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Optimization of Surface Plasmon Resonance Band of Copper Nanoparticles Doping in Silica Xerogels

Copper nanoparticles were synthesized via chemical reduction method. Copper nitrate aqueous precursor using trisodium citrate as a reducing agent at boiling temperature. Structural and optical characteristics were determined as a function of copper nitrite concentration. The effect of concentration on the characteristics of the surface plasmon absorption band was determined and studied at 790 nm. The broadening of the surface plasmon resonance (SPR) band indicated the existence of larger particles in the solution. Silica xerogel doped with Copper nanoparticles by sol-gel route at specific preparation parameters. The absorption intensity reasonably increased for bulk samples (Cu NPs in xerogels) as compared to Cu NPs solution.

Keywords: Silica xerogel; Chemical reduction; Nanoparticles; Concentration
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1. Introduction

Nanomaterials are investigated widely at the present time because of their distinct optical, electronic and mechanical characteristics [1]. Noble metal nanoparticles, such as copper nanoparticles (Cu NPs), have been a source of great interest to their unusual physical features, particularly their strong Plasmon absorption peak in the visible region [2]. The resonance frequencies are determined by the particle form and size, and remain stable for months. Nobel metal nanoparticles show brilliant colors due to the surface plasmon resonance absorption [3]. The examination of the surface plasmon resonance absorption is part of a large ongoing research field to investigate properties on the nanometer scale [4]. The color of metal nanoparticles depends on the shape and size of the nanoparticles and dielectric constant of the surrounding medium, leading to many studies on their synthesis and applications [5]. Copper is a relatively rare element with an estimate of copper atoms comprising 22 parts per million (ppm) of the Earth's crust (68 ppm by weight); making it the eighth most abundant metal. Bulk copper has good conductive properties, but not when synthesized as nanoparticles. Despite that, Cu NPs have superior antibacterial, deodorant, catalysis, lubricant and conductive links [6-9]. In the past few years, the synthesis of Cu NPs has attracted much attention because of its huge potential for replacing expensive nano silver inks used in conductive printing. If a suitable protective coating is applied on copper nanoparticles, they can withstand oxidation in the environment [6]. An organic polymer, alkene chains, graphene or amorphous carbon, inorganic substances like silica, or an inert metal could all be present in this layer. By directly printing conductive patterns, such coated copper nanoparticles allow for the achievement of high conductivities. By employing copper-based inkjet inks to create solar cells, RFID tags, and electroluminescence devices, among other gadgets, this method creates new opportunities in printed electronics [8-10]. To develop nanoparticles, ultrasonic irradiation, electrochemical synthesis, thermal decomposition, radiolysis, and chemical reduction of metal salts had been used [11,12]. Chemical reduction is one of the most important technique for preparing Ag, Au and Cu colloids [7]. In the present study, copper nanoparticles were synthesized from copper nitrate salt solution with trisodium citrate as a reducing agent. This approach allows regulating particle size and form by varying the molar concentration of reactants. Metal salt precursor, reducing agent, and stabilizing/surfactants/capping agent are the three key components used in this procedure. The two stages of the copper reduction process are nucleation and particle growth [13]. When compared to the physical approach, the chemical method is characterized by high yield, cost-effective and easy particle size control [14]. Despite numerous attempts, preparing NPs with a well-defined size remains difficult, necessitating a second procedure to prevent particle aggregation [15]. Synthesis of NPs utilizing stabilizers, surfactants, and capping agents has been evaluated and reported to prevent aggregation [16]. A metal alkoxide and an organic alkoxysilane precursor are combined with water and a solvent in the presence of an acid or base catalyst to hydrolyze and condense to create sol-gel materials, which are inorganic/organic hybrid compounds [17]. It can

create extremely porous, stiff membranes that are useful for a variety of purposes, including the entrapment or immobilization of biomolecules like proteins and enzymes that maintain their biological function and may be released from fouling. [18]. In order to optimize the surface plasmon resonance band of Cu NPs, the later was doped in silica xerogel for the development of future anti - bacteria agent.

