

# Ferromagnetism and Giant Paramagnetism in Cu@C nanocomposites

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## ABSTRACT

Different size copper nanoparticles coated by carbon are synthesized by solid phase pyrolysis of polycrystalline phthalocyanine (CuPc, Pc=C<sub>32</sub>N<sub>8</sub>H<sub>16</sub>). The structural properties of obtained powder products are characterized by XRD and Raman spectroscopy. The morphologies of obtained Cu@C nanocomposites studied by TEM, HRSEM, and HRTEM suggest a core shell structure. The unpaired electron states and electron transfer by changes in g-values, hyperfine splitting constants at various copper concentration are also analyzed by EPR and FMR spectra. Measurements of magnetization carried out by vibrational PPMS magnetometer provide strong evidence for coexistence of ferromagnetism and giant paramagnetism in wide range of temperatures. The values of the specific susceptibility at T=10K show a record high giant paramagnetism with magnetic specific susceptibility of  $\chi_m^{PM} \approx 1.5 \times 10^{-4}$  emu/gOe order while ferromagnetic behavior with hysteresis is preserved up to the room temperature.

**Keywords:** Cu@C nanocomposites, size and surface effects, carbon matrix, room temperature ferromagnetism, giant paramagnetism, charge transfer, core-shell structure

## 1 INTRODUCTION

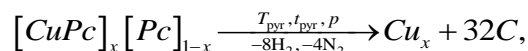
In recent years the emergence of ferromagnetism has been intensively studied at the nanoscale level in metals and/or other compounds, whose bulk (massive) samples with electronic configuration  $3d^9 4s^1$  are diamagnetic as a result of delocalization of the free electron density in the s band. These are primarily gold nanoparticles (NPs) - Au, as well as other non-magnetic elements such as Ag, Cu, Pd, and ZnO compounds with functionalized surfaces and linear dimensions falling within the range of 2-10 nm [1-6]. Several explanations for magnetism in these nanomaterials have been proposed, such as the competing magnetic contributions of the nanoparticle core and its surface [7], the formation of a magnetic moment due to the exchange of charges at the nanoparticle-ligand interface [1, 2]. In this paper we investigate the magnetic properties of Cu NPs in carbon matrix - Cu@C nanocomposites. The copper NPs encapsulated by graphite-like carbon shell show clear evidence for hysteretic behavior with room temperature ferromagnetism and giant paramagnetism. Magnetization

study reveals that at low concentration of Cu nanoparticles provide giant enhancement of magnetization. At low temperatures a giant paramagnetism is observed for small average sizes of copper nanoparticles in the range of 2-6 nm, apparently due to the (ballistic) conduction electron (large orbital magnetism). Until now the origin of this unexpected magnetism has not yet been fully understood. Three important factors can contribute to the magnetic properties of the material in the nano-metric scale: quantum-size, surface and ligand effects. Magnetic properties of Cu nanoparticles and carbon matrix are affected by quantum confinement of the conduction electrons and 3d-electrons. Magnetic properties of coated NPs are different from their bare form. In the bulk form copper is known to be weakly diamagnetic, because of diamagnetic response from the completely filled ions core and 3d-band while the ultra small Cu nanoparticles overcome the diamagnetic responses from the inner core by exhibiting giant paramagnetic and ferromagnetic responses at low temperatures. Here the nanoparticle size and concentration dependences of Cu nanoparticles on the magnetic properties of nanoparticles are analyzed. The study of nature of ferromagnetism in Cu@C nanocomposites, consisting of otherwise diamagnetic metal and carbon and the role of core shell magnetic nanoparticles in surface magnetism are the key goal of proposed project.

