Supporting Information for

Cu Nanoclusters in Ion Exchanged Soda-lime Glass: Study of SPR and Nonlinear Optical Behavior for Photonics

Promod Kumar[1]*, Mohan Chandra Mathpal[2], Syed Hamad[3], Soma Venugopal Rao[3], J.H. Neethling[4], A. Janse van Vuuren[4], E.G. Njoroge[5], R.E. Kroon[1], W.D. Roos[1], H.C. Swart[1*]

[1]Department of Physics, University of the Free State, Bloemfontein, ZA9300, South Africa.

[3]Department of Physics, Universidade de Brasília, Brasilia, DF, Brazil-70910900.

[3]Advanced Centre for Research in High Energy Materials (ACRHEM), University of Hyderabad, Telangana, India.

[4]Centre for HRTEM, Nelson Mandela University, Port Elizabeth, ZA6031, South Africa

[5]7 ENGAGE, University of Pretoria, Pretoria 0002, South Africa.

***Corresponding authors;**

Promod Kumar, Email: *talk2promodthakur@gmail.com; pkpmcm@gmail.com*

Hendrik Swart; Email: SwartHC@ufs.ac.za

Tel: 051 4012926, Fax: 0514013507

ESM-1: Table 1 SPR peak position and width as well as NCs size for different post heat treatment temperatures:

Temperature (°C)	SPR Wavelength (nm)	FWHM (eV)	NCs Size (nm)
none	568	0.33	6.2
450	566	0.31	6.6
500	565	0.29	7.1
550	565	0.26	7.9
600	563	0.24	8.6
650	561	0.21	9.8

ESM-2: Cu diffusion - RBS:

The RBS spectra of the pristine and heat-treated samples are shown in figure S1(a). The Cu peak height near the surface of the pristine sample was much higher than that of the post heat-treatment samples as shown in the magnified image of the Cu peak in Figure S1(b). This confirmed that the Cu concentration was higher at the surface directly after the Cu^{+}-Na^{+} ion exchange experiment and was reduced by post heat-treatment. We have shown that Ag atoms also accumulated near the glass surface during Ag ion exchange process[1]. The Cu peak height was reduced systematically due to Cu diffusion into the glass matrix during heat-treatment. The glass provides the essential electrons required for the conversion of Cu ions into Cu neutral atoms. The Cu ions (Cu^{+}/Cu^{2+}) captured the electrons from the glass impurities or defects during the post heat treatment to reduce the Cu^{+} ions and in the process formed Cu neutral atoms. The population of Cu^{+} ions on the surface was reduced as a function of annealing and the Cu neutral atoms diffused into the bulk.

