

## Preparation, optical and non-linear optical power limiting properties of Cu, CuNi nanowires

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Metallic nanowires show excellent Plasmon absorption which is tunable based on its aspect ratio and alloying nature. We prepared Cu and CuNi metallic nanowires and studied its optical and nonlinear optical behavior. Optical properties of nanowires are theoretically explained using Gans theory. Nonlinear optical behavior is studied using a single beam open aperture z-scan method with the use of 5 ns Nd: YAG laser. Optical limiting is found to arise from two-photon absorption.

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Advances in optics based technologies require efficient nonlinear optical materials which can be used as all-optical switches,<sup>1</sup> memory elements,<sup>2</sup> and materials for enhancement of fluorescence<sup>3</sup> etc. These materials are also essential in optical imaging,<sup>4</sup> steady state and ultrafast spectroscopy,<sup>5</sup> quantum communications and quantum entanglement.<sup>6</sup> Metal and metallic alloy nanostructures show enhanced third-order nonlinearities and fast electronic response (through temporal studies).<sup>5</sup> These attractive behaviors make these materials potential candidates for the optical limiting applications.<sup>7</sup> Optical power limiters gained wide attention due to their use in protecting optical components, sensors and human eyes from rapid exposure of ultra intense laser light. Optical limiters with high damage threshold are well suited for these applications.<sup>8</sup> One of the main reasons for these interesting optical properties is surface Plasmon resonance (SPR) present in these kind of materials. Even though it is free from quantum size effects,<sup>9</sup> it mainly depends on the free conduction electrons which oscillate with the external applied optical field. These oscillations depend on the size and shape of the nanometals and their hosts where they are suspended. So tuning size and shape will alter the optical response by changing the number of conduction electrons, which are responsible for the optical and chemical properties. Optical absorption of these metallic nanoparticles can be explained through Mie equation.<sup>10</sup> Alloy nanostructures show the peculiar optical properties which differ from their parent metals. Ratio of composition and types of metals determine the surface Plasmon band. In this letter, we report preparation of Cu and CuNi nanowires and their optical limiting properties. It is evident from the experiments that the shape and alloy composition play an important role in deciding the non-linear optical properties of these materials.

Preparation of these metallic nanowires is as follows: Synthesis of Cu nanowires were carried out by reducing the copper nitrate in the aqueous solution of sodium hydroxide (NaOH) and ethylenediamine (EDA) using hydrazine. 20 ml (0.2 M) copper (II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) prepared using double distilled water (DDW) is added to 100 ml (15 M) aqueous solution (DDW) of NaOH followed by

addition of 1.5 ml EDA and 250  $\mu\text{l}$  hydrazine (35 wt. %) into the reaction flask. The mixture is then kept at  $\sim 80^\circ\text{C}$  for  $\sim 1$  h under constant stirring. After the addition of hydrazine the royal blue color of  $\text{Cu}^{2+}$  changes to reddish brown indicating the formation of Cu nanowires in the solution. Cu Ni wires were prepared by mixing 0.01 M, 0.03 M, and 0.05 M solutions of nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) with 0.19 M, 0.17 M, and 0.15 M of copper nitrate, respectively, in the above mentioned reaction sequence. The precipitates were washed several times and dried in hot air oven at  $50^\circ\text{C}$  for  $\sim 2$  h. Samples prepared were named CuNi0, CuNi1, CuNi3, and CuNi5 with respect to the amount of Ni present in the samples. CuNi0 is the sample with no Nickel content. X-ray diffraction (XRD) studies show that the prepared metallic nanowires are of pure Cu and CuNi. Prolonged exposure of the powder samples to atmospheric conditions will result in surface oxidation.

The crystal structures investigations have been carried out with Rigaku Dmax 2000 XRD instrument in  $20^\circ$ – $80^\circ$  diffraction angle range ( $2\theta$ ). Optical absorption measurements carried out on water suspensions of the metal nanowires (MNWs) at room temperature using the dual beam Perkin Elmer UV-Visible spectrophotometer in the range 200–1100 nm. Nd:YAG laser emitting 5 ns pulses of second harmonic wavelength (532 nm) [Continuum, Minilite] used for the nonlinear absorption studies in z-scan technique. Open aperture z-scan method is used to measure intensity dependent transmission. Plano convex lens with 200 mm focal length is used to focus the laser beam and a pyroelectric energy probe is used for measuring the transmittance while translating the sample along the beam axis (z-axis) using an automated translation stage which makes the sample to face different fluence through the translation path of the sample (along z-axis). Neutral density filters were used in reducing the energy reaching the sample. In order to account the minute fluctuations in energy of the pulses, reference energy probe is used and beam splitter is employed to direct the pulses for the reference and detector probes.