## 2 EXPERIMENTAL RESULTS

### 2.1 Synthesis of samples

To obtain very fine dispersed copper nanoparticles, as well as to study size effects, we first synthesized solid solutions of phthalocyanines: copper phthalocyanine (CuPc) – and metal free phthalocyanine (H<sub>2</sub>Pc). Solid-phase pyrolysis of these solid solutions (CuPc) x (H<sub>2</sub>Pc) 1-x, where  $0 \leq x \leq 1$  can be represented using the following chemical reaction:



where  $T_{pyr}$  - pyrolysis temperature - 850°C,  $t_{pyr}$  - pyrolysis time - 3-15 min and  $p$  - pressure in the reaction ampoule, and the value of x is in the interval  $0 \leq x \leq 1$ . A set of synthesized samples have been prepared with atomic Cu concentrations in nanocompositions equal to 0; 0.5; 1; 2;

and 3 at%. The weight percent corresponds to  $\text{Cu}_n/\text{C}$  samples with  $n=0, 2, 4, 8$  and  $12$  wt% respectively.

## 2.2 Morphology and structure

Morphology and sizes of prepared samples were investigated by varying nanoparticle sizes and compositions using a FEI Talos F200X field-emission high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) at an accelerating voltage of 200 kV. The structure of the nanocomposites was determined using X-ray diffractometer Bruker D2 Phase rmodel # A26X1 (radiation of  $\text{CuK}\alpha$ ,  $1.54060 \text{ \AA}$ ). EDS spectroscopy of characteristic X rays used for compositional mapping. Table shows the result of elemental analyses of Cu sample with 2 wt%, i.e., 0.5 at% of Cu.

Element	Series	Net	Mass C. [wt.%]	norm. C. [wt.%]	Atom C. [at.%]	Error (3 Sigma) [wt.%]
Cl	K series	130	0.28	0.28	0.10	0.16
C	K series	18009	87.91	87.91	92.28	8.23
O	K series	1226	2.68	2.68	2.11	0.41
N	K series	1750	5.27	5.27	4.74	0.68
Cu	K series	1140	3.86	3.86	0.77	0.58
<b>Total</b>			<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	

The prepared powdered samples are represented by air-stable black powders of copper nanocrystals. The HRTEM image of  $\text{Cu}@C$  nanocomposites with  $\text{Cu}_n$  concentrations with  $n=0, 2, 4, 8$  and  $12$  wt% demonstrate a uniform distribution of Cu nanoparticles in carbon matrix.

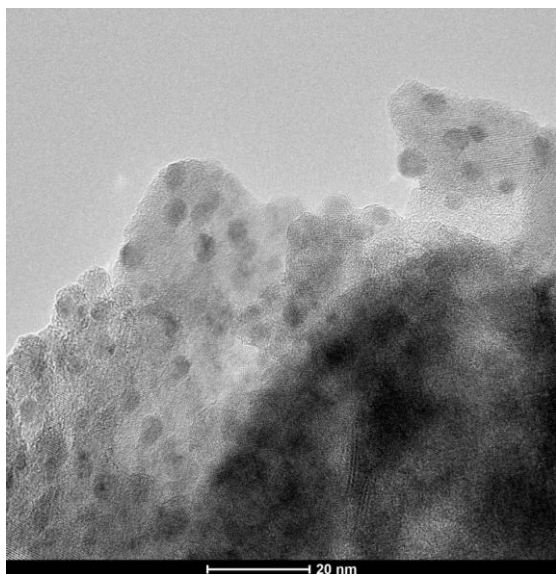


Fig. 1 HRTEM micrographs of the sample  $\text{Cu}_2/\text{C}$  indicate Cu nanoparticles capped by the carbon shell

The shape of nanoparticles is close to spherical. It should be noted that Cu nanoparticles are coated with

graphite-like carbon and a core-shell NP structure is observed. Fig. 1 shows the HAADF-STEM image of  $\text{Cu}_2$  for nanoparticles coated by carbon. The homogeneity of the carbon coated core-shell structures was confirmed by transmission electron microscopy. Using the data of HRTEM and STEM measurements, the corresponding particle size distribution histogram of  $\text{Cu}_n$  nanoparticles in  $\text{Cu}_n/\text{C}$  sample are constructed. Fig. 2 presents the size distribution histogram for Cu in  $\text{Cu}_2/\text{C}$  nanocomposite. According to the TEM images, the estimated average size for most of core-shell NPs is about 4-6 nm.