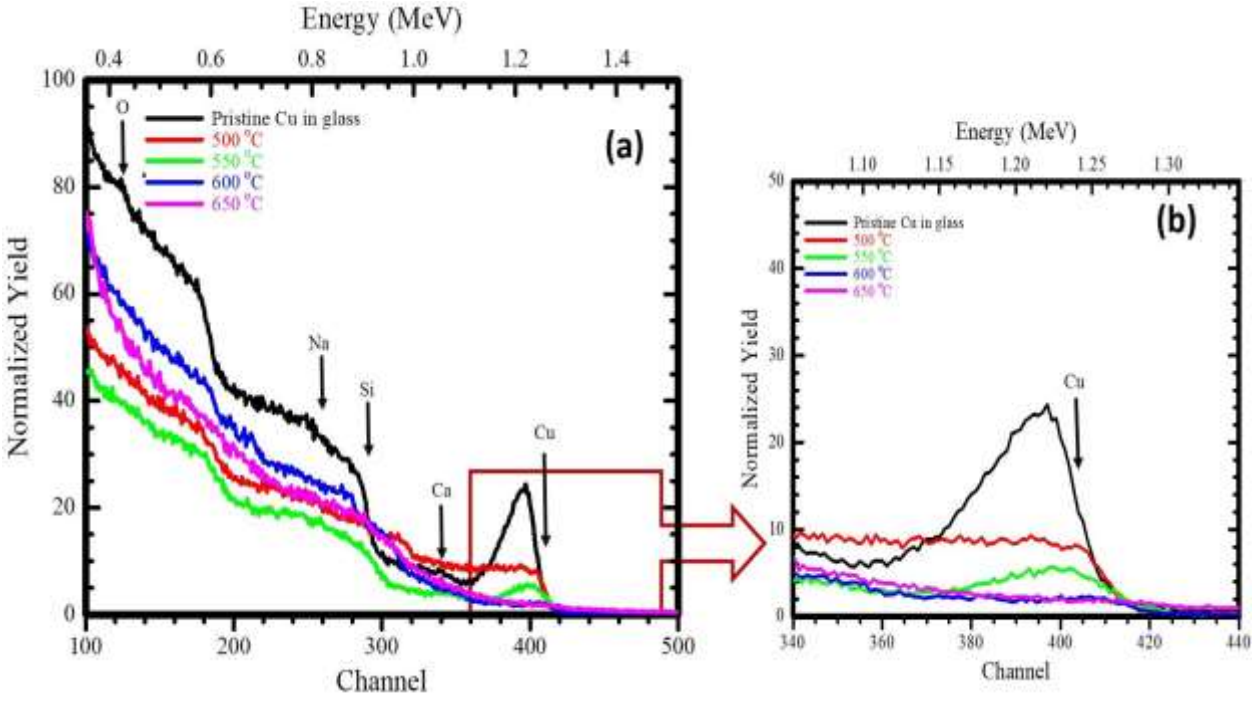

Figure S1: (a) RBS spectra of the pristine Cu ion exchanged glass and heat treated samples from 500°C up to 650°C and (b) magnified image of Cu peak has been shown for clarity.

The Cu atoms diffused deeper into the bulk after the post heat-treatment process as shown in figure S1. The tensile stress produced by the different ionic radius of the ions (Cu^{+}, Cu^{2+} and Na^{+}) during the ion exchange experiment was still present after cooling the furnace[2]. The Cu^{+}/Cu^{2+} ions could trap electrons from the glass impurities to form Cu atoms near the glass surface. Conversely, more Cu–O bonds were broken while heating and Cu atoms were formed and as a result a net loss in the system free energy[2, 3].

ESM-3: Structural studies of Cu NCs - XRD:

Figure S 2 shows the XRD patterns of the pristine sample and the 600 ºC and 650 ºC heat treated samples. The pristine sample did not show any diffraction peaks of pure Cu, but rather an amorphous behavior. This may be due to no accumulation of Cu crystals during the ion-exchange process or Cu crystal formation with a very small size causing broad diffraction peaks as shown

in figure 2. The samples heated at 600 °C showed low intensity peaks corresponding to Cu_2O (111), Cu_2O (002), Cu (111) and Cu (200) located at 36.3, 42.2, 43.5 and 51.1°, respectively[2, 4].

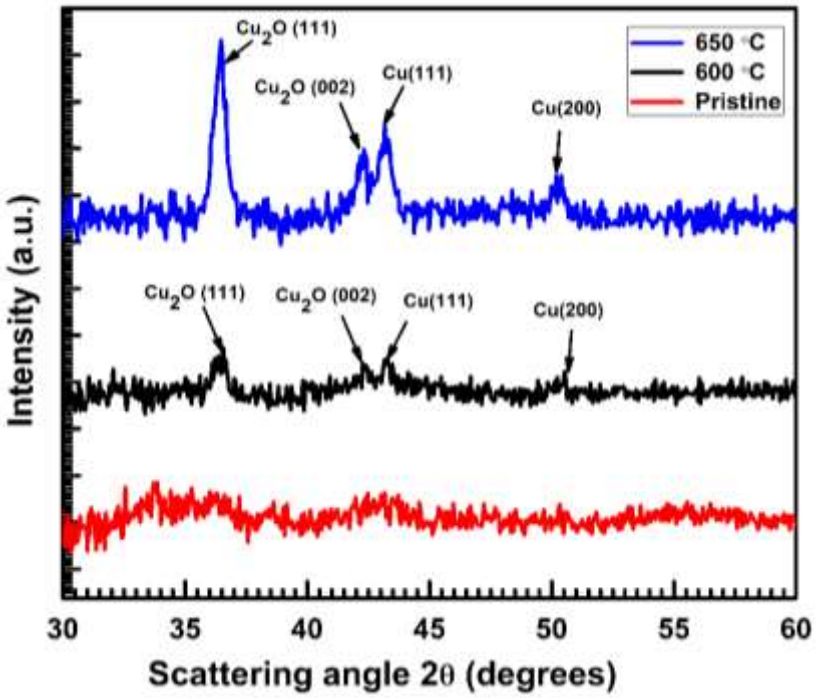

Figure S 2**:** XRD patterns of the pristine Cu ion exchanged sample and 600 °C and 650 °C heat treated samples.

