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Size-selective synthesis of immobilized copper oxide nanoclusters on silica

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Abstract

We report a straightforward route for preparing bulk quantities of size-controlled and low size dispersity copper oxide nanoclusters on amorphous silica. Adsorption of the copper–dendrimer complex on the silica surface minimizes aggregation, which results in previously unachieved low size dispersity of the nanoclusters. Copper oxide nanoclusters with mean diameters of 1–5 nm with size dispersities of only 8–15% were prepared by calcination of silica impregnated with Cu(II)–poly(propylene imine) dendrimer complexes of varying stoichiometry. The size and size distribution of the copper oxide nanoparticles are tunably controlled by the ratio of the Cu(II) to the terminal primary amines in the copper–dendrimer complex, DAB-Am_n–Cu(II)_x, the surface coverage of the DAB-Am_n–Cu(II)_x, and the impregnation procedure. This method is anticipated to be useful in the preparation of other metal oxide nanoparticles, e.g., Ni and Fe, and with other oxide substrates.

Keywords

Copper oxide nanoclusters; Nanocluster size control; Dendrimer

1. Introduction

Convenient preparations of well-defined nanoscale metal oxides have significant applications, including catalysis [1], sensor development [2,3], semiconductor manufacturing [4], and environmental research [5–7]. While there has been progress in the preparation of a variety of metal oxide nanoparticles, a major obstacle to their widespread use is limited control over their size and size dispersity [8,9]. For the past 15 years, a considerable amount of research has been performed on nanomaterials and nanoclusters, particularly metal oxide nanoparticles. As a result, a generally unfounded perception exists that size control has in general been achieved for the production of metal oxide nanoparticles. However, a thorough review of the available literature reveals a different

picture, viz. synthetic methods that result in size control of metal oxide nanoparticles do not currently exist.

With that said, significant advances have been made in the synthesis of metal nanoparticles by application of template-based methods that utilize precursors composed of metal ion containers, e.g. dendrimers, micelles, and organometallic complexes [10–20]. Application of these template-based and other approaches to the synthesis of metal oxide nanoparticles has led to a great deal of research focused on attempts to fabricate metal oxide nanoparticles [8,13,19,21–24]. However, a straightforward method for size-controlled synthesis of metal oxide nanoclusters (or, in fact, any size control method) has proven elusive. In this manuscript we present a method developed in our laboratory that achieves precisely that – control over the size of metal oxide nanoparticles supported on silica.

Dendrimer-based methods offer a variety of synthetic approaches for production of zero-valent metal nanoparticles and have the potential to significantly impact metal oxide nanoparticle synthesis. An important property of certain classes of dendrimers is their ability to form complexes with well-defined stoichiometry with transition metal ions in solution [11,25]. Depending on the number of pendant, terminal coordinating groups in a dendrimer (varied by branching level, viz., “generation”), the number of the metal ions complexed with the dendrimer can be precisely controlled. Sub-stoichiometric substitution by metal ions can be used to further control the number of metal ions in a dendrimer [26]. Chemical reduction [11,27] of these template complexes results in the formation of metal nanoparticles that ideally are of specific size depending upon the selected generation or substitution ratio of the dendrimer. Only few reported studies had the aim of synthesis of metal oxide nanoparticles using metal ion–dendrimer complexes [13,28,29].

Due to the well-known, and well-controlled coordinating ability of diaminobutane-core poly(propylene imine) dendrimers (referred to here as DAB- Am_n) with respect to metal ions, we explored the development of a robust and simple method for the synthesis of metal oxide nanoparticles of specified size and narrow size distribution. Here, we describe the synthesis of monodisperse copper oxide nanoparticles supported on silica via calcination of DAB- Am_n - Cu(II)_x complexes of varying metal ion–dendrimer substitution levels. To prevent aggregation of the resulting nanoparticles during oxidative/thermal decomposition of the dendrimer carbon skeleton, an amorphous silica matrix was impregnated with the DAB- Am_n - Cu(II)_x and thermally oxidized under controlled temperature conditions to ensure complete removal of carbon. In addition, select protocols for the adsorption of DAB- Am_n - Cu(II)_x on the silica resulted in significant decreases in nanoparticle migration/aggregation as judged by the observed control of size and size dispersity of the copper oxide nanoparticles.