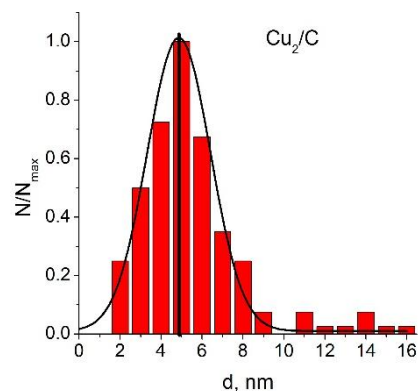


Fig. 2 The corresponding particle size distributions histogram of Cu in  $\text{Cu}_2/\text{C}$  nanocomposite.

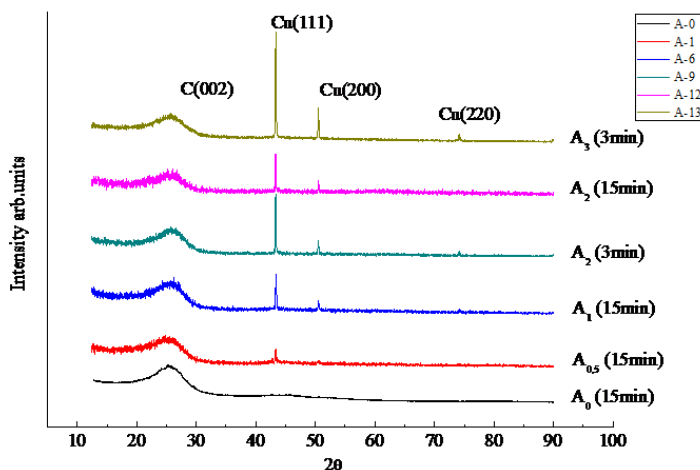


Fig. 3 Room-temperature XRD patterns from samples of A0 to A3 series indicating the peaks of Cu and C

Room-temperature XRD patterns of  $\text{Cu}@C$  powder nanocomposites display the characteristic peaks of Cu and C in multilayered graphene-coated copper nanoparticles. The XRD spectra of each sample were scanned at the Chemistry Department in California State University, Los Angeles using Bruker D2 Phaser model #A26X1 at  $15^\circ/\text{min}$ ,  $1.4\text{ s/step}$ , each step being  $0.01$  degrees. Fig. 3 represents X-ray diffraction spectra (XRD) of samples with close masses recorded at room temperature, where one can see the peak

patterns from Cu and carbon. The typical broad peak pattern at about  $25.5^\circ$  has been observed in the XRD spectra for all A series, which could be attributed to the formation of graphite-like carbon structures. A five narrow peaks with angles  $2\theta = 43.4^\circ$  (111),  $50.5^\circ$  (200),  $74.2^\circ$  (220),  $90^\circ$  (311) and  $95.2^\circ$  (222) which correspond to Cu nanoparticles with a face-centered cubic (fcc) crystalline structure.

## 2.4 Magnetic measurements

Both structural and magnetic data show that our samples are actually consist of single-domain ensembles of Cu nanoparticles embedded in a carbon matrix. Core-shell structures with copper nanoparticle core and surrounding carbon shell matrix is clearly seen. The carbon shell prevents Cu nanoparticles from oxidation and aggregation.

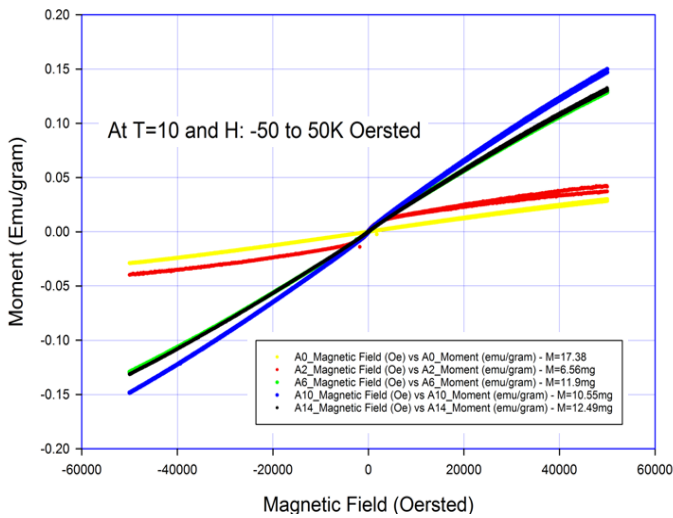


Fig. 4 Magnetization versus magnetic field in series of  $Cu_n/C$  samples with 2wt% at  $T = 10$ .

