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Copper nanoparticles functionalized PE: Preparation, characterization and magnetic properties

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ABSTRACT

We report grafting of copper nanoparticles (CuNP) on plasma activated high density polyethylene (HDPE) *via* dithiol interlayer pointing out to the structural and magnetic properties of those composites. The as-synthesized Cu nanoparticles have been characterized by high-resolution transmission electron microscopy (HRTEM/TEM) and UV–vis spectroscopy. Properties of pristine PE and their plasma treated counterparts were studied by different experimental techniques: X-ray photoelectron spectroscopy (XPS), UV–vis spectroscopy, energy dispersive X-ray spectroscopy (EDS), zeta potential, electron spin resonance (ESR) and SQUID magnetometry. From TEM and HRTEM analyses, it is found that the size of high purity Cu nanoparticles is (12.2 ± 5.2) nm. It was determined that in the CuNPs, the copper atoms are arranged mostly in the (111) and (200) planes. Absorption in UV–vis region by these nanoparticles is ranging from 570 to 670 nm. EDS revealed that after 1 h of grafting are Cu nanoparticles homogeneously distributed over the whole surface and after 24 h of grafting Cu nanoparticles tend to aggregate slightly. The combined investigation of magnetic properties using ESR spectrometry and SQUID magnetometry confirmed the presence of copper nanoparticles anchored on PE substrate and indicated ferromagnetic interactions.

1. Introduction

Immobilization of microspheres and nanoparticles (NPs) is the subject of numerous studies pertaining to the design of polymer nanocomposites [1], supported catalysts [2], bioactive colloidal crystals [3], inverse opals for novel optical materials [4], latex templated-hollow inorganic capsules [5], immunodiagnostic assays; “Pickering” emulsion polymerization for making latex particles and film-forming composites [6] or Janus particles [7]; chemo- [8] and biosensors [9], tunable plasmonic nanostructures [10], hybrid porous monoliths for separation science and technology [11], biocidal polymer/metal nanoparticle composite coatings, and so on. Particularly, in the recent years, the literature has witnessed an impressive progress of investigations on polymer coatings, grafts and particles as supports for anchoring nanoparticles. Reason for the rush in designing polymeric platforms for anchoring nanoparticles is the ease of preparation *via* well established chemical [12], electrochemical and radiation-induced routes [11,13]. Adsorption behaviours of MNPs can be easily controlled by incorporating desired functional groups, such as mercapto, nitrile, and amine, onto the surface of porous polymers [11,14].

Metal nanoparticles (NPs) *i.e.* Au, Ag, Cu *etc.* due to their small dimensions, high surface/volume ratio and interesting properties, are promising candidates for a variety of applications, which include optical, magnetic, thermal, sensoric devices, catalysis, etc. [15–17]. Among them, copper plays a distinctive role due to its availability, electrical, transport and catalytic properties. In a bulk form, if nuclear degrees of freedom are neglected, copper represents a diamagnet, whose properties are given by Lenz response of completely filled ions core and *3d* band.

However, in a nanoparticle the magnetic properties are strongly affected by the large proportion of surface spins which face an entirely different environment in comparison to the particle's core. The transfer of charge from surface atoms to inner parts of the core was found to become stabilizing factor of the nanoparticle [18]. The spins near the surface are imbalanced by image charges of the surface electrons, namely Fermi holes [19]. Experimentally,

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superparamagnetic behavior was reported for amine – capped Cu NPs, whereas thiol – capped Cu NPs displayed ferromagnetic behavior [20]. Systematic studies of bare Cu NPs of various sizes revealed the existence of ferromagnetic superspins. Pronounced redistribution of charge density from areas close to lattice sites in the bulk towards their neighbors in NPs was found. The formation of localized *3d* holes arising from the extended 3*d* and 4*s* band mixture was proposed to be responsible for ferromagnetic particle superspins in Cu nanoparticles [21].

In contrast, there is strikingly different situation in CuO NPs. Unlike bare Cu, bulk CuO represents an antiferromagentic system with two distinct critical temperatures. At higher temperatures CuO behaves as one – dimensional magnetic system. If the temperature is lowered, at $T_{N1} = 231$ K three – dimensional non collinear antiferromagnetic state with helical magnetic state is developed. Subsequently, for temperatures lower than $T_{N2} = 213$ K, three – dimensional collinear antiferromagnetic state is formed [22]. Paramagnetic response was found for CuO NPs annealed in the air at room temperature, whereas weak ferromagnetic component appeared for those annealed in reducing atmosphere. The effect was attributed to oxygen vacancies generating free carriers, which mediate ferromagnetic interactions among Cu spins. Both critical temperatures were revealed by alternating susceptibility studies [23]. Systematic study of dynamic properties of CuO NPs of various sizes revealed anomalous behavior. More specifically, FC and ZFC magnetization curves were found to bifurcate even at room temperature, *i.e.* well above T_{N1} and peak in ZFC curve usually found for other nanoparticle systems was absent. In addition, the absence of memory effects suggested neither superparamagnetic nor spin glass – like state for non – equilibrium behavior of CuO NPs [24].

