



## Review

## Atomically precise copper nanoclusters and their applications

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## ABSTRACT

Although Cu nanoparticles (CuNPs) have been subjected to broad investigations, especially viewing their easy access, low cost and rich catalytic properties, atomically precise copper nanoclusters (CuNCs) are less often examined due to the difficulties of their isolation in pure form. Yet their study is essential for a better understanding of the molecular, physical and catalytic properties of CuNPs that are in fact mixtures of CuNCs. The review highlights the background and recent progress in CuNCs including the structural and physico-chemical properties and new applications to galvanic reactions, fluorescence and catalysis. Particular emphasis is placed on catalysis for which hydrogen evolution reaction, reduction of CO<sub>2</sub> and recent comparative results from our group concerning 1,3-dipolar cycloaddition of organic azides and alkynes (CuAAC, “click reaction”) are detailed. In this latter sub-field the key role of the relative stabilities of the CuNCs on their performances is emphasized as shown with Clayborne and Chen’s nanocluster anion [Cu<sub>6</sub>(SR)<sub>6</sub>]<sup>−</sup> [Na<sup>+</sup>, solvent], R = C<sub>7</sub>H<sub>4</sub>NO, solvent = acetone or THF, that shows excellent efficiency for the CuAAC reaction.

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## 1. Introduction

The concentration of Cu in the Earth's crust is around 60 g/ton. Cu-based nanomaterials with plenty of morphologies involving copper (0), copper oxide, cupric oxide, tricopper nitride and supported copper complexes have been shown to catalyze a great deal of reactions due to their environmentally benign character, low cost, easy availability and excellent efficiency [1–5]. This reaction diversity includes *N*- and *O*-arylation, CuAAC reaction, nitrophenol reduction, hydrogen generation, CO and alcohol oxidation, oxygen reduction reaction, oxidative carbonylation, amination, epoxidation, aza-Michael reaction, carbon–carbon, carbon–sulphur, carbon–nitrogen, carbon–oxygen, carbon–selenium and sulphur–sulphur coupling, homocoupling of terminal alkynes, hydrogenation and hydrogenolysis. Among these Cu-based nanomaterials, Cu nanoparticles (CuNPs) occupy a large part, because their formation is very straightforward by reduction of a cheap and readily available Cu salt and a common reductant such as sodium borohydride. The CuNPs have been recently reviewed including their applications in catalysis [6]. CuNPs, as other kinds of NPs, are mixtures of nanoclusters (NCs), and these NPs have variable undefined polydispersities. For a better definition and understanding of the properties of each cluster, however, the isolation of atomically precise NCs is essential. Thus in the course of the present review, the abbreviation CuNC(s) is exclusively reserved to atomically precise nanoclusters (not only superatoms, but also including Cu(I) NCs), whereas the abbreviation CuNP is used for a copper nanoparticle consisting of a mixture of CuNCs with variable undefined dispersity.

In recent years, the rapid development of CuNCs stabilized mainly by thiolate or phosphate ligands has yielded a library of new model precatalysts with specific and uniform nanostructures [7–10], although a mere handful of CuNCs without any surfactant or protective agent have also been reported in the literature [11]. In general, CuNCs have a diameter less than 2 nm (excluding the ligand shell) and a metal core with tens to a few hundreds of metal atoms. These CuNCs have attracted wide attention due to their unique physical and chemical characteristics with potential applications in medical diagnostics and therapeutics [12], catalysis, chemical sensors, fluoroscopy and nanodevices [13–30]. In addition, CuNCs have become an ideal model for studying the structure and size-dependent characteristics of metal NPs because of their the atomically precise composition and determined atom packing structure. Similarly, these CuNCs have shown some very intriguing core size-dependent electronic and optical properties and quantum size effect [31–35].

