

19

20 **Figure ESI1.** (a) Photograph of liquid samples taken at different pH using 9 mM of Cu^{2+} as
 21 metal precursor (orange line) according to increasing charge density (0 to 3100 $C L^{-1}$). (b) Effect
 22 of single Cu^{2+} concentration on charge density consumption using $CuCl_2$ as metal precursor.

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

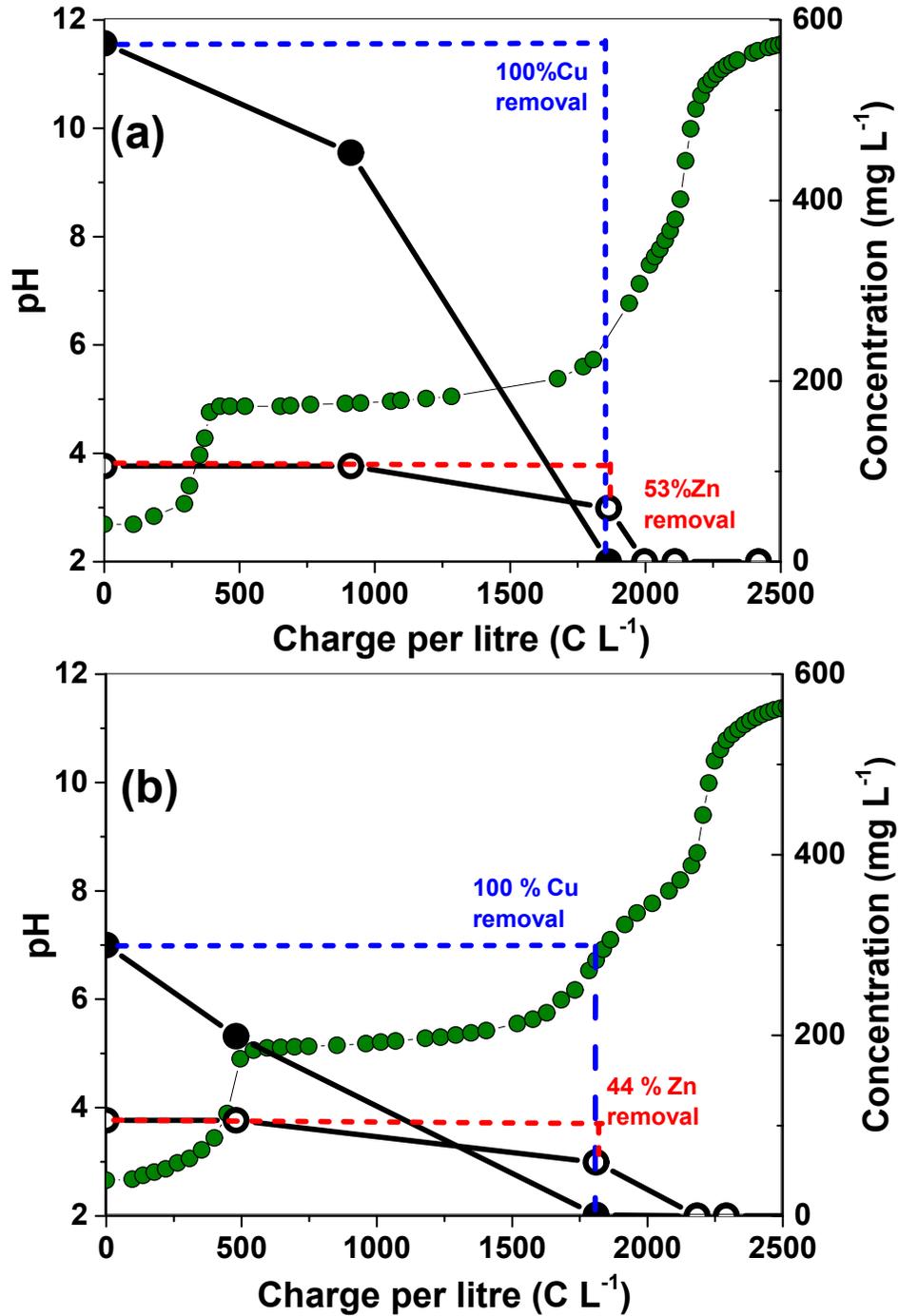
41

42

43

44

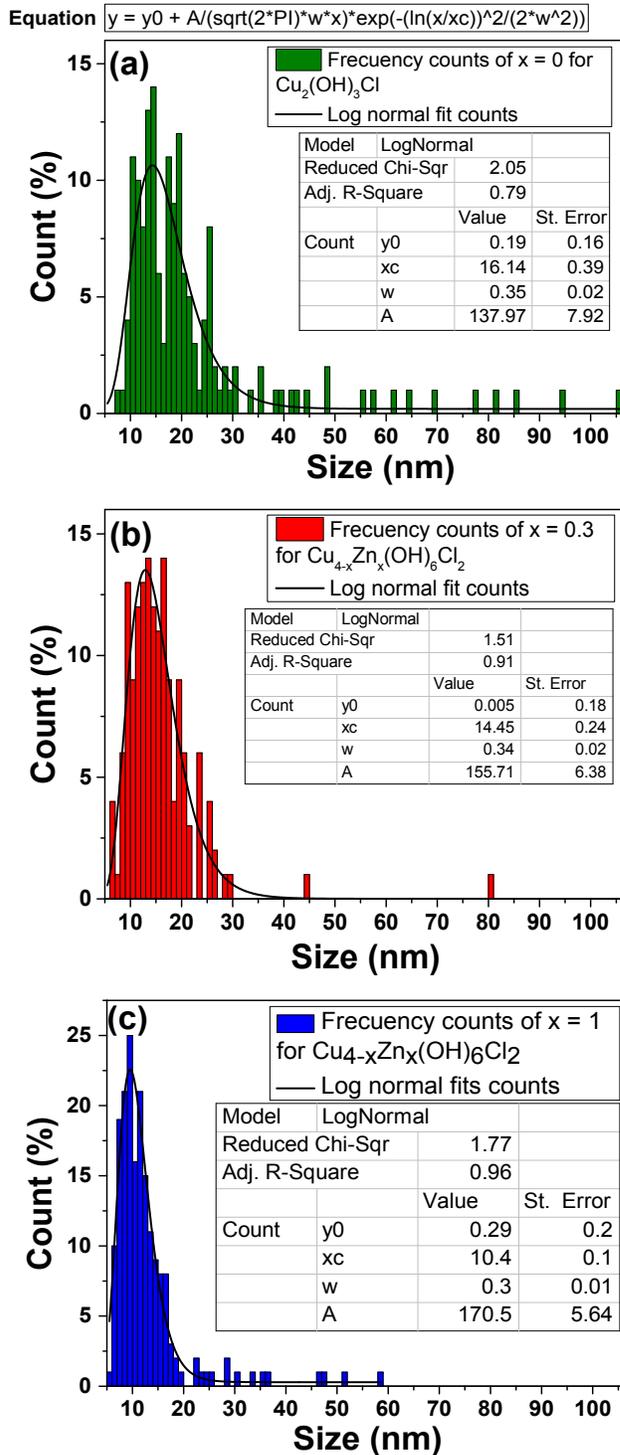
45



46 **Figure ESI2.** Effect of mixed Cu²⁺ and Zn²⁺ concentration on charge consumption during the

47 synthesis of herberthsmithite. (a) High initial Cu²⁺ concentration ; (b) Low initial Cu²⁺

