



Synthesis of copper nanostructures on silica-based particles for antimicrobial organic coatings



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ABSTRACT

Sol–gel based silica nanoparticles of 100 nm were used to interact with copper ions from the dissolution of CuCl_2 allowing the synthesis of paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) nanocrystals of around 20 nm. The method produced well dispersed copper nanostructures directly supported on the surface of the SiO_2 particles and was generalized by using a natural zeolite microparticle as support with similar results. These hybrid Cu based nanoparticles released copper ions when immersed in water explaining their antimicrobial behavior against *Escherichia coli* and *Staphylococcus aureus* as measured by the minimum inhibitory and minimum bactericidal concentrations (MIC and MBC). Noteworthy, when these nanostructured particles were mixed with an organic coating the resulting film eliminated until a 99% of both bacteria at concentrations as low as 0.01 wt%.

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1. Introduction

Synthesis of metal based nanoparticles on the surface of a supporting particle is a relevant approach producing nanomaterials with improved characteristics such as stability and reactivity [1,2]. Metal nanoparticles supported on metal oxides and carbon surfaces are the basis for many catalysts of importance in energy technologies, pollution prevention, and environmental cleanup [2]. From the different kinds of supported metal nanoparticles, those having copper are highlighted due to their wide range of applications, especially in catalysts [3–10]. Dispersed copper catalysts have been of great interest in several reactions from steam reforming to biosensing applications [11]. However, copper nanoparticles also emerge as an active and strong antimicrobial agent that can be supported on different nanostructures toward the development of novel biocide materials [12–16]. Noteworthy, copper nanoparticles can be embedded in polymer matrices allowing the development of novel antimicrobial polymeric materials [17–20]. The relevance of nanotechnology in this area relates with larger release of the active agent (Cu^{2+}) from nanoparticles than from microparticles [21,22]. Moreover, by supporting copper nanoparticles the aggregation is decreased avoiding the deterioration of its chemical properties and therefore of its antimicrobial behavior [14]. For instance, a direct relationship between nanoparticle dispersion and release of metal

ions was found in polymer/copper composites [23]. Moreover, the release of the active agent is delayed when these particles are supported [14]. Therefore, the ion release from copper nanoparticles can be controlled by a proper support design.

From the different kinds of copper particles, stoichiometric $\text{Cu}_2(\text{OH})_3\text{Cl}$ basic copper(II) chloride is stressed due to its unique chemistry and physical properties. $\text{Cu}_2(\text{OH})_3\text{Cl}$ is known to have four types of crystal structures, including orthorhombic atacamite, monoclinic botallackite, rhombohedral paratacamite, and monoclinic clinoatacamite [24]. For instance, $\text{Cu}_2(\text{OH})_3\text{Cl}$ paratacamite can be used in a wide range of applications such as a catalysts [25], corrosion prevention [26], agriculture [27], and hydrogen uptake and storage [28]. $\text{Cu}_2(\text{OH})_3\text{Cl}$ was superior to the traditional $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for reoxidizing reduced palladium catalysts [26]. Unlike botallackite [29], nanoparticles based on paratacamite have not been published focusing on their support neither on its antimicrobial activity [24,25,28,30–32]. These nanostructures are synthesized from copper salt solutions through pH regulation and, for instance, paratacamite is usually produced from copper chloride solution under basic condition [24]. Other methods based on hydrothermal and heat-treatment reactions have also been reported using urea as reagent [28].

Based on the above mentioned, the goal of the present manuscript was to synthesize paratacamite nanostructures on the surface of silica-based particles. These supported nanostructures were able to both release copper ions when immersed in water and eliminate bacteria. Moreover, these nanoparticles were used to produce antimicrobial organic coatings.

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2. Experimental

2.1. Synthesis of nanoparticles

Spherical silica nanoparticles of 100 nm were synthesized by the sol–gel method using a two-stage mixed semi-batch method, as previously reported [33,34]. In the first stage, Solutions A and B were prepared. For Solution A, 0.5 M of tetraethylortosilicate (TEOS) was dissolved in 22 mL of ethanol whereas in Solution B, 0.2 M of aqueous ammonia solution was added to 23 mL of ethanol and 2 mL of water. Solution B was then added dropwise to Solution A. The resulting mixture was allowed to react for 60 min at 40 °C under a N₂ atmosphere. In the second stage, Solutions A and B were again prepared and added to the reactor containing the solution and the particles prepared in the first stage. The solutions were separated by centrifugation (10,000 RPM, 20 min) and washed three times with ethanol. The methodology used for the synthesis of paratacamite nanostructures was based on the results from Kim et al. [14]. In particular, 1.56 g of CuCl₂ (from Sigma–Aldrich), 0.5 mL of ammonia solution (from Sigma–Aldrich) and 1.5 g of silica nanoparticles were mixed in 100 mL of deionized water during 6 h at pH 4. Afterward, the solution was filtered and dried at room temperature. The same procedure was used for zeolite microparticles. In this case, a natural mordenite was used.

2.2. Particle characterization

The morphology of the particles was characterized by a FEI microscope model G2 F20 S-Twin high-resolution transmission electron microscopy (HRTEM) at 200 kV. The samples were dispersed in ethanol previous to the observation. Wide angle X-ray diffraction analysis was carried out using a Siemens D-5000 diffractometer with CuK α =1.54 Å and a step scan of 0.02° at room temperature. Elemental analyses for the particles were carried out with inductively coupled plasma mass spectrometry (ICP-MS) Neptune Plus model. The thermal stability was evaluated by calcination of obtained particles at temperature 450 °C at a heating rate of 10 °C/min during 4 h using a Thermo Fisher Scientific Thermolyne.

