

Supporting Information for

Uniform Cu/Chitosan Beads as Green and Reusable Catalyst for Facile Synthesis of Imines via Oxidative Coupling Reaction

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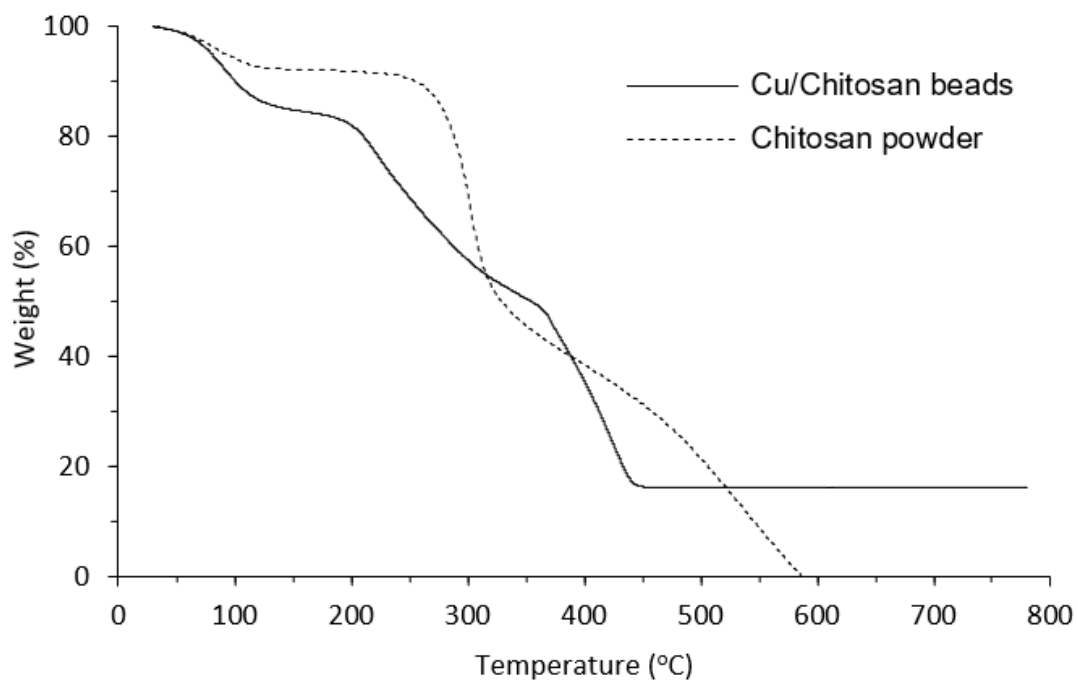


Figure S1 TGA diagrams of Cu/Chitosan beads prepared from $\text{Cu}(\text{OAc})_2$ and Chitosan powder