X ray diffraction study shows diffraction peaks (Figure 1) are observed at angles of  $43.6^\circ$ ,  $50.7^\circ$ , and  $74.3^\circ$  correspond to the (111), (200), and (220) planes of Cu metal. The 5% doped Ni wires show an additional peak at  $44.2^\circ$  which is due to (111) plane of Ni metal. This confirms that doping yields

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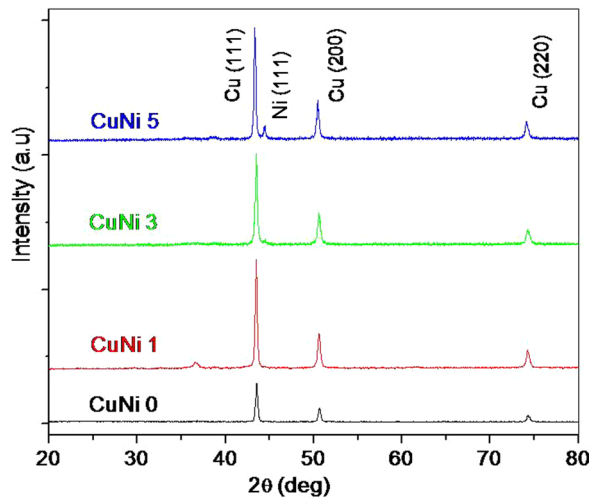


FIG. 1. X-ray diffraction pattern of the prepared Cu and CuNi nanowires. CuNi5 shows the bimetallic nature where peaks correspond to Ni also seen. All the other peaks agree well with the metallic phase of Cu.

the bimetallic nature of MNWs. Peaks correspond to oxide forms of the metals may appear with long time of exposure to the atmosphere.

To identify the morphology and shape, we carried out the Field Emission Scanning Electron Microscopy (FESEM) studies. The FESEM images shown in Fig. 2 tells that the prepared particles are  $\sim 200$  nm in diameter and  $1 \mu\text{m}$  in length. Spherical particles on the surface of MNW arise by the doping with Ni. Optical absorption spectra of MNWs suspended in DDW is shown in Fig. 3. The strong absorption band centered at 560 nm and broad band centered at 800 nm are due to transverse and longitudinal surface plasmon absorption<sup>5</sup> of Cu nanowires, respectively. Usually Mie theory gives clear picture about the optical absorption coefficient, which is expressed through the relation<sup>10</sup>

$$\alpha = 9p\epsilon_d^{3/2} \frac{\omega}{c} \frac{\epsilon_{m(I)}(\omega)}{[\epsilon_{m(R)}(\omega) + 2\epsilon_d]^2 + \epsilon_{m(I)}^2(\omega)}, \quad (1)$$

where  $p$  is the volume fraction of the nanoparticles,  $\omega$  is the applied optical frequency, and  $c$  is the speed of light in vacuum. Here,  $\epsilon_m(\omega) = \epsilon_{m(R)}(\omega) + i\epsilon_{m(I)}(\omega)$  is the frequency

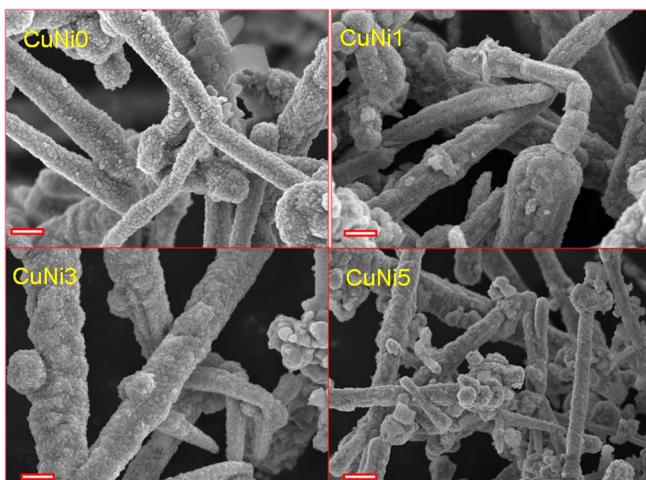


FIG. 2. SEM images of the prepared nanowires. Scale bar for all the images is 200 nm.

