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Copper nanoparticles catalyzed oxidation of threonine by peroxomonosulfate

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Abstract The undertaken study describes the synthesis of copper nanoparticles (Cunps) in an aqueous medium using ascorbic acid as a reducing agent via the chemical reduction method. The synthesized copper nanoparticles have resistance to oxidation by atmospheric oxygen for two months. The copper nanoparticles were characterized by UV–Visible spectrophotometry, FTIR spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The average sizes of copper nanoparticles were found to be 28, 16, 12 nm at increasing concentrations of L-ascorbic acid respectively. Interestingly, it was found that, the catalytic activity depends on the size of nanoparticles. The catalysis by colloidal copper nanoparticles was studied kinetically with the oxidation of L-threonine (Thr) by peroxomonosulfate (PMS) in aqueous medium. The oxidation rate was found to follow first order kinetics with respect to threonine and peroxomonosulfate. The copper nanoparticles are expected to be a suitable alternative and play an important role in the field of catalysis and environmental remediation.

1. Introduction

Research on nanoparticles has received considerable attention since they have unique properties and numerous applications in different areas [1,2]. Metallic nanoparticles are of great interest due to their excellent chemical, physical and catalytic properties [3]. Among colloidal transition metal nanoparticles, copper nanoparticles receive considerable attention since they are used as an advanced material with electronic, optical and thermal properties [4]. In addition to their interesting physical properties exhibited due to quantum size effect, they also have applications in catalysis due to their large surface area and special morphologies. Copper nanoparticles were assumed to be cost effective as compared to noble metals like Ag, Au and Pt. Hence, they are potentially applied in the field of catalysis, cooling fluids and conductive links [5]. Among various methods, the chemical reduction method is widely selected for the synthesis of copper nanoparticles because it is of low cost, efficient in yield and requires limited equipment. It is simple and control of size and shape of particles obtained under controlled parameters is seen [6]. Although the synthesis of copper nanoparticles has been carried via numerous routes [7], very less is known about the size dependent performance of copper nanoparticles as a suitable catalyst. The main question arises

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from the stability of copper nanoparticles including the extreme sensitivity to oxygen and colloidal agglomeration. Therefore there are several approaches related to the dispersion and oxidation resistance that needs to be solved before application. Some studies reveal that to protect copper nanoparticles against oxidation, ascorbic acid is utilized as a reductant and antioxidant [8–10]. The L-ascorbic acid (hydrogen potential of +0.08 V) can easily reduce metal ions with standard reduction potential higher than 0 V, such as Cu^{2+}, Ag^{+}, Au^{3+} and Pt^{4+} but cannot reduce these ions with potential less than 0 V such as Fe^{2+}, Co^{2+}, Ni^{2+}. Hydrogen free radicals released from ascorbic acid react rapidly with hydroxyl free radicals and oxygen, whose existence is usually related to the oxidation of the nanoparticles. So our experiment was performed without inert gas protection.

The oxidative decarboxylation of amino acid is of importance both from a photochemical view point and also from the view point of the mechanism of amino acid metabolism. Metallic ions play a significant role in the oxidative decarboxylation of amino acids. Kinetics of oxidation of amino acids by a variety of oxidants like hexacyanoferrate(III) [11], peroxomonosulfate [12], peroxodisulfate [13], cerium(IV) [14], chromium(VI) [15] in the presence of transition metal catalysts as well as hexacyanoferrate(III) [16], hydrogen peroxide [17], peroxomonosulfate [18] in the presence of transition metal nanoparticles in both acid and alkaline media have been studied. There are still controversies reported regarding the oxidation product of amino acids as keto acids [19], both as intermediate and also as the oxidation product. In most of the reaction, the end product is the aldehyde [20], the intermediate R–CH = $N^{+}H_2$ undergoes hydrolysis to yield aldehyde whereas its interaction with the oxidant yields nitrile as an end product. However, various types of reaction mechanisms have been suggested but the specific details are yet to be found out. Peroxomonosulfate can be considered as a monosubstituted hydrogen peroxide in which one hydrogen is replaced by the SO_3 group, the other hydrogen comes from the acid group. Peroxide act as an oxygen donor to the organic substrate [21]. In fact, it is the peroxide bond in these peracids that is mainly responsible for its reactions. Study of kinetics of oxidation of amino acids by peroxo oxidants is an area of intensive research because peroxo oxidants are environmentally benign and do not produce toxic compounds during the reaction. The applications of transition metal nanoparticles as catalyst for organic transformations include condensation [22], hydrosilation [23] and hydration reaction of unsaturated organic molecules [24] as well as redox [25] and other electron transfer process [26]. Though studies on kinetics of oxidation of amino acid with peroxomonosulfate have been widely carried out, very few attempts have been made so far on the oxidative deamination of amino acids in the presence of metal nanoparticles. In this work, an attempt has been made to construct a model.