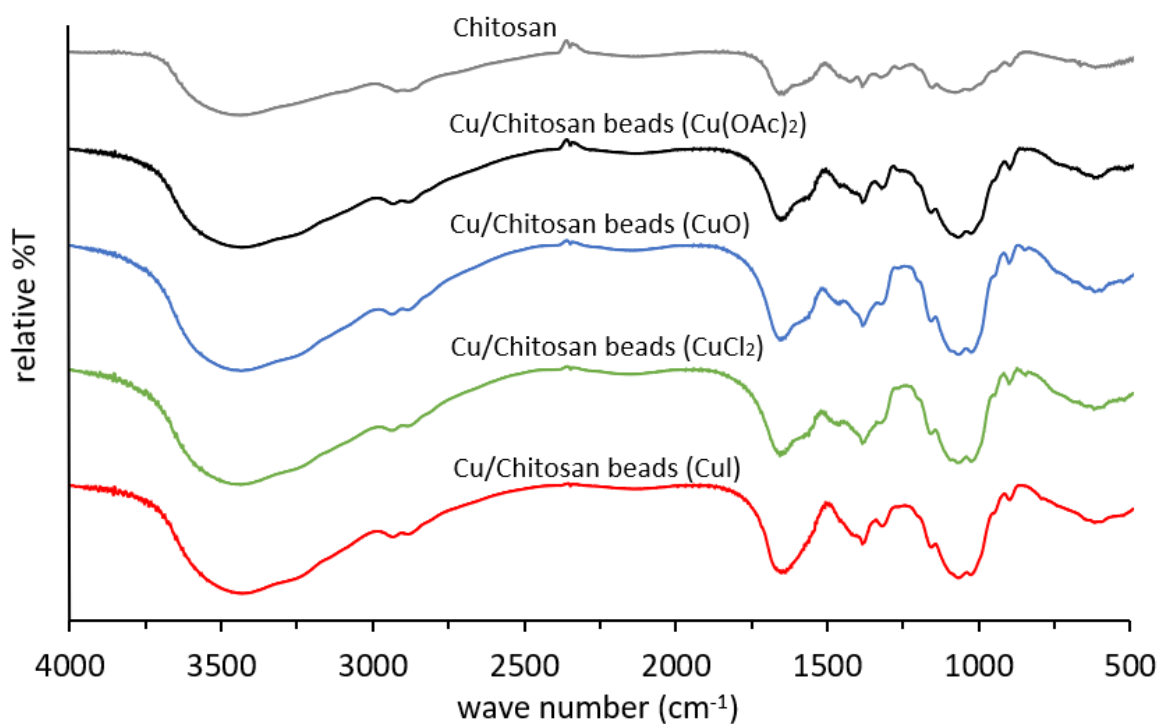


Figure S2 FTIR spectra of Cu/Chitosan beads prepared from different Cu precursors

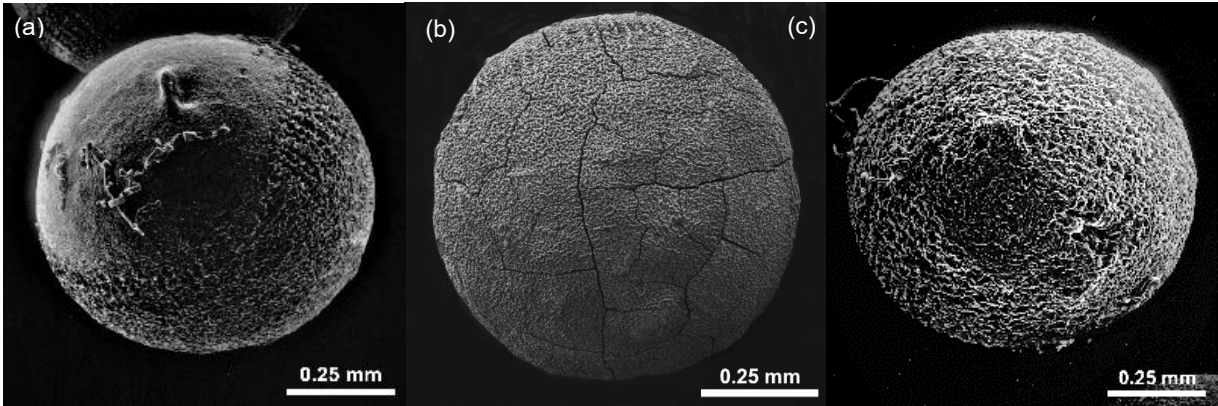


Figure S3 SEM images of Cu/Chitosan beads prepared from $\text{Cu}(\text{OAc})_2$ with copper content of (a) 6, (b) 11, and (c) 14 %wt.

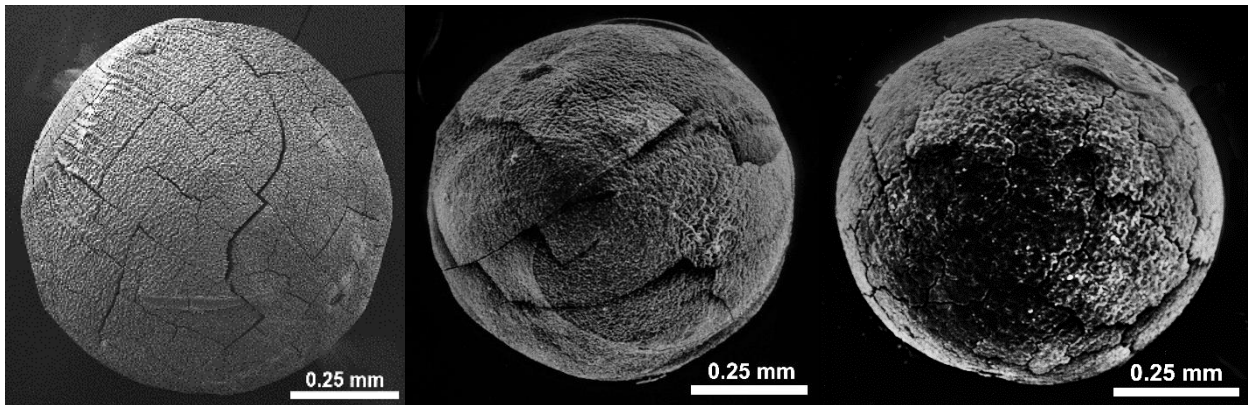


Figure S4 SEM images of Cu/Chitosan beads: (a) fresh, (b) after 1st use, and (c) after 10th use