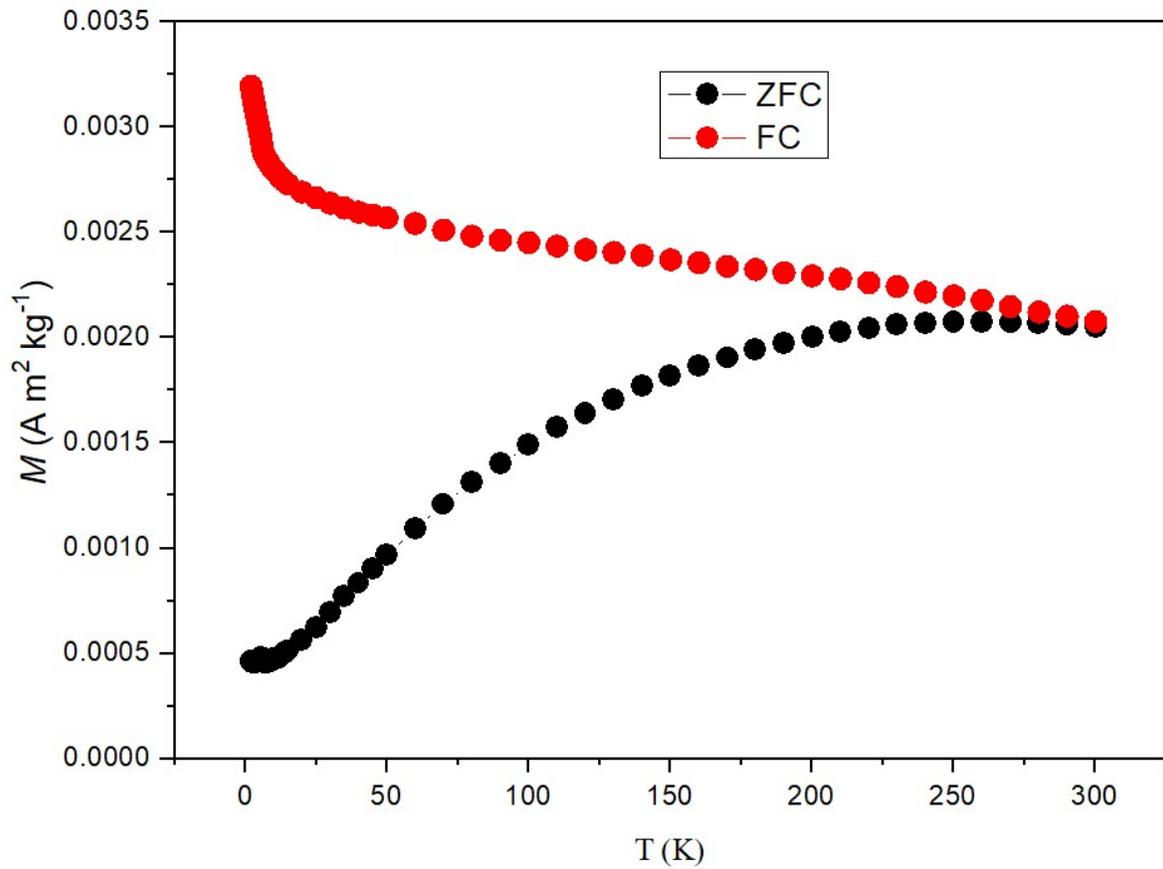
48 concentration.



69 **Figure ESI3.** Mean particle size and distribution of $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ products with a desired
 70 value for x , a) $x = 0$ for clinoatacamite ; b) $x = 0.3$ for paratacamite and c) $x = 1$ for
 71 herbertsmithite.

72

73



74

75 **Figure ESI4.** Temperature dependence of mass magnetization (M) at 8 kA/m (100 Oe) for CuO
76 as measured under ZFC-FC conditions.

77

78

79

80

81

82

83

84 **Table S1.** Quantitative phase analysis (QPA) by Rietveld method and ICP-OES of powder samples.

Sample code	Charge consumed (C L ⁻¹)	ICP powder mg g ⁻¹ solid		(mmol)		Cu/Zn ratio	Phase percentage (%)				Cu and Zn in Cu _{4-x} Zn _x (OH) ₆ Cl ₂		Stoichiometric coefficient (x)
		Cu	Zn	Cu	Zn		Cu _{4-x} Zn _x (OH) ₆ Cl ₂	ZnO	Cu(OH) ₂	CuO	Cu (mM)	Zn (mM)	
Sample (a)	987	546		8.6			100	0	0	0	8.6		0
Sample (b)	1876	783		12.3						100	12.3		0
Sample (c1)	778	469	64	7.4	1.0	7.3	82	3.2	15	0	7.1	0.8	0.3
Sample (c2)	850	524	72	8.3	1.1	7.3	98	1.6	1.8	0	8.2	1.1	0.4
Sample (d1)	2000	462	150	7.3	2.3	3.1	77	15	8	0	6.2	2.1	1.0
Sample (d2)	2018	467	144	7.4	2.2	3.2	80	16	4	0	6.2	2.1	1.0