2. Experimental Part

The synthesis of $CuNO_3$ NPs was carried out using chemical reduction method. At first, a solution of 6.7×10^{-3}, 5×10^{-3}, c= 5×10^{-1} , d=8.5 $\times$ 10^{-1} , e =9×10^{-1} & f= 1 $mol\backslash L$ $CuNO_3$ were prepared by dissolving the copper nitrate precursor in water. Besides; 0.5g sodium citrate was dissolved in 50mL of H_2O to obtain 5% solution. Copper nanoparticles were synthesized by heating the diluted solution of $CuNO_3$ until it begins to boil, then 2.5 mL of 0.5% sodium citrate solution was added drop by drop, as soon as boiling commences. The heating process continued until a pale blue color change was seen. 3 minutes after the boiling point, heating was seized but stirring the solution continued until reaching room temperature as shown in Fig. (1). Drop casting method was used to coat glass substrates with the prepared colloidal copper nanoparticles in order to characterize the samples [19].

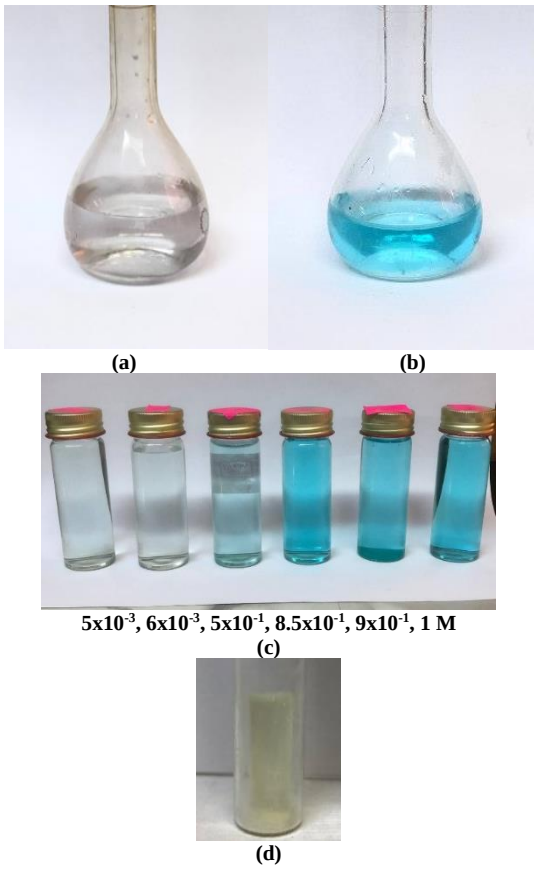

Fig. (1) (a) $CuNO_3$ solution (b) Cu NPs solution (c) Copper NPs prepared by chemical reduction at different concentrations (d) Cu NPs doped silica xerogel

The silica xerogel sol-gel rod samples were prepared under selected reaction conditions in order to prepare a suitable transparent host for Cu, TEOS and absolute EthOH after mixing them 1:5:10 volume ratio and pH of 1.5. For Cu doping, 1 ml of CuNPs solution, at different Cu concentrations, was added to the mixture of TEOS and absolute EthOH before the hydrolysis and this was denoted as sol (I). This was homogenized by stirring it obtained for 15 min by a magnetic stirrer. A mixture of 0.6 ml deionized water and 1.2 ml absolute EthOH was prepared and denoted as sol (Π) which was slowly added to the sol (I) for the hydrolysis process. The final solution was left for (30 min) under magnetic stirrer, and this was followed by adding 0.5 ml of N,N-dimethylformamide. The solution was poured in a closed glass tube and kept under 80 ºC reaction temperature. After aging and drying, the xerogel bulk rod samples was sintered by increasing the temperature from 110 to 250°C within 48 hours [20].

3. Results and discussions

In order to investigate the phase structure of the synthesized Cu nanoparticles (NPs), the XRD pattern in Fig. (2) shows three peaks with their corresponding planes; obtained at diffraction angles 35.55° (111), 41.40° (200), 72.73° (220) Bragg's reflections planes which represent (111), (200), and (220) planes of FCC crystal structure of metal copper. No extra/impurity peaks are observed in XRD pattern and this means there is no impurity present in the prepared samples. The sharp and strong peaks reveal that Cu nanocrystals are highly oriented. The patterns reveal that all the diffraction peaks are indexed to the characterization of metal copper, which are similar to the prepared pure copper samples. The analysis reveals that the as prepared samples have a crystallite size of 26.86 nm; calculated by using Debye-Scherrer's equation [21].

