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Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis

BINGHAM, LAURA, MARIA

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Appendix: Chapter 4

Full list all preparation conditions trialled

A full list of all preparation conditions trialled in Chapter 4 are given below (Table 4A.1) along with the corresponding Figure numbers (Chapter 4) and the file location for full transmission electron microscopy (TEM) data (electronic supplementary information).

Table 4A.1. Full list of experimental conditions tried for copper nanoparticle (Cu) synthesis, along with the corresponding Figure numbers (Chapter 4) and the file location for full TEM data (referring to locations within the electronic supplementary information). The corresponding Figure numbers (Chapter 4) and the file locations for full TEM data (Electronic Supplementary Information) are given where Section-Figure refers to the Section of Chapter 4 and the parameter being varied and, Figure is the Figure number and Spectra letter (A, B, C etc.) of interest (e.g. 4.2 is Figure 4.2). Within this terminology the following section abbreviations were used: T=temperature variation, RT=ripening time variation, CA=capping agent variation, RA=reducing agent. Experiments were undertaken for the following capping agents: oleylamine (OAm), oleic acid (OAc), octadecylamine (ODA), and the following reducing agents morpholine borane complex (mbc), 1,2-tetradecanediol (1,2-td). It should be noted that OAm and OAc refers to both capping agents being present in the ripening period. Whereas OAm then OAc refers to ripening in the presence of OAm only and the subsequent addition of OAc to terminate ripening. An N/A entry, in the particle diameter and standard deviation columns, corresponds to no nanoparticles being received and so no TEM imaging undertaken. It should be noted that for all TEM data given particle size for spherical or oval shapes were counted by their typical diameter. Hexagonal shapes were calculated using their long diameter (perhaps resulting in very slightly overestimating their size), but for cubes a mathematical average of their longest (corner to corner) and shortest (side to side) cross particle lengths was taken.

Sample	Section-Figure	Temperature / °C	Ripening time / h	Capping agent	Moles capping agent / mmol	Reducing agent	Moles reducing agent / mmol	Colour of solution	Diameter from TEM / nm	Standard deviation / nm	Tem location
Cu-031215_1	T-4.2A	200	1	OAm	1.1	none	0	green/brown	39	5	microscopy-2015-dec-04/12/15
Cu-120716_1	T-4.2B	200	1	OAm	1.1	none	0	pale brown/yellow	38	5	microscopy-2016-18/7/16
Cu-240316-2	T-4.2C	200	1	OAm	1.1	none	0		43	5	microscopy-2016-5/4/16, 6/4/16
Cu-180216_1	T-4.3D	210	1	OAm	1.1	none	0	brown/yellow	39	6	microscopy-2016-19/2/16
Cu-210716_1	T-4.3E	220	1	OAm	1.1	none	0	brown	48	7	microscopy-2016-22/07/16

Cu-180216_2	T-4.3F	220	1	OAm	1.1	none	0	brown/ yellow	42	9	<i>microscopy-2016-19/2/16</i>
Cu-190216_1	T-4.3G	230	1	OAm	1.1	none	0	brown/ green/ black	39	4	<i>microscopy-2016-26/2/16</i>
Cu-080316_1	T-4.4H	230	1	OAm	1.1	none	0	dark green	29	6	<i>microscopy-2016-14/3/16</i>
Cu-091215_1	T-4.4I	240	1	OAm	1.1	none	0	green/ black	18	2	<i>microscopy-2015-dec-10/12/15</i>
Cu-020216_1	T-4.4J	240	1	OAm	1.1	none	0	dark green	40	6	<i>microscopy-2016-2/2/16</i>
Cu-170216_1	T-4.4K	240	1	OAm	1.1	none	0	black	41	6	<i>microscopy-2016-18/2/16</i>
Cu-161215_1	T-4.6A	200	1/6	OAm	1.1	none	0	dark green	26	4	<i>microscopy-2016-6/1/16</i>
Cu-161215_2	T-4.6B	240	1/6	OAm	1.1	none	0	deep brown	29	4	<i>microscopy-2016-6/1/16</i>
Cu-200116_1	T-4.6C	240	1/6	OAm	1.1	none	0	dark green/ black	16	5	<i>microscopy-2016-28/1/16</i>
Cu-010216_1	T-4.6D	240	1/6	OAm	1.1	none	0	green/ brown	41	6	<i>microscopy-2016-2/2/16</i>

Cu-091215_2	T-4.7A	200	1/2	OAm	1.1	none	0		29	4	<i>microscopy-2015-10/12/15</i>
Cu-010216_2	T-4.7B	240	1/2	OAm	1.1	none	0	green/brown solution	40	7	<i>microscopy-2016-2/2/16</i>
Cu-010216_5	RT-4.9A	240	2	OAm	1.1	none	0	dark green/black solution	34	4	<i>microscopy-2016-2/2/16</i>
Cu-010216_6	RT-4.9B	240	3	OAm	1.1	none	0	black solution	35	5	<i>microscopy-2016-2/2/16</i>
Cu-010216_7	RT-4.9C	240	4	OAm	1.1	none	0	black solution	28	3	<i>microscopy-2016-2/2/16</i>
Cu-031215_1	CA-4.11A	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-120716_1	CA-4.11B	200	1	OAm	1.1	none	0	pale brown/yellow	38	5	<i>microscopy-2016-18/7/16</i>
Cu-010316_1	CA-4.11C	200	1	OAm	2.2	none	0	dark green/brown solution	34	5	<i>microscopy-2016-2/3/16</i>
Cu-020216_1	CA-4.10A	240	1	OAm	1.1	none	0	dark green	40	6	<i>microscopy-2016-2/2/16</i>
Cu-170216_1	CA-4.12B	240	1	OAm	1.1	none	0	black	41	6	<i>microscopy-2016-18/2/16</i>

