Physica E 77 (2016) 65–71

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Air stable colloidal copper nanoparticles: Synthesis, characterization and their surface-enhanced Raman scattering properties

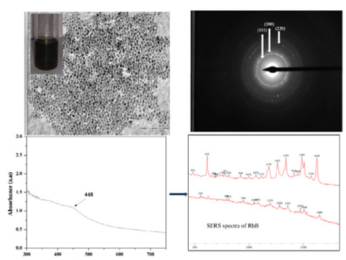
Thekkathu Ramani [a,*], K. Leon Prasanth [b], Bojja Sreedhar [a]

[a] Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India
[b] Department of Chemistry, The Zamorin's Guruvayurappan College, Calicut 673014, India

HIGHLIGHTS

- Air stable colloidal copper nanoparticles are synthesized by a simple chemical reduction method without any inert gas.
- The resulting nanoparticles were characterized by various spectroscopic techniques such as UV-visible, FT-IR, XRD and TEM.
- The copper nanoparticles do not suffer significant oxidation even after being stored for 6 months under ambient conditions.
- They exhibit large surface-enhanced Raman scattering (SERS) signals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form
9 October 2015
Accepted 4 November 2015
Available online 10 November 2015

Keywords:
Nanomaterials
Copper nanoparticles
X-ray techniques
SERS
Electron microscopy

ABSTRACT

Air stable colloidal copper nanoparticles are synthesized by a simple chemical reduction method using octadecylsilane as a reducing agent and octadecylamine as a stabilizing agent in toluene without any inert gas. The formation of nanosized copper was confirmed by its characteristic surface plasmon absorption peaks in UV–visible spectra. The transmission electron microscopic (TEM) images show that the resulting copper nanoparticles are distributed uniformly with a narrow size distribution. The X-ray diffraction (XRD) demonstrated that the obtained copper nanoparticles are single crystalline nanoparticles. Fourier transform infra-red (FT-IR) spectroscopic data suggested that the silane Si–H is responsible for the reduction of copper ions. And also the resulting colloidal copper nanoparticles exhibit large surface-enhanced Raman scattering (SERS) signals.

1. Introduction

Metallic nanoparticles (MNPs) have been the subject of intense research during the recent years because of their unique properties compared to bulk metals [1–6]. Among the different metal particles, copper nanoparticles have received considerable attention because copper is a versatile material which finds various applications in different fields of research like advanced microelectronics for conductive lines, medicine as an antibacterial agent, catalytic and biocatalytic transformations [1–8] or for surface-enhanced Raman spectroscopy applications [9,10]. It is well known that Raman spectroscopy is one of the nondestructive spectroscopic techniques widely used to characterize the dynamic behavior of molecules interacting with the electromagnetic radiation. The Raman vibrational spectrum is a molecular “fingerprint” that often provides unambiguous sample (solids, liquids, and gases) identification. Unfortunately, Raman scattering is an

* Corresponding author.
E-mail addresses: ramaniiict@gmail.com (T. Ramani), leonprasanthk@gmail.com (K. Leon Prasanth).

http://dx.doi.org/10.1016/j.physe.2015.11.002
1386-9477/

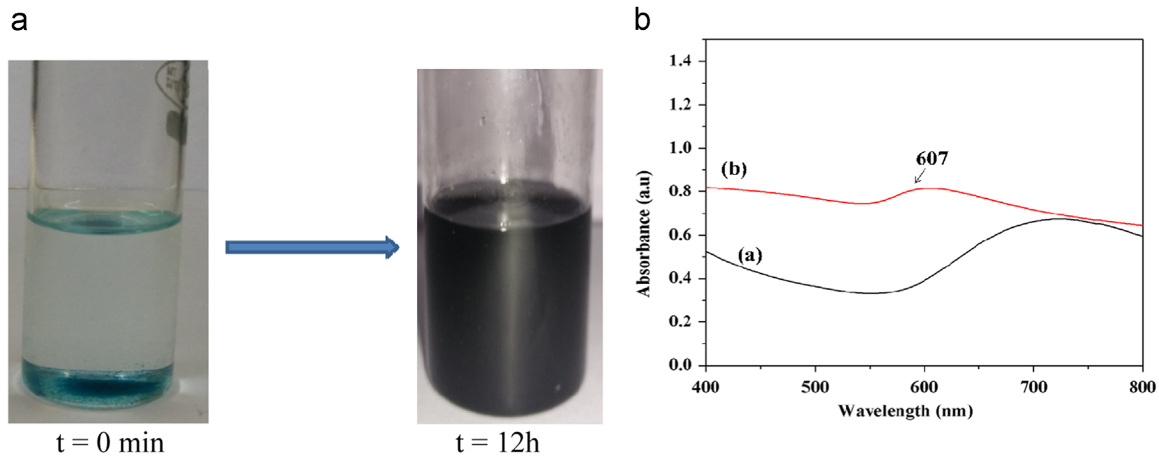


Fig. 1. (A) Reaction mixture at 0 min and 12 h respectively; (B) UV–vis spectra of (a) $Cu(OAc)_2$ and (b) CuNPs in toluene.