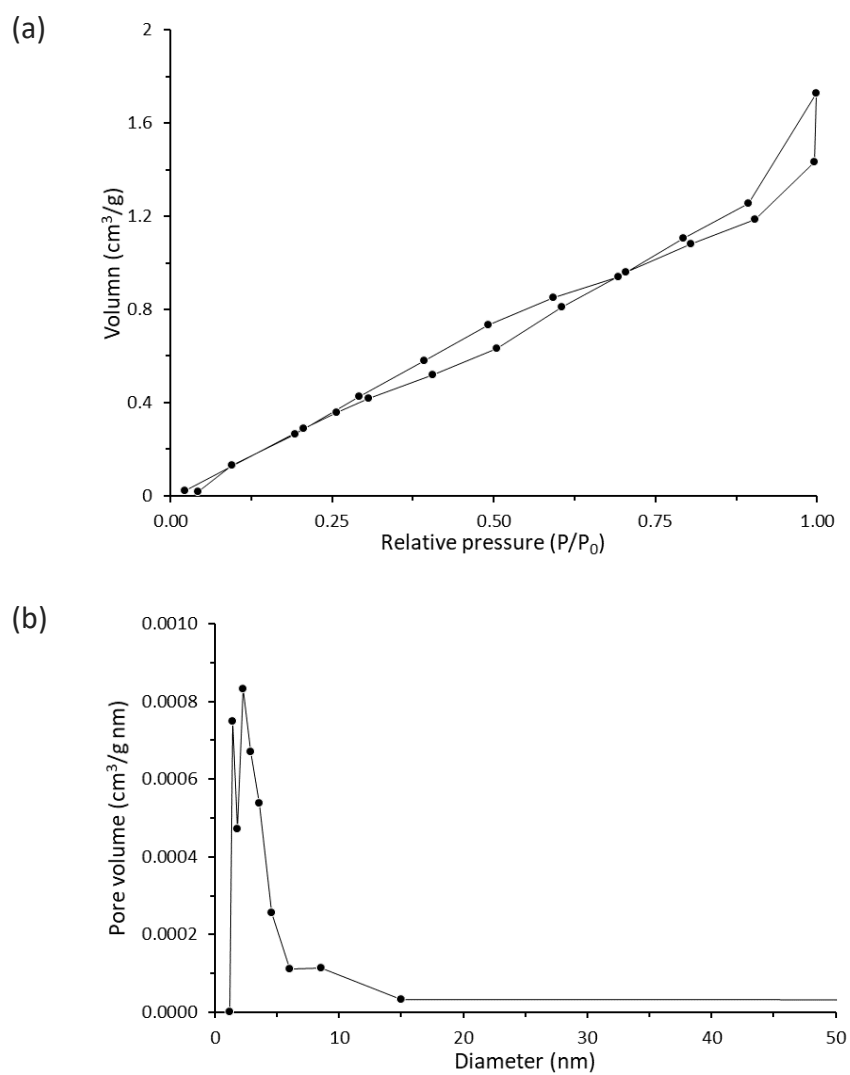


Figure S5 (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of Cu/Chitosan beads prepared from Cu(OAc)₂