2. Materials and methods

2.1. Synthesis of the supported copper oxide nanoparticles

Amine-terminated poly(propylene imine), generation-4 dendrimer (DAB- Am_{32}), was purchased from SyMO-CHEM (CAS# 163611-04-9). Cab-O-Sil, a high purity (>99.8%) fumed silica powder with a high surface area of $380 \text{ m}^2 \text{ g}^{-1}$ (CABOT Corp., EH-5) was the

support matrix. Copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, was used as received (Aldrich, CAS# 19004-19-4).

The DAB- Am_{32} dendrimer possesses 32 primary amine terminal groups that are able to coordinate Cu^{2+} ions up to a 2:1 stoichiometric ratio. For example, in the case of the fully stoichiometric process, one DAB- Am_{32} molecule complexes 16 Cu^{2+} ions [11,25]. The ratio of z Cu^{2+} ions complexed to the number of available bidentate-binding Am groups ($n/2$ per dendrimer molecule) can be used as a measure of the “degree of substitution of the dendrimer”, $X = z \times 2/n$. $X = 1$ for stoichiometric substitution, and $X < 1$ for less than stoichiometric substitution.

DAB- $\text{Am}_n\text{-Cu(II)}_x$ was synthesized by first adding a methanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1×10^{-2} M) to DAB-Am (1.56×10^{-3} M) in methanol. The resulting solution was thoroughly stirred for 30 min to ensure complete coordination between Cu ions and dendrimer [11]. The quantities of the $\text{Cu}(\text{NO}_3)_2$ and dendrimer solutions were adjusted to obtain the a 2×10^{-2} M concentration of Cu(II) in the final solution for the desired value of X .

To impregnate the silica matrix with the dendrimer-Cu(II) complex, Cab-O-Sil powder, in the amount corresponding to a final 5% (w/w) CuO/SiO_2 system, was suspended in methanol and sonicated for 20 min. DAB- $\text{Am}_n\text{-Cu(II)}_x$ solution was added, and the solvent was removed by rotary vacuum evaporation to form the DAB- $\text{Am}_n\text{-Cu(II)}_x$ impregnated silica powder. The impregnated material was calcined for fixed times in ambient air at a prescribed temperature. Except for experiments focusing on the effect of temperature on nanoparticle size, calcination at 450°C for 5 h was used.

To study the possible surface migration and agglomeration of the nanoclusters during the calcination procedure, a revised preparation approach was used. In the “pre-adsorption technique, the suspension containing dendrimer-Cu(II) complex and Cab-OSil was shaken for 24 h prior to solvent removal. This procedure was explored to determine if diffusional/adsorption processes of the dendrimer-Cu(II) complexes on the silica surfaces or possible aggregation of the DAB- $\text{Am}_n\text{-Cu(II)}_x$ in methanol during the previously employed fast solvent evaporation process (*vide supra*) affected the final size distributions.

2.2. Characterization of materials

Images of supported metal oxide nanoclusters were obtained on a JEOL-2010 HRTEM (high-resolution transmission electron microscope) operated at 200 kV with a LaB_6 source. The powder samples were suspended in methanol and treated in an ultrasonic bath for 1 min. A holey carbon-coated nickel TEM grid was dipped into the resulting suspension and dried in air to remove the solvent. The digitized images were imported into the program, ImageJ [30,31], and the populations of particles with respect to mean particle diameter were determined. For each sample, 150–500 particles were measured from several HRTEM micrographs to establish particle size distribution histograms. The populations of particle sizes were tabulated, and histograms were created using IGOR PRO 5 software (WaveMetrics, Inc.) with binning widths of 0.2 nm. The data were plotted and fitted to a standard Gaussian function. The reported mean sizes and standard deviations resulted from

mathematical Gaussian fits. Energy dispersive X-ray spectroscopy (EDAX) measurements were obtained using an EDAX DX-4 attachment on the TEM to obtain atomic speciation information for the region of interest in the TEM images. The measured area was typically 200 nm.

