



# Carbon as reducing agent for the precipitation of plasmonic Cu particles in glass



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## ABSTRACT

The first investigation on the use of carbon to produce metal nanocomposite glasses with plasmonic properties is reported. It is demonstrated how the reducing properties of graphite powder allow for producing Cu nanocomposite glasses in a controlled manner during heat treatment. Cu–C containing phosphate glasses were prepared by melting in ambient atmosphere having copper introduced in its highest oxidation state as CuO. Optical absorption and photoluminescence spectroscopy were employed in assessing material optical properties as a function of graphite contents and thermal processing. The processes likely resulting in copper valence state changes leading to the plasmonic material are discussed.

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## 1. Introduction

Under rapid development, the field of plasmonics holds promise for advancing technologies of current interest such as chemical and biological sensing [1,2], optoelectronics [3], photovoltaic devices [4], and nonlinear optics [5]. Particularly, the field of nonlinear plasmonics, which exploits the large optical nonlinearities of the metal nanostructures with their ultrafast optical responses, make plasmonic materials attractive for all-optical signal processing and ultrafast switching [5,6]. In such context, plasmonic metal nanocomposites fabricated in a robust inorganic host such as glass are very attractive [7,8]. Within noble metals Cu, Ag, Au, it is noteworthy that Cu nanoparticles (NPs) offer the most cost-effective alternative with plasmonic properties similar to the less abundant element gold [9]. Yet, the preparation of Cu nanocomposites is a difficult task given that copper can acquire various oxidation states ( $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^0$ ), and the predominant stability is for the  $\text{Cu}^{2+}$  ion especially for syntheses carried out under ambient atmosphere [10]. Appropriately, reducing agents such as tin (II) oxide [11,12] or antimony (III) oxide [13,14] have been proposed to be included as part of the glass material, aiming for control over the oxidation states of copper. The use of sucrose on top of well-mixed reagents has been also proposed to assist as an antioxidant preventing oxidation of tin (II) by atmospheric oxygen during melting in air [15]. Nevertheless, the sole use of carbon powder as reducing

agent for the controlled production of plasmonic nanocomposite glasses is not yet reported to the best of the author's knowledge. Thus, such an investigation is herein reported for the first time regarding the use of graphite as carbon source for producing plasmonic Cu nanocomposite glasses. A barium–phosphate glass prepared by melting in ambient atmosphere is chosen as matrix, and the worst-case scenario is considered by having the noble metal introduced in its highest oxidation state as copper (II) oxide. An optical spectroscopy study is conducted, aiming for the characterization of the melt-quenched glass, and for investigating on the influence of heat treatment (HT) on material optical properties. It is shown how the inclusion of graphite in the batches allows for reducing the  $\text{Cu}^{2+}$  ions during melting, ultimately allowing for the controlled precipitation of the plasmonic copper particles in the glass system during subsequent thermal processing.

## 2. Materials and methods

Barium–phosphate glasses with a  $50\text{P}_2\text{O}_5:50\text{BaO}$  (mol%) composition were prepared from high purity Alfa Aesar chemicals ( $\text{P}_2\text{O}_5$ ,  $\geq 98\%$  and  $\text{BaCO}_3$ , 99.8%) by the melt-quenching technique. Batch materials (about 25 g batches) were thoroughly mixed and melted at 1150 °C between 15 and 25 min under normal atmospheric conditions and immediately quenched. Copper and carbon were added as CuO (Alfa Aesar, 97%) and graphite powder (Alfa Aesar, crystalline, –300 mesh, 99%). Copper (II) oxide concentration was held constant in all Cu-doped samples at 0.5 mol% (relative to network former  $\text{P}_2\text{O}_5$ ). A glass containing only 0.5% CuO was made,

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labeled Cu glass. A set of glasses were prepared having the fixed 0.5% CuO concentration with different amounts of graphite as part of the batch materials, added as 1.0, 1.5 and 2.0 wt%, referred to as CuC1.0, CuC1.5, and CuC2.0, respectively. All glasses were cut and polished in order to produce glass slabs with final thicknesses of about 1.0 mm.

Optical absorption measurements were performed using a Perkin–Elmer 35 UV/vis double-beam spectrophotometer. The absorption spectra were recorded with air as reference. Photoluminescence (PL) emission and excitation spectra were obtained with a Photon Technology International QuantaMaster 30 spectrofluorometer equipped with a Xenon flash lamp having a pulse width of about 2  $\mu$ s (L4633, Hamamatsu Photonics K.K.) and a photomultiplier tube (R1527P, Hamamatsu Photonics K.K.). The flash lamp was kept operating at a frequency of 125 Hz with the total period of data collection set to 8 ms. The step size used for all spectral acquisitions was 1 nm. All PL measurements were recorded with samples mounted in a solid sample holder at an angle of 40° with particular attention given to keep conditions constant during experiments. All measurements were carried out at room temperature.