When the neutral clusters only bear neutral ligands such as phosphines, amines, *N*-heterocyclic carbenes, etc. the oxidation state of all the metal atoms is zero. On the other hand, when the metal atoms bear formally anionic (in fact radical type) ligands such as H, halogeno, phosphido, thiolate, etc. that are bridging surface atoms, these surface atoms are in the oxidation state I. In these Cu(I)NCs, the stability is provided by the bridging ligands, and there are no real Cu–Cu bonds, but only some cuprophily, i.e.  $d^{10}$ – $d^{10}$  van der Waals interactions. In large NCs where there are both inner and ligand bridged surface atoms, the average oxidation state becomes intermediate between 0 and I.

This review will cover the most significant developments of CuNCs in the last 5 years with a special emphasis on the syntheses, structures and applications of the CuNCs in catalysis. CuNCs are discussed as parts of CuNPs with similar properties in the fluorescence section. Previously, the review of Yan [9] and Jin [14] have provided a good summary of the recent developments in the synthesis, stable sizes and properties of ligand protected, atomically precise NCs of Au, Pt, Ag, Cu and Ni. Fenske's group has also shown a long-term interest in metal NCs, and in 2013 they reported a

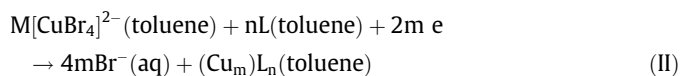
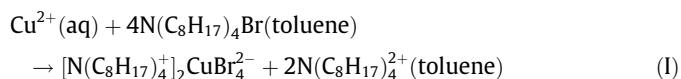
summary of the rich structural properties of Cu and Ag chalcogenide NCs with protecting phosphane or organic ligand shells generated from silylated chalcogenide sources [7]. Liu et al. also reported an account on the polyhydrido CuNCs and compared their syntheses, structures, stabilities, reactivities and transformations [10]. In the present review the recent progresses concerning the syntheses, structures, galvanic reactions, fluorescence properties, small molecule activation and catalytic applications of CuNCs in the literature are discussed, and some recent catalysis results from our groups on CuNCs are detailed.

## 2. Synthesis

The various synthetic approaches of atomically precise CuNCs that have been reported include those used for the synthesis of CuNPs. In this section, the commonly used effective methods including the Brust–Schiffrin method, the water-in-oil (w/o) microemulsion strategy, electrochemical techniques and microwave-assisted polyol synthesis method are summarized. In Sections 3 and 4, selective reactions leading to the isolation of a single CuNC are detailed.

### 2.1. Brust–Schiffrin method

Since the report by the Schiffrin group of the two-phase method to synthesize AuNPs in 1994 [36], the so-called Brust–Schiffrin method has been widely utilized to synthesize ligand-protected metal (Au, Ag or Cu) NPs due to the high stability of the AuNPs obtained and simplicity of the procedure. In general, the Brust–Schiffrin method involves the assistance of a phase-transfer agent such as  $N(C_8H_{17})_4 Br$ . The chloro-metal anions are initially transferred to the organic phase from the aqueous phase, and these ions are then reduced to metal NPs in the presence of a reducing agent (sodium borohydride). The metal NPs are simultaneously passivated and protected by ligands. For example, in 2011, Chen and coworkers reported the use of 2-mercapto-5-*n*-propylpyrimidine (MPP) as the protecting ligand to synthesize stable  $Cu_n$  ( $n \leq 8$ ) NCs using a modified Brust–Schiffrin method (Eqs. (I) and (II)).



The obtained  $Cu_n$  nanoclusters exhibited significant luminescence at 425 and 593 nm, with 3.5% and 0.9% quantum yields, respectively. Moreover, these CuNCs were shown to be efficient catalysts in the  $O_2$  electroreduction (*vide infra*) [37].

### 2.2. Water-in-oil (w/o) microemulsion strategy

The use of an inorganic phase in water-in-oil (w/o) microemulsions (the liquid mixture of aqueous and organic phases) has attracted wide attention for the preparation of metallic NPs with precise control of the NP shape, size and narrow size distributions [38]. Recently, Vazquez-Vazquez and coworkers successfully synthesized a battery of small CuNCs using the w/o microemulsion strategy [39]. In addition, they also found that the core size of the CuNCs was highly associated with the amount of reducing agent during the synthesis procedure.

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