X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos AXIS 165 X-ray photoelectron spectrometer equipped with an Mg/Al source. Powdered samples were fixed on a steel holder with double-sided adhesive tape (Type 415 acrylic, 3 M) and inserted into the ultra-high vacuum (UHV) chamber of the instrument (10^{-9} Torr). In order to remove the charging effect that results from examination of insulating samples, the spectrometer's charge neutralization function was used for all analyses. For determination of the carbon content of samples calcined at different temperatures, metal stubs were used as the sample holder rather than conductive adhesive tape. Survey and high-resolution scans were collected with analyzer pass energies of 160 and 40 eV, respectively. The spectrometer utilized the hybrid magnification mode, providing for an analysis area of about 700 by 300 μm , which is suitable for survey mode spectroscopic XPS analysis.

XANES (X-ray absorption near edge structure) spectra at the Cu K-edge were collected using the Double Crystal Monochromator (DCM) beam line at LSU's Center for Advanced Microstructures and Devices [32]. A 20% (w/w) sample of CuO or Cu₂O mechanically mixed with Cab-O-Sil was used as a reference sample. Each test or reference sample was packed into a 15 mm $\times$ 2 mm window in an aluminum sample holder with both sides of the opening sealed with Kapton tape. The reported spectra are the sum of 3–5 scans. The data reduction and analysis, including background subtraction and normalization, were performed using standard methods included in the commercial analysis program WinXAS, Version 3.0 [33]. Pre-edge absorption due to the background and detector was subtracted using a linear fit to the data in the range of –150 to –50 eV relative to the sample edge energy (E_0). Each spectrum was then normalized using a constant determined by the average absorption in the range of 25–300 eV relative to E_0 .

3. Theory

We have selected diaminobutane-core poly(propylene imine) dendrimers, DAB-Am_n, as a metal oxide precursor matrix because DAB-Am_n forms well-defined stoichiometric complexes with metal ions [25,34]. Control over the stoichiometry of the dendrimer–metal complex is a critical factor for the size control of the supported metal oxide nanoclusters using our method. It is assumed that the metal-substituted dendrimer interacts with the silanol groups of the silica particles so as to immobilize them on the silica surface, similar to what is known for end-capped DAB-Am_n on other oxide surfaces [35]. Furthermore, we posit that during the calcination process, dendrimers undergo the well-known reverse Michael addition, with the resulting fragments being oxidized to CO/CO₂ to yield metal oxide nuclei composed of those metal ions from an individual DAB-Am_n–Cu(II)_x molecule. These nuclei then diffuse to yield the resulting metal oxide nanoparticles.

Fig. 1 is a schematic diagram of the fully substituted, generation-4 DAB-Am₃₂ molecule with Cu(II) ions. It has been shown that Cu(II) coordinates with 2 terminal amino groups of

DAB-Am_n molecules, forming a square-based pyramidal coordination [11]. As a result, the number of copper atoms per dendrimer molecule can be, at maximum, half of the total number of terminal amino groups. It has also been shown, that in the sub-stoichiometric concentrations of copper ions, the number of copper atoms per dendrimer molecule is constant in the whole solution, and no mixed copper–dendrimer stoichiometries are formed [25]. No formation of dendrimer–metal–dendrimer dimers has been reported.

4. Results and discussion

4.1. Impact of calcination temperature on removal of organic matter and oxidation state of Cu for DAB-Am_n–Cu(II)_x/silica

In order to determine the preparation conditions necessary for complete removal of the dendrimer skeleton from the metal ion–dendrimer complexes adsorbed on silica, the effect of calcination temperature on the XPS-determined elemental composition of the CuO/silica particles was studied. Table 1 summarizes the XPS-based compositional analysis for representative Cu–dendrimer/silica samples prepared at different calcination temperatures. Treatment at 450°C for 5 h resulted in carbon and nitrogen being reduced to below detection limits. Consequently, all the subsequent samples were prepared by calcination at 450°C for 5 h.

To determine if the Cu was reduced during calcination by carbonaceous species in the DAB-Am₃₂–Cu(II)₁₆/silica materials, XANES and XPS spectroscopic analyses were performed (cf. Fig. 2). The similarity of the XANES spectra for the calcined DAB Am₃₂–Cu(II)₁₆/silica sample and the Cu(II) oxide reference standard is striking and indicates that CuO is the dominant constituent of the copper-containing species present on the silica support.