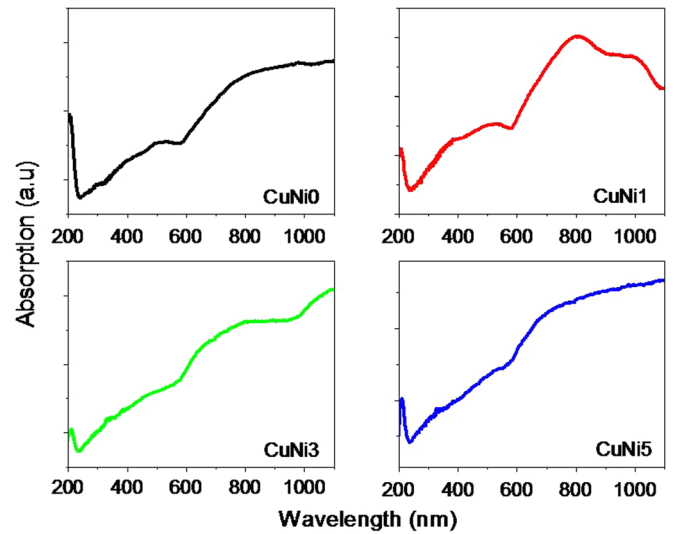


FIG. 3. Optical absorption spectra of the prepared nanowires dispersed in DDW. The band at  $\sim 530$  nm and 800 nm is attributed to transverse and longitudinal vibrations of surface electrons (Plasmon resonance).

dependent, complex dielectric constant of the metallic particle,  $\epsilon_d$  is the dielectric constant of the host matrix which is real. SPR maximum occurs when  $\epsilon_{m(R)}(\omega) + 2\epsilon_d = 0$ . This equation is valid only for small particles with diameter  $< \lambda/10$  in which only dipolar oscillations occur. On the contrary, if the diameter is more than  $\lambda/10$  and the particle is non-spherical, quadrupolar, and higher order polar oscillations will also be present. Gans<sup>11</sup> by extending Mie theory, introduced geometrical factor “ $P$ ” treated Plasmon oscillations by randomly oriented non-spherical particles. According to this theory, extinction coefficient  $\gamma$  relates with the geometrical factor “ $P$ ,” complex dielectric constant of the metallic particle and medium dielectric constant by the relation

$$\gamma \propto \frac{\epsilon_d^{3/2}}{\lambda} \sum_j \frac{\left(\frac{1}{P_j}\right) \epsilon_{m(I)}}{\left[\epsilon_{m(R)} + \left(\frac{1-P_j}{P_j}\right) \epsilon_d\right]^2 + \epsilon_{m(I)}^2}. \quad (2)$$

In case of non-spherical particles (elongated ellipsoids or rods/wires) ( $A$ ,  $B$ , and  $C$  axes), the geometrical factor  $P_j$  along the three axes ( $A > B = C$ ) has the values given by the relation

$$P_A = \frac{1 - e^2}{e^2} \left( \frac{1}{2e} \ln \left( \frac{1+e}{1-e} \right) - 1 \right) \text{ and } P_B = P_C = \frac{1 - P_A}{2}, \quad (3)$$

where  $e$  is a function of the aspect ratio ( $Q$ ), which can be written as

$$e = \left( \frac{L^2 - d^2}{L^2} \right)^{1/2} = \left( 1 - \frac{d^2}{L^2} \right)^{1/2} = \left( 1 - \frac{1}{Q^2} \right)^{1/2}. \quad (4)$$

For the particles with sphere like nature ( $A = B = C$ ) geometrical factor will become  $P_A = P_B = P_C = 1/3$  and extinction coefficient reduces to Mie form<sup>27</sup>

$$\gamma \propto \frac{\varepsilon_d^{3/2}}{\lambda} \frac{\varepsilon_m(I)}{[\varepsilon_m(R) + 2\varepsilon_d]^2 + \varepsilon_m^2(I)}. \quad (5)$$

For the calculations, bulk optical parameters for copper<sup>12</sup> and medium dielectric constant of 1.33 are used. Calculated spectra for different aspect ratio show two bands related to transverse resonance and longitudinal surface Plasmon resonance modes in the lower and higher wavelength range, respectively.<sup>27</sup>

From the experimental optical absorption observations, two broad bands present in all the samples. Gans theory predicted two bands corresponds to the two modes of oscillations, one which has peak around  $\sim 530$  nm and the other mode is around  $\sim 830$  nm for the aspect ratio of 5. Polydispersity in the shape of the particles governs the discrepancy between experimental and theoretical optical absorption results. Both theory and measured spectra are shown in Ref. 27 for comparison.