The magnetic characteristics of the carbon microspheres were taken on a vibrating magnetometer (Quantum Design)

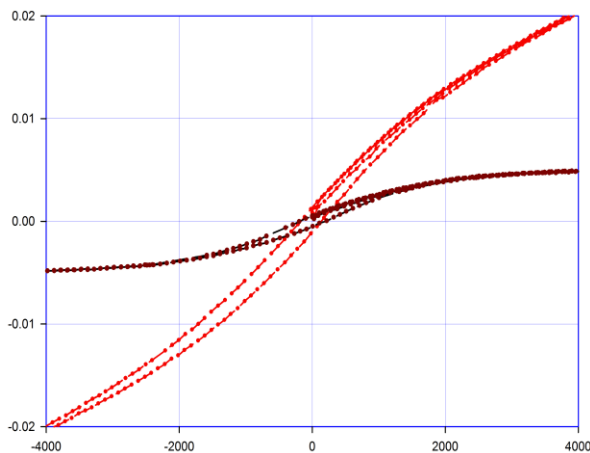


Fig. 5 Magnetization versus magnetic field in of  $Cu_2/C$  sample at room temperature and  $T = 10$

in magnetic fields to 60 kOe in a temperature range 5–300 K [8,9].

In ferromagnetic nanoparticles a magnetization are randomly distributed along their easy axes. The dependence of magnetization from the magnetic field in  $Cu_n/C$  series are performed at temperatures of 10 and 300 K, respectively. Analysis of the magnetization versus field curves lead to the following conclusions: a) the paramagnetic magnetization at  $T = 10$  K is linear function of field up to  $H = 50$  kOe and it is far from saturation b) paramagnetic magnetizations at  $H = 50$  kOe and  $T = 10$  K practically in all the samples are an order of magnitude higher than the corresponding magnetizations at ferromagnetic saturation c) the ratio of the proportions of the paramagnetic fraction to the ferromagnetic fraction, are approximately the same for all samples. It is also seen that a considerable fraction of the magnetization at low temperatures due to superparamagnetic nanoparticles. Fig. 5 for comparison shows the variation of magnetization at  $T=10$  K and the room temperature in  $Cu_2/C$ . The characteristic features of a ferromagnetic material, namely a hysteretic behavior with a coercive field and permanent magnetization even in zero applied field, are clearly seen for both temperatures. Variation of saturation magnetization values is observed with changing a copper content and nanoparticle size. The observed size-dependent behavior of magnetization in nanoparticles can be attributed to the relative surface area-to-volume ( $A/V$ ) ratio.

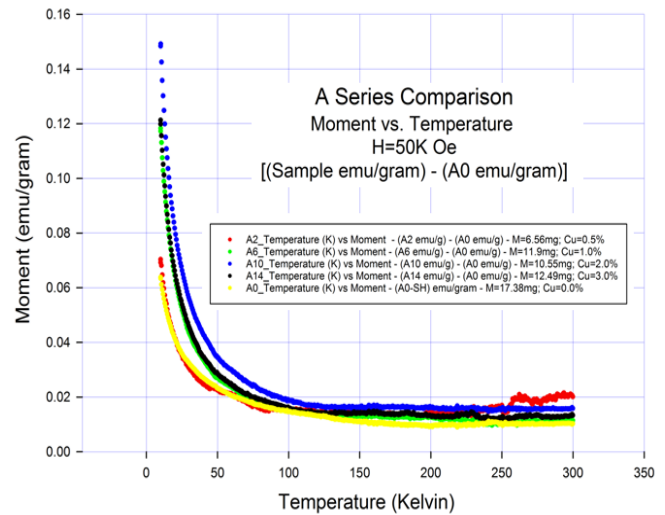


Fig. 6 Magnetization  $M$  versus temperature in  $Cu_n/C$  samples ( $m = 0, 2, 4, 8$  and  $12\text{wt}\%$ ) at  $H=50\text{kOe}=50$  kOe.