XPS data obtained for the calcined DAB-Am_n–Cu(II)_x/silica materials presented in Fig. 2 also pointed to Cu(II) as the major copper constituent. The Cu 2p_{3/2} transition at 933.8 eV and the 2p_{1/2} peak at 954 eV is characteristic of copper(II) [36]. In addition, the presence of Cu(II) in the calcined dendrimer complexes was supported by observation of satellite transitions at 940.3 and 943.1 eV that are uniquely characteristic of Cu(II) [36,37]. Cu(I) possesses a full 3d shell and does not display these transitions. Because the 2p_{3/2} transition is broad, some Cu(I) may have been present in the calcined samples; however, the peak analysis and fitting procedure (see supporting materials for XPS spectra peak fitting) confirmed the 2+ oxidation state of copper ions for $X = 1$ and $X = 0.5$. For these samples, the spectrum could be fitted to a single peak at 933.7 ($X = 1$) and 934.1 ($X = 0.5$) with the presence of satellites centered at 941.4–941.9 eV. Such energies are consistent with the presence of Cu(II). A small amount of Cu(I) was detected for clusters formed at $X = 0.25$ where, apart from the peak centered at 933.8 eV typical of Cu(II), peak fitting resulted in a second smaller peak at 931.8 eV. The peak position at ~932 eV is typical for the presence of Cu(I) or metallic copper [34,38]. It was difficult to ascertain if any Cu(I) present in the calcined samples was the result of the synthetic process or X-ray-induced reduction that has been previously observed for Cu₂O particles [37].

4.2. Microscopic examination of calcined DAB-Am_n-Cu(II)_x/silica

Fig. 3 depicts representative HRTEM images of silica impregnated with dendrimer-Cu(II) complexes and subsequently thermal oxidized at 450°C for 5 h. When calcined samples of silica impregnated with DAB-Am₃₂ were examined by HRTEM, images characteristic of untreated Cab-O-Sil silica were obtained. However, HRTEM evaluation of calcined Cu(II)-dendrimer/silica samples revealed silica surfaces highly populated with nanometer-sized dark spots that were identified as CuO nanoparticles. Additional control experiments with non-calcined DAB-Am₃₂-Cu(II)₂/silica samples did not exhibit the characteristic dark features. Impregnation using copper nitrate methanol solution followed by calcination produced CuO clusters with a broad size range of 10–100 nm. In contrast, calculation of the size distributions of the particles in Fig. 3 prepared using the dendrimer technique demonstrated the CuO nanoparticles possessed a low size dispersity (8–15%), and their size was a function of the copper doping stoichiometry, X (cf. Fig. 4). These results indicate the dendrimer technique is necessary for size selectivity and the control to prevent broad size distributions. Although very small, the observed size dispersities were indicative of a particle nucleation and growth mechanism involving nuclei enlargement via a route that did not fully separate the nucleation and growth paths in a temporal or spatial manner [39]; *vide infra*. Statistical analysis of the average particle diameters and associated standard deviations indicated the observed differences in diameters were significant beyond the 99.9% confidence level (for t -test analysis see Supporting information). Thus, we can confidently state that the CuO nanoparticle size was dependent on the copper substitution stoichiometry in the DAB-Am₃₂-Cu(II) _{x} and is therefore exquisitely tunable.

The nanoparticle size tunability determined from the TEM measurements was consistent with the hypothesis that calcination of DAB-Am₃₂-Cu(II) _{x} complexes deposited on silica result in formation of near-monodisperse nanoparticles of copper oxide, where the number of copper ions in each dendrimer complex controls the size of the particles. However, based on dendrimer substitution only, the sizes of the nanoparticles were larger than anticipated. The generation-4, DAB dendrimer, with 32 terminal amino groups, can complex up to a maximum of 16 copper ions (2:1 ratio). Thus for the fully-, half- and quarter substituted-dendrimers, one dendrimer-copper complex contains 16, 8, and 4 copper ions, respectively. Thus a single nanoparticle on silica should also contain 16, 8 or 4 copper atoms depending the stoichiometry of the dendrimer. Cu–O bond distances in copper(II) oxide range from 0.195 to 0.216 nm [40]. For example, a particle of Cu₄O₄ should have a diameter of on the order of 0.5 nm and, depending upon the geometry of the particle, certainly no greater than 1 nm. The observed mean diameter of CuO particles on silica resulting from calcination of our $X = 0.25$ dendrimer complexes that contained 4 copper ions per single complex was 1.68 nm. The roughly 2-fold difference between theoretical and observed sizes indicated that either some aggregation of dendrimer-Cu occurred during the synthetic process or that some limited diffusion of Cu ions/CuO nuclei took place during calcination. A similar conclusion was reached for particles resulting from calcination of the half and fully Cu-substituted complexes. However, the extent and nature of Cu-dendrimer aggregation or Cu ion/CuO diffusion was small enough that narrow particle size distributions were still observed. The larger than expected CuO particle sizes may be the result of diffusion of Cu ions on the

