuPd work (11 kDa)	50.2	42.5	/

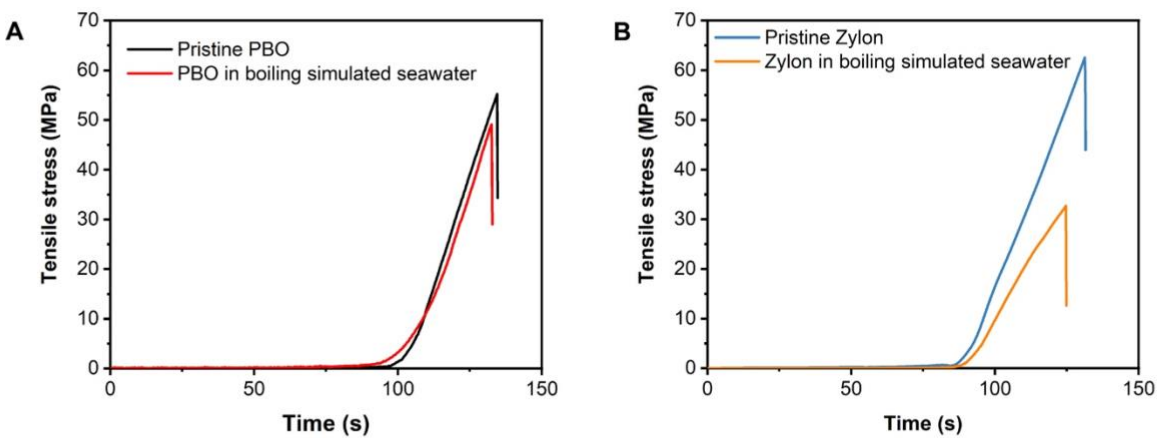

Figure S15. Stability of PBO mechanical properties. The stress-strain curve for (A) as-prepared PBO and (B) commercial Zylon films.

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