The temperature dependences of the magnetization in series of the  $Cu_n/C$  samples ( $m = 0, 2, 4, 8$  and  $12\text{wt}\%$ ) are given, measured in a magnetic field of 50 kiloersteds. Samples in

which there is no copper nanoparticles ( $n=0$ ,  $x=0$ ) correspond to the pyrolysis of the non-metal phthalocyanine. Estimation of the concentration of paramagnetic centers of the carbon matrix is about  $10^{18}$ - $10^{19}$  CE/g.

EPR spectra of samples obtained by pyrolysis are exhibiting an intense electron paramagnetic resonance (EPR) signal at varies temperatures. All of these materials exhibited similar broad, featureless slightly axial ( $g_x = g_y \neq g_z$ ) signals near  $g = 2$ . These are probably broad because there is a high density of  $S = 1/2$  Cu(II) centers which interact through dipolar magnetic interactions - this induces broadening even at very low temperatures as it is merely a through space interaction. The Cu<sub>2</sub>/C samples showed a little change in the signal intensity or lineshape (the room temperature sample had to be shifted because of significant conductivity causing difficulties with tuning. The size effects and the influence of surface magnetic anisotropy in Cu@C nanocomposites are also revealed in measurements of coercive field, susceptibility, blocking temperatures and spectra of ferromagnetic resonance.

### 3 CONCLUSION

In the present work the two-phase pyrolysis, provide samples in which the weight concentrations of copper in carbon can be varied from 0 to 12 wt%, and the nanoparticle sizes are from 2 to 500 nm. Our structural studies show that copper nanoparticles form an fcc lattice structure and that they are encapsulated in nano-graphite-like carbon shells. Despite the filled  $d$  shells the small Cu nanoclusters Cu@C nanocomposites possess magnetic moments and can reveal even room temperature ferromagnetism. Band paramagnetism overcomes the combined core diamagnetism, and, as result, carbon coated copper NPs become paramagnetic. We found that copper capped NPs have a marked ferromagnetic and giant paramagnetic behavior dependent on the NPs size. Giant paramagnetism was found in all Cu/C samples, whose paramagnetic susceptibilities are half the order of magnitude more than the paramagnetism observed in the carbon matrix. The paramagnetic susceptibilities of Cu@C nanocomposites are of the order of  $(0.3-1) 10^{-4}$  emu/g<sub>Cu</sub>Oe. In nanocomposite Cu@C, ferromagnetism is also found, which is apparent due to small copper nanoparticles, the sizes of which are about 2-5 nm. The amount of ferromagnetic and/or giant paramagnetic magnetizations observed in Cu@C nanostructures cannot be attributed to the small amount of iron or any other magnetic elements that was justified by our STEM and XRD element analyses. The saturation magnetization of ferromagnetic nanoparticles in the studied samples falls in the range 0.2-1.5 emu/g and depends little on the temperature in entire range of temperatures from helium to room temperatures. One can assume that the introduction of carbon into

the metal can be realized at boundaries, which are inevitably present in the copper NPs. The mechanism of magnetism and the role of the graphene/metal interface still remains unclear. The magnetic properties and changes in the electronic structure of Cu@C nanocomposites can be attributed to the charge transfer through core-shell interface from copper to carbon or vice-versa. On the basis of the present analysis the conclusion can be made that the thorough and detailed experimental studies of these problems using electron spectroscopy measurements can provide explanation to this very complicated problem of magnetism of non magnetic metals coated by carbon-based material. Unusual ferromagnetism and giant paramagnetism displayed by nanocomposites of non-magnetic copper surrounded by carbon environment is novel interesting phenomenon in physics of condensed state and might have potential applications in electronics, spintronics and quantum information processing.

### 4 ACKNOWLEDGEMENT

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