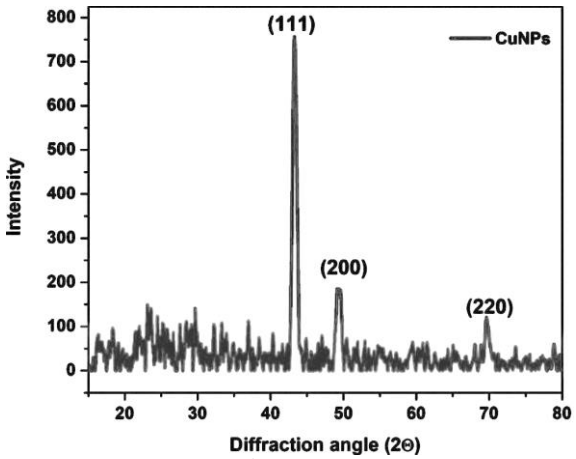

Fig. (2) The XRD pattern of Cu NPs were prepared by chemical reduction method

In order to explore the influence of preparations conditions on the characterization of such nanostructures, the absorption of Cu colloidal was

recorded as a function of $CuNO_3$ concentrations. Figure (3) shows that the absorption intensity increases with concentration while the maximum peak surface absorption of plasmon copper nanoparticles (at 1 $mol\backslash l$ as a concentration) occurred at 797 nm and for $9\times 10^{-1}, 8.5\times 10^{-1} mol\backslash l$ & $0.5\times 10^{-1} mol\backslash l$ concentration, it occurred at 790, 793 and 781 nm, respectively. At low concentration (0.5×10^{-3}& 6.7×10^{-3} 1 $mol\backslash l$) no absorption peak was observed. Figure (4) represents the absorbance as a function of concentrations which increased with concentration; a result that agrees well with Beer-Lambert laws.

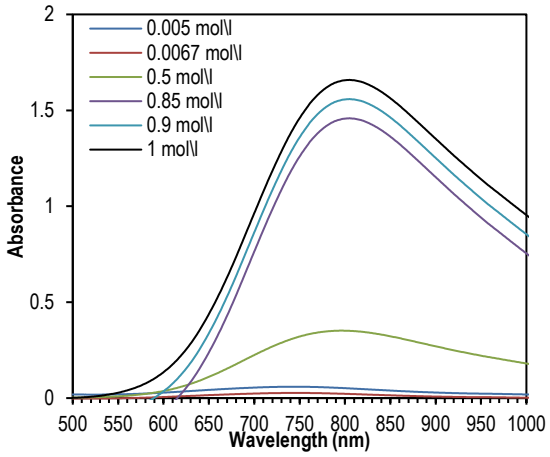

Fig. (3) The absorption spectra of Cu colloidal were prepared by chemical for different concentrations

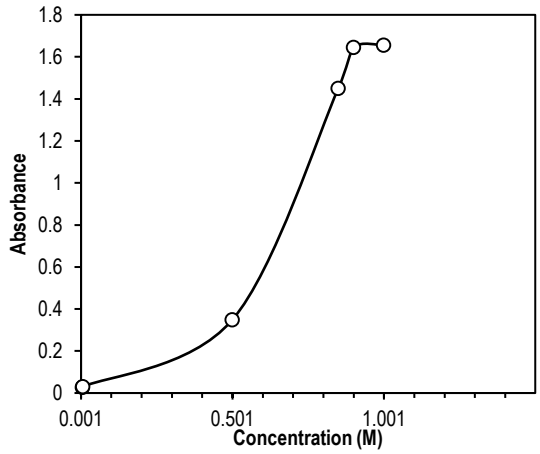

Fig. (4) The absorption spectra of Cu colloidal were prepared by chemical for different concentrations

To prevent decomposing the Cu-NPs, the liquid colloidal must be incorporated into a solid host by caging it into solid network; such as polymer or sol-gel host whereas its stability in liquid phase is a global problem. Cu-NPs dopant has been added to increase absorbance of silica xerogel. Figure (5) shows the absorption coefficient against the wavelength of the silica xerogels doped with different Cu-NPs concentrations. It shows the peak absorption coefficient α (λ), of each band increases steadily with Cu concentration.