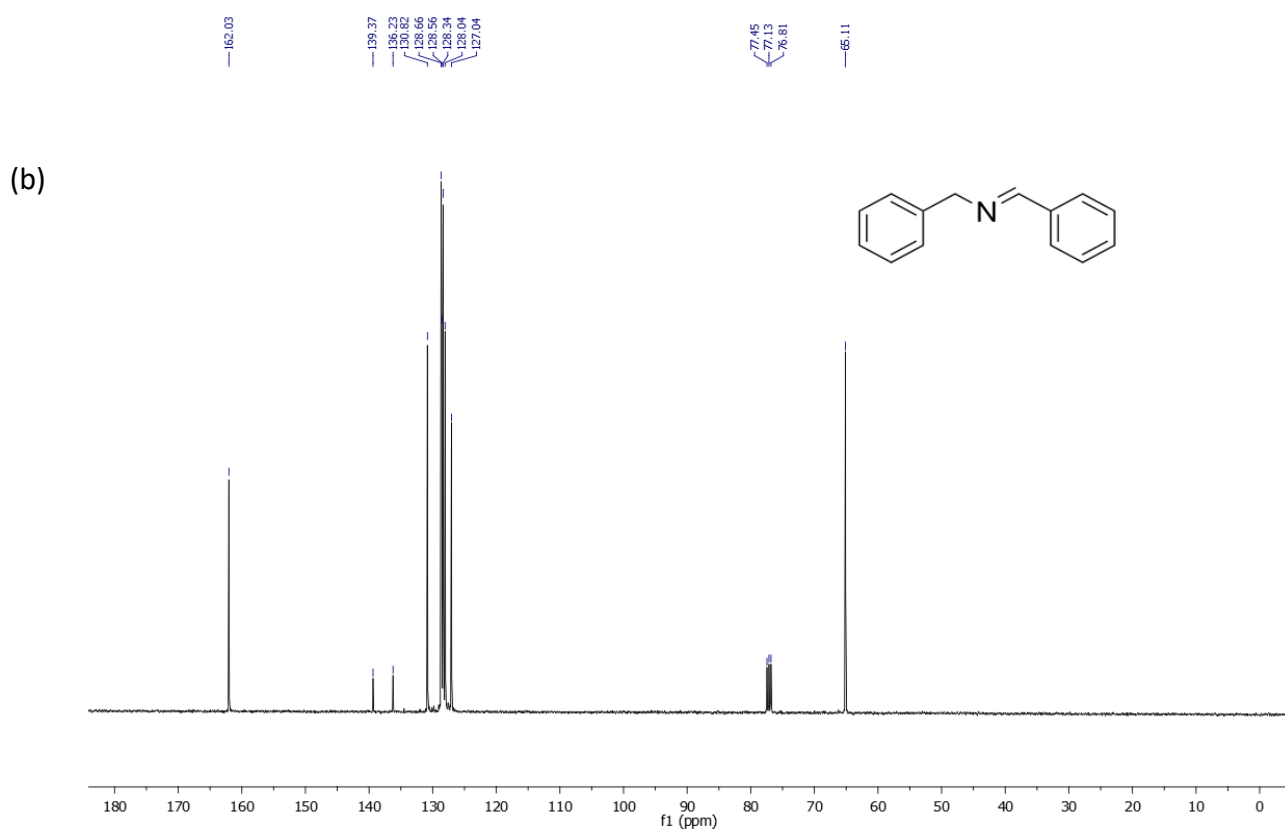
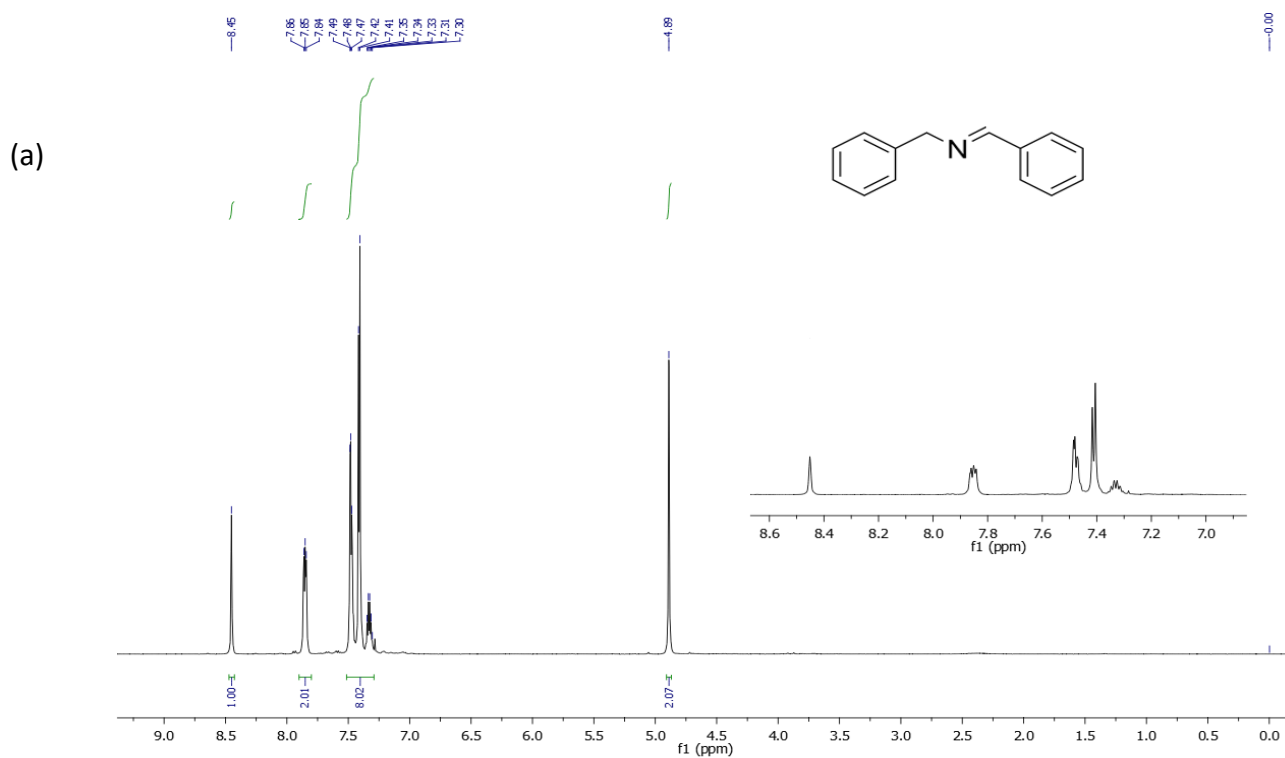