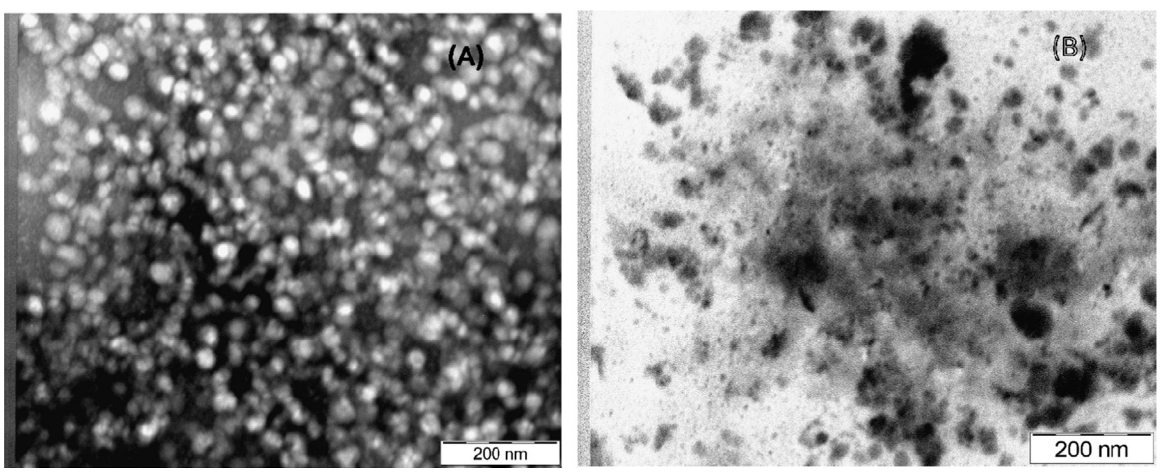


Fig. 2. TEM images of CuNPs stabilized by ODS: mainly focused on (A) PODS micelles network and (B) CuNPs respectively.

inherently weak process, unable to provide spectral information from very small amounts of sample. However, the sensitivity problems can be overcome by the employment of surface-enhanced Raman scattering spectroscopy (SERS) [11]. SERS enhancement effect has been observed with alkaline metals [12], various transition and noble metals [12,13], metal oxides [14] and even semiconductor materials like silicone and graphene [14,15]. Typically, large SERS is observed with coinage metals such as gold, silver, and copper because they exhibit localized surface plasmon resonance (LSPR) bands in the visible region due to excitation of the conduction electrons after irradiation with light. Colloidal suspensions of metal nanoparticles are the most common SERS substrates, which enable us to provide Raman intensification up to 10^7–10^8 enhancement factors with respect to the normal Raman signal of non-adsorbed molecules. The colloidal suspensions of metal nanoparticles acquire intense Raman signals due to the Brownian motion of the metal particles in the colloidal dispersions compared to other SERS active substrates such as rough metal electrodes, and metal island films. Among the group 11 metals, Cu is significantly cheaper than Ag and Au but the formation of a surface oxide layer on Cu is inevitable in an ambient atmosphere because the oxide phases are thermodynamically more stable, consequently, they are hard to synthesize chemically.

Generally, colloidal copper nanoparticles are synthesized by the chemical reduction of copper salts with sodium borohydride or hydrazine in water, followed by stabilization of the metal clusters inside protective shells (reverse micelles, polymers or long alkane chains) and eventually transfer into an organic phase [16]. They can also be synthesized by other methods such as laser ablation [17], gamma irradiation [18], microwave [19], electron beam [20], thermal decomposition [21] or vapor deposition [22]. Among the above mentioned methods, the chemical reduction is an easy and rapid procedure to prepare quite stable metal nanoparticles. To better control the NP size and size distribution, which are fundamental prerequisites for their employment in SERS studies, their synthesis should be performed in a single organic solvent [23]. Monodisperse Au, Ag, and Au_3Pd nanoparticles with narrow size distribution were prepared by direct reaction of the related metal salt with oleylamine in toluene and studied their SERS properties using Rhodamine B and 2-naphthalenethiol as model substrates [24]. Zhang et. al. reported the large scale synthesis of monodisperse CuNPs with high purity using $Cu(OH)_2$ as the precursor, L-ascorbic acid as the reductant, and PEG-2000 as the protectant for the conductive ink applications [25]. However, the investigation of Cu nanoparticles synthesized in single organic phase as SERS substrate has remained largely unexplored. This has inspired us to develop synthetic methods for stable colloidal Cu nanoparticles in organic solvent and explore their SERS properties.

Polysilanes are known to have a reductive nature for reducing noble metal salts to form the corresponding noble metals by the high HOMO-electrons of the Si–Si σ-bonds [26]. However, metal salts, which can be reduced by polysilanes, are limited in metals which have high standard reduction potentials, i.e., noble metal salts, and reduction of metal salts having a low reduction potential, such as copper or nickel salts, into metals is considered to be very difficult using polysilanes [27]. Kamada group reported the