The release of cupric ion was measured using a UV–Visible (Model JENWAY 6320D) spectrophotometer. The ion concentration in 3 mL of sample solutions was determined by adding 1 mL of 10% hydroxylamine hydrochloride solution, 1 mL of sodium acetate–acetic acid buffer (pH 4.5) and 1 mL of 1.92×10^{-3} mol neocuproine (copper reagent). The neocuproine was used to form a yellow chelate with the cupric ions. Ions released from hybrid particles were determined by adding 0.05 g in 60 mL of deionized water. Before each measurement at time, the solution was centrifuged for 15 min at $19,000 \text{ rev min}^{-1}$.

The antibacterial activity was determined by turbidimetric method. The *Escherichia coli* (K-12 DH5 α) and *Staphylococcus aureus* (isolated strain) were tested. A pure culture of the specified bacteria was grown overnight then diluted in growth-supporting Muller Hinton broth to a concentration between 1×10^6 and 1×10^9 CFU/mL. A stock of tubes with a dilution of the antimicrobial substance were prepared in low-phosphate Tris-buffered mineral salts (LPTMS) medium. The dilutions were from 0 to 2000 mg/L of the particles, increasing by 125 mg/L. An aliquot of 100 μ L of bacteria was incubated in each tube overnight in a shaking incubator at 37 °C and 200 rpm. Inoculated broths without antimicrobial substance were used as blank. The tubes were then characterized by turbidity. Turbidity indicates growth of the microorganism and the MIC (minimum inhibitory concentration) is the lowest concentration where no growth is visually observed. The MIC is therefore defined as the lowest concentration of the antimicrobial substance which will inhibit the *in vitro* growth of the bacteria. An aliquot of 100 μ L of the dilution representing the MIC was incubated in a plate

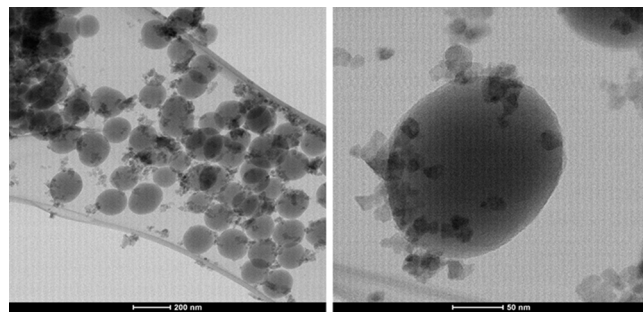


Fig. 1. TEM images for hybrid particles synthesized by using silica nanoparticles of 100 nm. Copper nanostructures are mainly formed on the surface of the silica-based particles.

and enumerated to determine viable CFU/mL. The MBC (minimum bactericidal concentration) otherwise was defined as the lowest concentration of the antimicrobial substance to kill 99.9 percent of the initial bacterial inoculum. MBC was determined from the tubes showing no turbidity. An aliquot of 100 μ L of the dilution representing the MBC was incubated in a plate and enumerated to determine viable CFU/mL. All the experiments were repeated at least twice.

2.3. Organic coating

A latex paint was used as a standard organic coating where particles were dispersed at concentrations of 0.01 and 0.1 wt%. The solution was stirred by a magnetic mixer for 10 min and the final composites were stable without any evidence of particle precipitation. After mixing, the dispersion was coated on a wood surface where a homogeneous film was obtained.

The antibacterial activity was determined by plate method. *E. coli* (K-12 DH5 α) and *S. aureus* (isolated strain) were tested. A pure culture of specified bacteria was grown overnight then diluted in growth-supporting Muller Hinton broth to a concentration between 1×10^6 and 1×10^9 CFU/mL. The initial concentration of bacteria was determined by incubated in a plate for 24 h at 37 °C. An aliquot of 100 μ L of the bacteria broth was poured into the wood surface and covered with a glass during 6 h at 37 °C. After the prescribed time had elapsed, the samples were thoroughly washed with 5 mL solution of 0.88 wt% NaCl and 1 wt% of Tween 80 to remove the bacteria. An aliquot of 100 μ L of the each sample was diluted 0.1, 0.01 and 0.001 in low-phosphate Tris-buffered mineral salts (LPTMS) medium. From these dilutions, a 100 μ L was incubated in a plate for 24 h at 37 °C and the bacteria colonies were enumerated to determine viable CFU/mL. All the experiments were repeated at least twice.

3. Results

Fig. 1 displays TEM images of the nanostructures synthesized using SiO₂ nanoparticles as support. Sol–gel method was able to produce well defined and homogeneous spherical silica nanoparticles with diameters around 100 ± 8 nm. Noteworthy, by adding CuCl₂ salt to a solution having these silica nanoparticles, well dispersed copper nanoparticles were obtained, as observed in **Fig. 1**. These nanostructures were mostly absorbed on the support although coexisting with unanchored particles. The method produced a mono-dispersed particle size distribution with values around 20 nm. The interaction between the metal ions and the oxide surfaces of the silica, for instance the terminal OH groups formed by dissociative adsorption of water molecules, can explain the presence of copper nanoparticles [14]. In a similar system, the formation of copper nanoparticles on a silica surface was summarized in three steps [14]: (1) deprotonation of hydroxyl ligand

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