Optical limiting properties are examined through open aperture z-scan method. The normalized transmittance is plotted against intensity of the laser beam (Figs. 4 and 5). Experiment was carried out on MNWs using DD Water suspension. Optical nonlinearity will be enhanced when excited near the SPR due to the local field enhancement. If metal particles with dielectric constant  $\varepsilon_m$  is distributed uniformly and randomly in the dielectric host having dielectric constant  $\varepsilon_d$ , then the local field is given by<sup>13</sup>

$$E_l = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0,$$

where  $E_0$  is the applied optical field. Near SPR  $\varepsilon_m + 2\varepsilon_d$  is minimum and hence  $E_l$  becomes maximum. Corresponding polarization is given by

$$P_{NLS} = 3p \left( \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right)^4 \chi_m^{(3)} E_0^3,$$

which scales as the fourth power of the term in the bracket and consequently, when the frequency  $\omega$  satisfies the

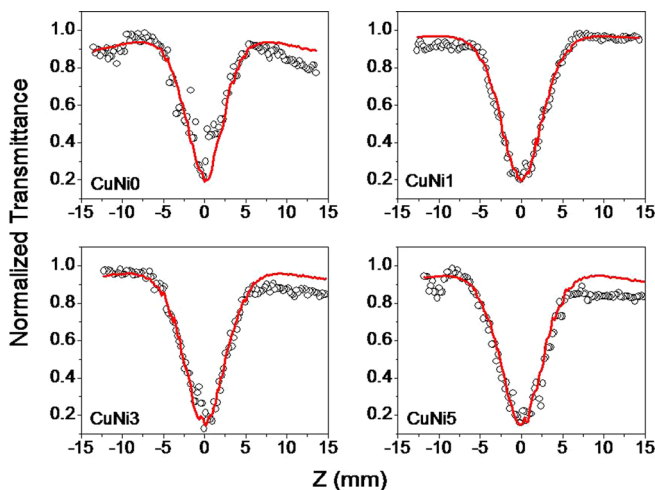


FIG. 4. Optical power limiting properties of pure Cu (CuNi0) and Ni doped Cu metallic nanowires (CuNi1, CuNi3, and CuNi5). (Limiting studies were carried out with the help of 532 nm, 7 ns laser used as excitation source by suspending the samples in solvent.)

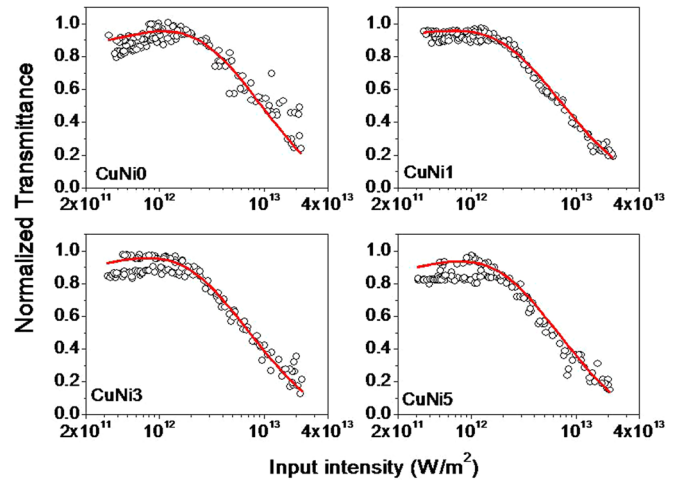


FIG. 5. Intensity dependent transmission of the pure Cu (CuNi0) and Ni doped Cu metallic wires (CuNi1, CuNi3, and CuNi5) samples (data extracted from the Figure 4).

resonance condition the enhancement in the optical nonlinearity is greatly amplified.