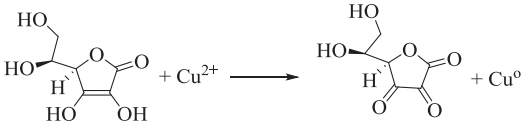
2. Experimental

2.1. Materials

Peroxomonosulfate (PMS) was obtained from Sigma–Aldrich under the trade name "Oxone". The purity of the triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ was estimated by iodometry and found to be 98%. However, the presence of H_2O_2 in the oxone sample was tested. Tests with permanganate showed the absence of free hydrogen peroxide and hence this reagent was used without further purification. A fresh solution of oxone was prepared before starting the experiments. Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$-97%), L-ascorbic acid (vitamin C-98%), and threonine were obtained from E. Merck. All other chemicals used in this study were of Analar grade and used as such without any further treatment. Double distilled water was employed throughout the study.

2.2. Synthesis of copper nanoparticles

In a synthetic procedure, the wet chemical reduction route was used for synthesis of the copper nanoparticles. $CuCl_2{\cdot}2H_2O$ aqueous solution was prepared by dissolving $CuCl_2{\cdot}2H_2O$ (0.02 mol L^{-1}) in 50 ml deionized water. The flask containing aqueous solution of $CuCl_2{\cdot}2H_2O$ was heated to 353 K in an oil bath with magnetic stirring. 50 ml of L-ascorbic acid (0.1 mol L^{-1}) aqueous solution was added drop wise into the flask while stirring. With the passage of time, the color of the solution gradually changed from white to dark brown with a number of intermediate stages. The reduction process and copper nanoparticle growth process was completed after 24 h and the resulting dispersion was centrifuged for 15 min at 6000 rpm. The supernatant was placed under ambient conditions for 2 months. The redox equation of L-ascorbic acid and copper ion can be expressed by Eq. (1).



(1)

L-ascorbic acid dehydroascorbic acid

2.3. Characterization

UV–Visible spectrophotometer from a double beam spectrophotometer (U.V. 3000^{+} LABINDIA) was used for the preliminary estimation of copper nanoparticles synthesis. FTIR (ALPHA-T – Bruker) provided information about oxidation product of the reaction. Morphological study of the copper nanoparticles was carried out with scanning electron microscopy (SEM) (EVO 18 carlzeiss) image analysis, for which dispersed nanoparticles were centrifuged (Laboratory Centrifuges Remi, model R-8C) and ultrasonicated (Ultrasonic processor model EI-250UP) for 40 min. 30 µl aliquots were extracted and deposited on stub for SEM analysis. Transmission electron microscope (TEM) (FEI Techni G2S2 Twin) images were recorded to confirm size distribution and shape homogeneity of newly synthesized copper nanoparticles. Samples were prepared by taking small quantities of copper nanoparticles separated by centrifugation then ultrasonicated dispersed suspensions were mounted on carbon coated copper grids.

2.4. Kinetic measurements

Reaction mixture containing aqueous solution of all other reagents except peroxomonosulfate was adjusted to pH 7.0 employing potassium dihydrogen phosphate–sodium

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