The sample heated at 650 °C shows higher intensity peaks, which revealed the growing of the Cu-related NCs[2].

ESM-4: PL spectrum of pure soda-lime glass:

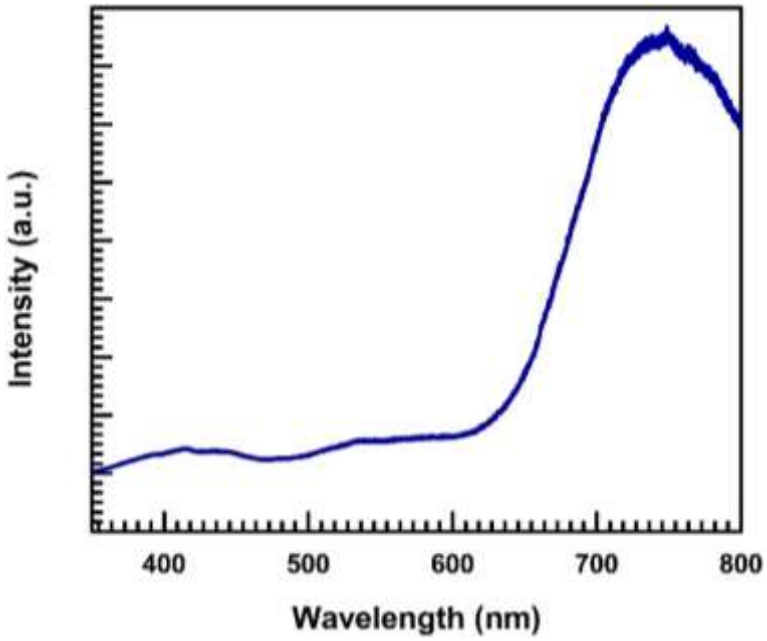

Figure S3: PL spectra of pure soda-lime glass slide; Exc. 325 nm.

ESM-5: Table 2: The different peak positions for the PL emission excited by two different wavelengths of 280 and 325 nm, respectively.

Sample ID/ Excited Wavelength (nm)		**Cu^{+} ions in distorted octahedral sites (nm).).**	**Cu_2O (nm).**	**Non-bridging oxygen center in the glass (nm)**
Pristine	Exc-280	517	611	
	Exc-325	530	620	724
450 °C	Exc-280	504	603	
	Exc-325	519	598	644
500 °C	Exc-280	508	606	
	Exc-325	534	616	665

550 °C	Exc-280	510	592, 617	644
	Exc-325	522	606	654
600 °C	Exc-280	501	602, 613	
	Exc-325	518	608	632
650 °C	Exc-280	501	594	
	Exc-325	509	583	681

References:

1. P. Kumar, M.C. Mathpal, A.K. Tripathi, J. Prakash, A. Agarwal, M.M. Ahmad, H.C. Swart, Plasmonic resonance of Ag nanoclusters diffused in soda-lime glasses, Phys. Chem. Chem. Phys., 2015, 17, 8596-8603.
2. P. Kumar, M.C. Mathpal, H.C. Swart, Multifunctional properties of plasmonic Cu nanoparticles embedded in a glass matrix and their thermodynamic behavior, J. Alloy Compd., 2018, 747, 530-542 .
3. F. Gonella, F. Caccavale, Experimental study of copper–alkali ion exchange in glass , J. Appl. Phys ,1998, 83, 1200-1206.
4. P. Liu, H. Wang, X. Li, M. Ruib, H. Zeng, Localized surface plasmon resonance of Cu nanoparticles by laser ablation in liquid media, RSC Adv., 2015, 5, 79738-79745 .