85

86

87

88

89

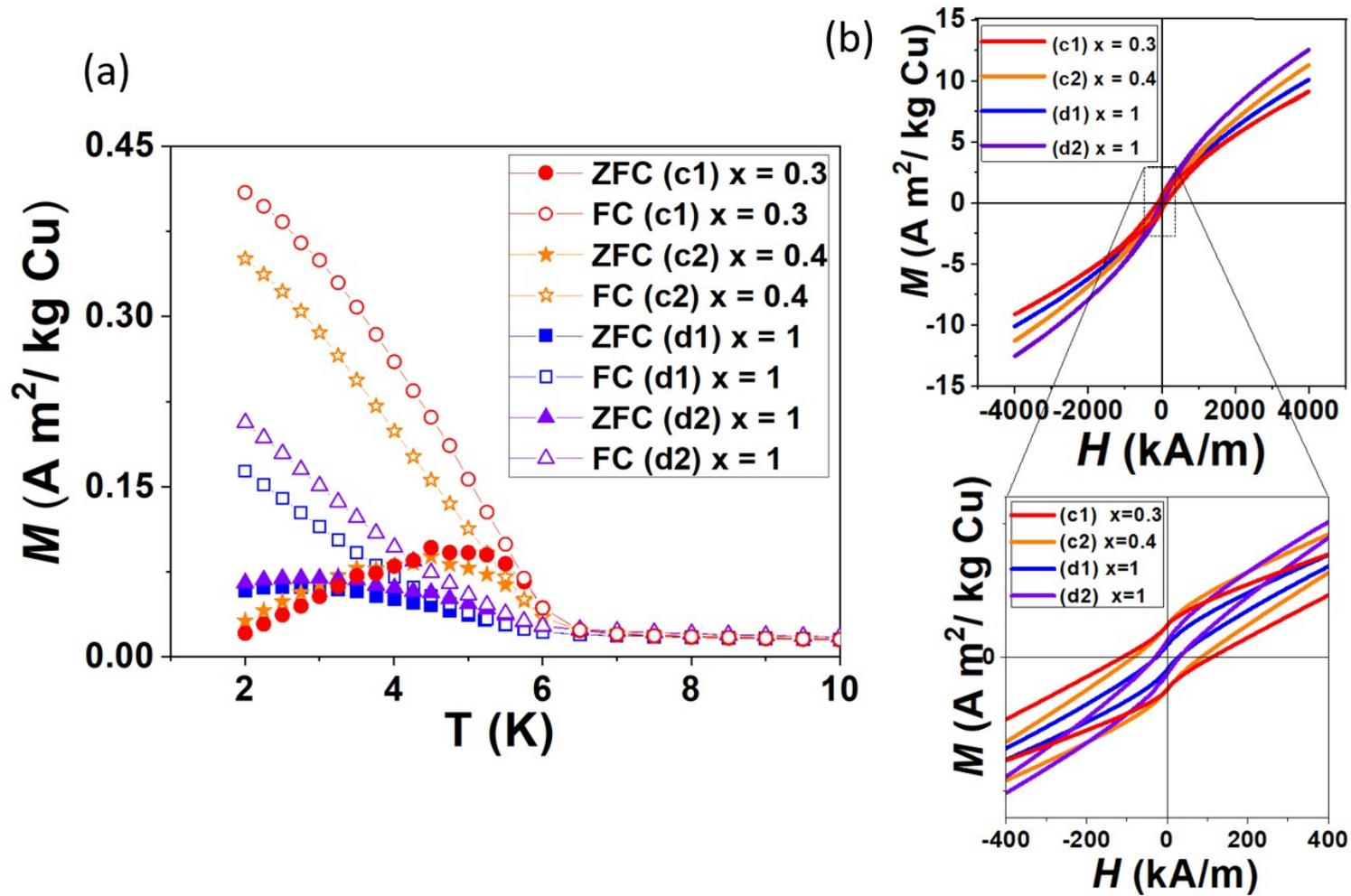
90

91

92

93

94



95

96 **Figure EIS5.** (a) ZFC-FC thermal magnetization of a duplicates sample with stoichiometric coefficient ($x = 1$ and $x = 0.3$). (b)

97 Magnetization against field over temperature sweep at 2.0 K in duplicate samples.