Figure S6 (a) ^1H and (b) ^{13}C NMR spectra of N-benzylidenebenzylamine in CDCl_3

Table S1 Computer-controlled sequential operational steps of the reversible-flow system (Figure 1) for preparation of Cu/Chitosan beads

Step	Description	Port number of multi-selection valve port	Flow rate ($\mu\text{L s}^{-1}$)	Operation (volume)
Aspiration of H₂O carrier into syringe pump (repeat steps 1-2 twice)				
1	Syringe pump valve in; aspirate of the H ₂ O	1	50	Aspirate (5000 μL)
2	Syringe pump valve out; dispense of the H ₂ O	4	50	Dispense (5000 μL)
Aspiration of air, Cu/Chitosan solution into holding coil				
3	Switched 3-port switching valve; dispense of air plug	4	10	Aspirate (200 μL)
4	Aspirate of Cu/Chitosan solution plug	4	10	Aspirate (4000 μL)
Dispersion of Cu/Chitosan solution, air to the tip of tubing				
5	Switched 3-port switching valve; dispense of Cu/Chitosan solution and air plug	4	10	Dispense (4200 μL)
Cleaning of holding coil by 0.2 M HCl solution and H₂O (repeat steps 6-9 twice)				
6	Syringe pump valve in; aspirate of the 0.2 M HCl solution plug	3	50	Aspirate (5000 μL)
7	Syringe pump valve out; dispense of 0.2 M HCl solution plug	4	50	Empty
8	Syringe pump valve in; aspirate of H ₂ O plug	1	50	Aspirate (5000 μL)
9	Syringe pump valve out; dispense of H ₂ O plug	1	50	Empty

Table S2 Effect of reaction conditions on the oxidative self-coupling reaction of benzylamine^a

Entry	Solvent	Oxidizing agent	Temp. (°C)	Catalyst loading	Conv. (%)	Yield ^b (%)
1	Neat	TBHP	80	10 mg	>99	55
2	Toluene	TBHP	80	10 mg	70	71
3	Acetonitrile	TBHP	80	10 mg	>99	98
4	Dimethyl formamide	TBHP	80	10 mg	62	62
5	Dimethyl sulfoxide	TBHP	80	10 mg	56	51
6	Ethyl acetate	TBHP	80	10 mg	49	46
7	Ethanol	TBHP	80	10 mg	91	28
8	Water	TBHP	80	10 mg	>99	24
9	Acetonitrile	ambient	80	10 mg	12	12
10	Acetonitrile	O₂ ^c	80	10 mg	16	14
11	Acetonitrile	H₂O₂	80	10 mg	62	46
12	Acetonitrile	TBHP	30	10 mg	13	10
13	Acetonitrile	TBHP	70	10 mg	25	22
14	Acetonitrile	TBHP	90	10 mg	97	96
15	Acetonitrile	TBHP	80	5 mg	76	73
16	Acetonitrile	TBHP	80	15 mg	96	94
17	Acetonitrile	TBHP	80	20 mg	95	95

^aReaction condition: benzylamine (0.5 mmol), solvent (2 mL), oxidizing agent (1 mmol), 30 min ^bGC yield calculated using hexamethylbenzene (10 mg) as internal standard ^cusing oxygen gas bubble as the oxidizing agent