Cu-091215_1	CA-4.12C	240	1	OAm	1.1	none	0	green/black	18	2	<i>microscopy-2015-dec-10/12/2015</i>
Cu-181215_1	CA-4.13D	240	1	OAm	2.2	none	0	blue/black	23	7	<i>microscopy-2016-6/1/16</i>
Cu-220116_1	CA-4.13E	240	1	OAm	2.2	none	0	dark green/blue	20	2	<i>microscopy-2016-28/1/16</i>
Cu-031215_1	CA-4.14A	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-190716_1	CA-4.14B	200	1	OAm then OAc	0.71 then 0.38	none	0	green	15	4	<i>microscopy-2016-21/7/16</i>
Cu-230316_1	CA-Table 4.3	200	1	OAm and OAc	0.55 and 0.55	none	0		N/A	N/A	N/A
Cu-240316_1	CA-4.15A	200	1	OAm and OAc	0.99 and 0.11	none	0		9	6	<i>microscopy-2016-5/4/16, 6/4/16</i>
Cu-031215_1	CA-4.15B	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-120716_1	CA-4.15C	200	1	OAm	1.1	none	0	pale brown/yellow	38	5	<i>microscopy-2016-18/7/16</i>

Cu-031215_1	CA-4.16A	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-120716_1	CA-4.16B	200	1	OAm	1.1	none	0	pale brown/yellow	38	5	microscopy-2016-18/7/16
Cu-100216_1	CA-4.16C	200	1	ODA	1.1	none	0	brown/green	33	4	<i>microscopy-2016-11/2/16</i>
Cu-170616_1	CA-4.16D	200	1	ODA	1.1	none	0	brown solution	52	6	<i>microscopy-2016-21/6/16</i>
Cu-031215_1	RA-4.18A	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-240616_1	RA-4.18B	200	1	OAm	1.1	mbc	0.115	pale brown/orange	38	8	microscopy-2016-18/07/16
Cu-040516_1	RA-4.18C	200	1	OAm	1.1	mbc	0.23		35	9	microscopy-2016-8/5/16
Cu-060516_1	RA-4.19D	200	1	OAm	1.1	mbc	0.46		4	1	microscopy-2016-8/5/16
Cu-140716_1	RA-4.19E	200	1	OAm	1.1	mbc	0.92	deep purple/black	8	2	microscopy-2016-18/07/16
Cu-100216_1	RA-4.24A	200	1	ODA	1.1	none	0	brown/green	33	4	<i>microscopy-2016-11/2/16</i>

Cu-170616_1	RA-4.24B	200	1	ODA	1.1	none	0	brown solution	52	6	<i>microscopy-2016-21/6/16</i>
Cu-310316_1	RA-4.24C	200	1	ODA	1.1	mbc	0.23		5	2	<i>microscopy-2016-4/4/16</i>
Cu-150716_1	RA-4.25D	200	1	ODA	1.1	mbc	0.46	black	6	1	<i>microscopy-2016-18/07/16</i>
Cu-190716_2	RA-4.25E	200	1	ODA	1.1	mbc	0.92	purple precipitate, clear solution	3	1	<i>microscopy-2016-22/07/16</i>
Cu-031215_1	RA-4.27A	200	1	OAm	1.1	none	0	green/brown	39	5	<i>microscopy-2015-dec-04/12/15</i>
Cu-040216_1	RA-4.27B	200	1	OAm	1.1	1,2-tdd	0.023	green/brown solution	42	7	<i>microscopy-2016-5/2/16</i>
Cu-110216_1	RA-4.27C	200	1	OAm	1.1	1,2-tdd	0.023	brown solution	35	7	<i>microscopy-2016-17/2/16</i>
Cu-260216_1	RA-4.27D	200	1	OAm	1.1	1,2-tdd	0.23	pink/red solution	280	60	<i>microscopy-2016-2/3/16</i>

Inductively coupled plasma-optical emission spectrometry (ICP-OES)
 All ICP-OES data obtained (for which a subsection was displayed in Chapter 4, Section
 4.2.3.2) is listed below in Table 4A.2.

Table 4A.2. ICP-OES data for monometallic copper nanoparticles (Cu) and silver and copper bimetallic nanoparticles (AgCu) digested in nitric acid and aqua regia respectively. All samples were washed thoroughly prior to ICP-OES (see Chapter 2, Sections 2.2.1.5 and 2.2.1.6 respectively for details) in order to remove any unreacted metal salt, or decomposed oxidised metal ions. The following sample identifiers and variations from standard reaction conditions were used: A) Cu-040516_1, 0.23 mmol morpholine borane complex, B) Cu-170616_1 octadecylamine capping agent, C) AgCu-150816_1 0.23 mmol morpholine borane complex with octadecylamine capping agent, D) Cu-120716_1 no deviation from standard conditions, E) Cu-150716_1 0.46 mmol morpholine borane complex with octadecylamine capping agent, F) Cu-210716_1, 220 °C ripening temperature, G) Cu-240316_1, oleylamine and oleic acid capping agents with a molar ratio of oleylamine : oleic acid of 0.9:0.1, H) Cu-190716_2, 0.92 mmol morpholine borane complex with octadecylamine capping agent.

Sample	Sample identifier	Yield Cu / %	Recovery Ag / %
A	Cu-040516_1	85	N/A
B	Cu-170616_1	66	N/A
C	AgCu-150816_1	62	93
D	Cu-120716_1	71	N/A
E	Cu-150716_1	92	N/A
F	Cu-210716_1	124	N/A
G	Cu-240316_1	9	N/A
H	Cu-190716_2	83	N/A