silica surface [26], or alternatively, aggregation of the dendrimer–Cu(II) precursor complexes in solution.

To test these hypotheses and possibly improve precursor adsorption on the silica, a room temperature, 24 h interaction of the precursor solution with the substrate was employed (“pre-adsorption”) to determine if these conditions would allow for more efficient/facile diffusion/adsorption of the dendrimer–Cu(II) complexes on the silica surface. This procedure resulted in a significant, 20–35% decrease in the size of the CuO nanoparticles (cf. Fig. 5). When copper oxide nanoparticles were prepared using the $X = 0.25$ dendrimer–Cu(II) complex, the EDAX measurements indicated the expected presence of copper associated with the silica. However, CuO nanoparticles were not discernable in the HRTEM micrographs. CuO nanoparticles were likely formed, but their contrast versus the silica background was not sufficient to be observable.

Decreasing the concentration of dendrimer–Cu(II) complexes on the silica surface resulted in smaller diameter nanoparticles (cf. Fig. 5). For $X = 1$, a decrease in the dendrimer–Cu(II) complex loading corresponding to 1% (w/w) CuO on the silica surface used in conjunction with the pre-adsorption deposition method resulted in the formation of nanoparticles with a mean diameter of 1.55 nm. These results suggested both solution aggregation of the dendrimer–Cu(II) complex in the final stages of impregnation and the surface concentrations of particle precursors were critical factors influencing the final size of the copper oxide nanoparticles. Higher surface concentrations of Cu(II)–dendrimer, resulting in close proximities of adsorbed dendrimer–Cu(II) complexes, appeared to enhance the migration of copper species that resulted in larger CuO particles during calcination. However, these results indicated that this phenomenon could be limited if the surface concentration of the Cu(II)–dendrimer precursor was lowered. Similarly, avoiding a fast solvent removal during deposition of the dendrimer–Cu(II) complex on the surface matrix and allowing sufficient time for diffusion and pre-adsorption of the complexes on the matrix reduced the final size of the oxide particles. The CuO nanoparticles resulting from the 1% Cu coverage and pre-adsorption technique (1.55-nm diameter) may have formed a structure that is close to that of a flat CuO nanoparticle [13], similar to that observed for iron oxide nanodisks made by solution-phase synthesis routes [41].

Thermal treatment at high temperatures is generally accepted to result in growth and sintering of metal oxide grains [42]; however, to our knowledge, there has been no systematic study of thermal growth of supported metal oxide nanoparticles. To increase the range of CuO nanoparticle sizes utilizing the same generation of the dendrimer precursor, we investigated what we refer to as the “annealed growth” approach. This technique takes advantage of the increased mobility of nuclei/particles/monomers (ions or atoms) with increased temperature to form particles with increased sizes. However, the use of elevated temperatures is expected to result in broader particle size distributions [43]. Two common mechanisms are known for particle growth during thermal annealing: Oswald ripening and particle migration and coalescence [43]. Particle migration/coalescence involves migration of multiple particles, while in Oswald ripening, monomers (ions/atoms) migrate along the surface to the immobile particle.

The shape of the particle size distribution curve can be used to distinguish the thermal mechanism of particle growth. Fig. 6 presents the particle sizes and distributions achieved in experiments in which the calcination temperature was varied. The nanoparticles resulting from oxidation of substituted dendrimer–Cu(II) complex ($X = 1$) were enlarged from 2.05 to 3.17, 4.09, and 5.64 at 550°C, 600°C and 650°C, respectively. However, although most of the nanoparticles were 2–4 nm in diameter, the size distribution became broader and the percentage of larger particles increased. The positively skewed size distribution is characteristic of the particle migration and coalescence mechanism of growth.