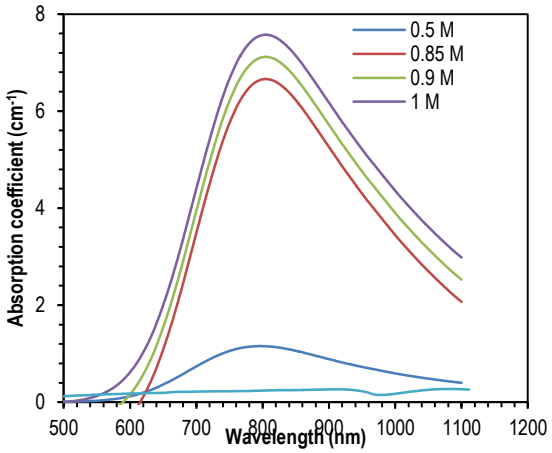

Fig. (5) The absorption spectra of silica xerogels doped with different concentrations of Cu NPs

The characteristic vibrational bands of silica were located in the FTIR spectra of silica xerogel and Cu-NPs doped silica xerogel samples as shown in Fig. (6). These samples were prepared at pH 1.5, 1:5:10 volume ratio and 80°C temperature. They were dried at 110°C and sintered at 250°C. The bending vibrations of Si-O-Si groups facilitate centering the absorption band at 460.2 cm^{-1}. The symmetric stretching Si-O-Si groups caused the absorption band peaking at 810.1 cm^{-1}. Lastly, the wide band round 1103.8 cm^{-1} is the distinctive Si-O-Si asymmetric stretching vibrations.

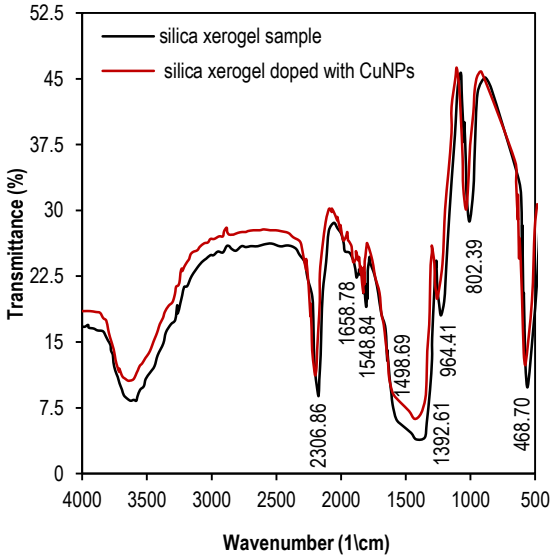

Fig. (6) FTIR transmission spectra of silica Xerogel and silica xerogel doped with CuNPs

The weak band at 964.8 cm^{-1}, attributed to stretching vibrations of silanol (Si-OH) groups which suggests a limited number of these groups in the silica network and implies a complete condensation reaction. The incomplete trapped water molecules in the pores of silica xerogel during the drying process at 110°C, two absorption bands appeared: 1640.7 cm^{-1} and 3440 cm^{-1}. The first band is caused by the bending vibrations of the O-H bond in the H_2O

molecules, whereas the second band is caused by stretching vibrations of the link. For glass sample sintered at 250°C, the first band became very weak and the second band vanished; indicating the driving out of most H_2O molecules as explained in Fig. (6).

4. Conclusions

It was found that the Copper nanoparticles were successfully prepared using a chemical reduction method based on varying the concentration of copper nitrate and studying its effect on the plasmon resonance band specification. In order to use such nanoparticles, they are embedded in a transparent host medium, silica xerogel. It turns out that these particles are concentrated within the pores that characterize the media prepared by the sol-gel method also, the absorption intensity reasonably increased for bulk samples (Cu NPs in xerogels) as compared to Cu NPs solution. Thus the possibility of using them in various applications.

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