### 3. Results and discussion

Fig. 1 shows the absorption profiles obtained for the melt-quenched Cu and CuC1.0–2.0 glasses. The spectrum of the Cu glass displays the broad absorption feature peaking around 850 nm ascribed to  $^2E \rightarrow ^2T_2$  intra-configurational (d–d) transitions in  $Cu^{2+}$  ions [13,15]. It is observed that for the lowest amount of graphite the intensity of the band is slightly decreased; yet, it remarkably vanishes when sufficient graphite is added at 1.5 and 2.0 wt%. Further, as shown in the inset, together with the disappearance of the  $Cu^{2+}$  absorption in the CuC2.0 glass, the surface plasmon resonance (SPR) absorption feature characteristic of plasmonic Cu clusters [11,16] is noticed. These results indicate that the reduction of copper (II) via carbon occurred effectively during the melting. It is also observed that with 1.5 and 2.0 wt% graphite, a blue shift is induced in the UV absorption edge of the glasses. This seems connected to a structural rearrangement produced by the incorporation of carbon into the glass network [17]. A more detailed investigation regarding this effect is currently in progress in our group. Hence, the following redox reactions producing tetravalent carbon can be considered possible during the melting



Another possibility would be further reduction of monovalent copper in the glass melt as



As considered, the generation of neutral copper [e.g., Eqs. (2) and (3)] is supported by the absorption data for the CuC2.0 glass in the inset of Fig. 1. PL spectroscopy (*vide infra*) provides further evidence in support of generation of copper (I).

Samples of the CuC1.5 glass were further subjected to HT at 460 °C for 7, 15, 22 and 30 min of holding time. This glass was selected since it is that with the smallest amount of graphite where complete disappearance of the  $Cu^{2+}$  absorption band was observed. The optical absorption spectra for the corresponding samples are shown in Fig. 2 together with the spectrum of the glass prior to HT for comparison. Noticeably, the well-known SPR peak of Cu NPs [9,11,16] grows steadily after 15 min. The accompanying rise in absorption observed at about 525 nm extending towards shorter wavelengths is due to the interband transitions in the metallic particles, as the threshold for the excitation of 3d-band electrons into the 4sp conduction band in copper is about 2.1 eV (~590 nm) [9]. Evidently,  $Cu^0$  atoms produced were effectively aggregated into NPs. The current results appear even more dramatic than those reported for the glass system when using SnO as reducing agent [16], as the plasmonic absorption herein grows at a lower temperature, in a shorter amount of time, and in a more controlled fashion. It is observed in Fig. 2 that the SPR peak is situated consistently around 565 nm and narrows with increasing holding time, in agreement with the dipole regime of Mie theory [9]. Accordingly, a mean particle ‘optical’ diameter,  $d$ , may be approximated as

$$d = 2v_f / \Delta\omega_{1/2} \quad (4)$$

where  $v_f$  is the Fermi velocity of the metal ( $1.57 \times 10^8$  cm/s for Cu) and  $\Delta\omega_{1/2}$  is the full-width at half-maximum of the absorption band in units of angular frequency [16,18]. The estimated diameters by Eq. (4) were 0.7, 1.4, and 2.0 nm for HT at 460 °C after 15, 22 and 30 min;

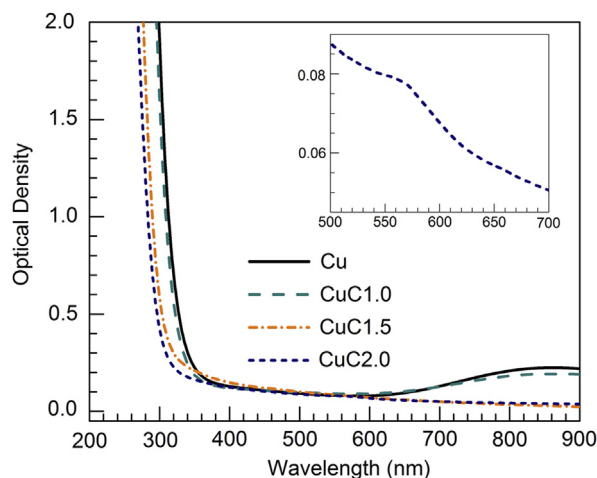


Fig. 1. Optical absorption spectra of Cu and CuC1.0–2.0 glasses. The inset shows the spectrum of the CuC2.0 glass enlarged in the region relevant to plasmonic Cu clusters absorption.

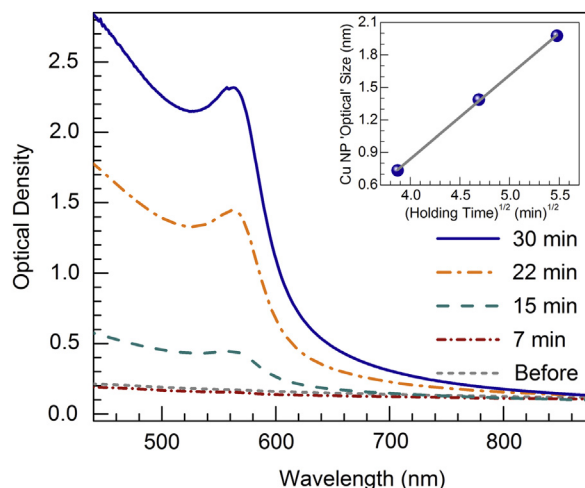


Fig. 2. Optical absorption spectra of CuC1.5 glass before and after HT at 460 °C for displayed holding times. The inset shows a plot of estimated Cu NP diameters as a function of the square root of holding time for the samples heat-treated for 15, 22 and 30 min; the solid trace is a linear fit to the data.

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