5. Conclusions

The use of the dendrimer-template methodology described here is a powerful tool for synthesis of CuO nanoparticles. As is evident from the summary in Table 2, particle sizes can be broadly tuned with low size disparities. The size range can be further expanded by use of different generations of dendrimers. Additional studies also indicate this method is robust and can be applied to other metal oxides such as iron and nickel and supports as varied as titania and alumina.

The applications of metal oxides nanoclusters are multiple, from catalytic processes to pharmacology, optical and electronic industries. With this work we are providing a new tool for applications that are strongly dependent on the size of the metal oxide nanoclusters. Because such narrow size distributions of metal oxide nanoclusters are currently unavailable, it is difficult to predict what these applications might be. However, it is generally acknowledged that small changes in the size of metal and metal oxide nanoclusters can result in dramatic changes in the chemical or physical properties of the materials. One can even imagine a small difference in the size of metal oxide nanoclusters can control site-specific bonding with target proteins.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Schematic diagram of the DAB-Am₃₂ dendrimer (generation-4) fully substituted with 16 copper ions.

Fig. 2. XANES (*upper*) and X-ray photoelectron (*lower*) spectra of calcined DABAm_n-Cu(II)_x/silica and those of powdered Cu₂O and CuO standards.

Fig. 3. High-resolution electron micrographs of thermally-treated (450°C, 5 h) DAB-Am₃₂ and DAB-Am₃₂-Cu(II)_z on Cab-O-Sil silica. The dark spots in the images for $X = 0.25$, 0.5 , and 1 are copper oxide nanoparticles, and the gray background results from the silica support. Cab-O-Sil impregnated with Cu(II)_z-DAB-Am₃₂, but not calcined (data not shown), did not result in nanoparticle formation.

Fig. 4. Size distribution of CuO nanoparticles on silica (5%, w/w) resulting from calcination of dendrimer-Cu(II)/silica of various substitution ratios ($X = 0.25, 0.5, \text{ and } 1$) of generation-4 dendrimer.

Fig. 5. Size distribution of CuO nanoclusters supported on silica as a function of preparation procedure. The purple and green curves compare the effects of deposition method. The green and red curves compare the effects of varying the stoichiometric ratio, X . The green and blue curves compare the effects of the metal concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 6. Size distribution of 5% CuO nanoclusters on silica achieved under higher calcination temperature using dendrimer-Cu(II) complex with $X = 1$ as precursor.

Table 1

Surface atomic composition (%) of DAB-Am₃₂-Cu(II)₁₆/silica as a function of calcination temperature.

Element	Calcination temperature					
	Initial sample ^a	250 °C	300 °C	350 °C	400 °C	450 °C
Carbon	13.18	2.21	0.98	0.82	0.28	<0.01
Nitrogen	3.51	0.92	0.27	n.d.	n.d.	n.d.
Oxygen	47.73	52.04	55.13	44.83	42.80	49.20
Copper	1.86	1.46	1.20	0.72	0.52	0.43
Silicon	33.72	43.37	42.42	53.62	56.40	50.4

n.d.: none detected. The detection limit for nitrogen was 0.001% for the Axis 165 instrument.

^a All samples were dried at 120 °C and calcined at a prescribed temperature for 5h.

Table 2

CuO cluster sizes and distributions achieved using methods described in this paper.

CuO loading (% w/w)	Substitution ratio (X)	T (°C)	Pre-adsorption	d_m (nm)	σ (nm)	Rsd ^a (%)
5	1	650	Yes	5.64	2.52	44.7
5	1	600	Yes	4.09	1.59	38.9
5	1	450	No	3.27	0.24	7.3
5	1	550	Yes	3.17	0.71	22.4
5	0.5	450	No	2.37	0.34	14.3
5	1	450	Yes	2.05	0.23	9.2
5	0.5	450	Yes	1.86	0.17	9.1
5	0.25	450	No	1.68	0.19	11.3
1	1	450	Yes	1.55	0.19	12.3
5	0.5	450	Yes	<1	NA	NA

Rsd: relative standard deviation.

^aDue to image contrast limitation, it was not possible to observe the CuO nanoclusters, pointing to particles smaller than 1 nm.