Flytzanis and co-workers have shown that there are three major electronic contributions to the Kerr nonlinearity in metal nanoclusters.<sup>14</sup> According to their explanations, the optical properties of noble metal clusters are primarily determined by the electrons occupying their “d” and conduction bands. First electronic contribution  $\chi^{(3)}_{intra}$  is derived from the intraband conduction electrons. It is electric dipolar in nature, and originates totally due to the confinement of the free electrons, and is strongly size dependent. The second term  $\chi^{(3)}_{inter}$  originates from inter-band transitions between the d-bands and the conduction band, which is size and shape independent for very small sizes. The third and most important contribution  $\chi^{(3)}_{hot}$  arises from conduction electrons that are easily elevated to temperatures of several hundred degrees by photo-excitation, as their specific heats are very small and these electrons are called hot electrons. Calculations and experiments show that the hot electron and interband contributions are mainly imaginary in nature, and much stronger than the intraband contribution. The Fermi-Dirac electron distribution will be modified within few picoseconds by hot electrons (after laser excitation) to thermalize with the lattice, since part of the one-electron levels below the Fermi level is emptied and part of those above is occupied. This leads to a modification of the dielectric constant  $\varepsilon_m$  that results in a transient re-distribution of the equilibrium plasmon band. In the present case, we excited at the Plasmon frequency in the transverse mode of excitation. This leads to the strong optical nonlinearity. The experimental plots were fitted theoretically to identify the effective absorption coefficients,  $\alpha(I)$ , which is a sum of independent negative and positive absorption coefficients<sup>15</sup>

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_s)} + \beta I,$$

where  $\alpha_0$  is the linear absorption coefficient,  $I$  is the laser intensity, and  $I_s$  is the saturation intensity. Here,  $\beta$  is the generalized coefficient for negative transmission. Now the open aperture normalized transmittance can be written as<sup>16,17</sup>

$$T(z) = \frac{1}{\sqrt{\pi}q(z)} \int_{-\infty}^{+\infty} \ln[1 + q(z)\exp(-\tau^2)]d\tau,$$

where  $q(z) = \beta I_0 L/[I + (z/z_0)^2]$ , with  $I_0$  being the peak intensity at the focal point.  $L = [I - \exp(-\alpha_0 l)]/\alpha_0$ , where  $l$  is the sample length; and  $z_0 = \pi\omega_0^2/\lambda$  is the Rayleigh range, where  $\omega_0$  is the beam waist radius at focus and  $\lambda$  is the light wavelength.

Non-linear parameters from the experimental data by performing theoretical fit are given in Table I.<sup>27</sup> It is seen that for 532 nm excitation the value of  $\beta$  and  $I_s$  for pure Cu MNW's (CuNi0) are  $14 \times 10^{-11}$  and  $91 \times 10^{10}$  and these values changes to  $21 \times 10^{-11}$  and  $110 \times 10^{10}$  for CuNi MNW's sample. More addition of Ni shows downward trend in the nonlinear parameters which might be due to formation of Ni related phase along with Cu in the samples. Thus, an obvious enhancement in the nonlinear parameter  $\beta$  is achieved with the presence of Ni in the MNW's system. In comparison when excited using 532 nm (5–10 ns pulses) laser, the  $\beta$  value for C60,<sup>18</sup> Single-walled carbon nanotubes (SWNTs),<sup>18</sup> Bi nanorods<sup>19</sup> are lesser than the values obtained from our study and saturation intensity  $I_s$  values are not available for comparison. ZnO added MoO3 Nanotubes,<sup>20</sup>  $\beta$ -AgVO3 nanobelts<sup>21</sup> systems having the lower values of  $\beta$  and  $I_s$  when compared with our samples data.

From the reported values (Refs. 21–26), the values of  $\beta$  are lower than our  $\beta$  values where as their reported  $I_s$  are higher when compared with our values. The higher values of  $I_s$  observed in the ZnO-GO hybrid system<sup>26</sup> which may be due to two photon absorption (TPA) with reverse saturable absorption and photo-induced photon transfer between ZnO and graphene sheets and direct comparison could not be made with other reported values.

In summary, we have prepared Cu and CuNi nanowires whose X-ray diffraction and FESEM studies confirm the crystalline nature and morphology of the prepared particle, respectively. Optical absorption measurements reveal that the strong and broad bands between 250 and 1100 nm is ascribed to surface Plasmon which is particularly the combination of transverse and longitudinal Plasmon oscillations. The optical absorption data with two broad bands are supported by our theoretical predictions by using Gans theory for MNW's. Open aperture Z scan measurements show that the strong optical limiting behavior is due to TPA and it increases with the increase in the MNW's concentration. The values of non-linear parameters values obtained show good enhancement against the values earlier obtained in certain other metal and semiconductor nanosystems. Observation of optical limiting at 532 wavelengths sounds the potential of these materials for optical limiters applications like eye and

sensor protection in optical systems. As these materials shows broad range of optical absorption, these materials will better perform as nonlinear optical materials in the other excitation wavelengths.

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- <sup>27</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4858406> for extinction spectra calculated from the Gans theory using Eqs. (2)–(4) and comparison of the obtained effective two-photon absorption coefficients values to the reported values in literature for a few other metal and semiconductor nanoparticles given in Table I.