In this paper we have investigated magnetic properties of CuNP coated polyethylene substrate for the first time. We have used the same coating strategy as in our previous papers because we found this procedure very effective [25,26]. Surface properties of pristine PE and its modified counterparts were studied by several experimental techniques: X–ray photoelectron spectroscopy (XPS), electrokinetic analysis and energy dispersive X-ray spectroscopy (EDS) were employed to study surface chemistry and copper distribution over the treated/grafted surface. Further, ultraviolet-visible spectroscopy (UV–vis) and Transmission Electron Microscopy (TEM/HRTEM) were used for characterization of copper nanoparticles. Magnetic properties of prepared samples were investigated by electron – spin resonance (ESR) and SQUID magnetometry.

2. Experimental part

2.1. Materials and sample preparation

High density polyethylene (HDPE, density 0.97 g cm^{-3}, 40 μm foil, supplied by Granitol Ltd., CZ) was used in this study. The samples were treated in Ar$^+$ plasma on Balzers SCD 050 device: the exposure time was 120 s, the discharge power was 8.3 W, gas purity was 99.997%, flow rate 0.3 l s^{-1}, pressure 10 Pa, electrode distance 50 mm and its area 48 cm^2, chamber volume approx. 1000 cm^3, plasma volume 240 cm^3 and treatment was accomplished at the laboratory temperature.

Immediately after exposition to plasma the samples were embed into methanol solution of biphenyl-4,4′-dithiol (1×10^{-4} mol l^{-1}; BPD; Sigma-Aldrich Corp.; US) for 24 h [27]. Thereafter the samples were inserted into colloidal solution of CuNPs for 1 or 24 h. Grafting times of 1 h and 24 h were chosen to estimate the influence of the duration of the immersion on the final concentration of nanoparticles on the surface of the polymer. A more detailed description of NPs preparation can be found in Ref. [28]. Finally, the samples were rinsed in methanol and then dried under nitrogen flow. Samples were kept under laboratory conditions.

2.2. Measurement and techniques

Ultraviolet-visible (UV–vis) absorption spectra were recorded using a Lambda 25 UV–vis spectrophotometer (PerkinElmer Inc., US). The colloidal solutions of CuNPs were kept in 1 cm quartz cell. Reference spectrum of solvent (water) was subtracted from spectra of colloidal solutions of CuNPs. Data were collected from 200 to 700 nm with 1-nm data step at the scan rate of 240 nm min^{-1}. The UV–vis absorption spectra were also measured on PE samples, pristine or modified by the plasma discharge and grafted with thiols and copper nanoparticles, too. Reference spectrum of pristine PE was subtracted from the spectra of modified PE samples.

The samples for transmission electron microscopy (TEM) were prepared by the deposition of a 6-μL drop of colloidal solution of copper nanoparticles onto a carbon-coated copper grid; excessive solution was removed and grids were dried by Whatman filtration paper. The samples were observed by transmission electron microscope (JEM-1010; JEOL Ltd., Tokyo, Japan) at an accelerating voltage 80 kV. Pictures were taken by SIS MegaView III digital camera (Soft Imaging Systems, Berlin, Germany) and analyzed by AnalySIS v. 2.0 software (Münster, Germany). More detailed structural characterization of copper nanoparticles was performed using the high resolution transmission electron microscope (HRTEM, JEOL JEM-2200FS, JEOL Ltd., Tokyo, Japan) operated at 200 kV.

Concentrations of C(1s), O(1s), S(2p), Cu(2p) atoms in the modified surface layer were measured by X-ray Photoelectron Spectroscopy (XPS). Omicron Nanotechnology ESCAProbe P spectrometer (Omicron Nanotechnology GmbH, DE) was used to measure photoelectron spectra (typical error of 5%). XPS analysis was performed at a pressure of 2×10^{-8} Pa. Exposed and analyzed area had dimension of 2×3 mm^2. X-ray source was monochromatic at 1486.7 eV with step size of 0.05 eV, take off angle was 0° with respect to the sample surface normal. High-resolution scans of the Cu *2p* XPS and Cu L2VV Auger regions were scanned. Peak line shapes and positions from X-ray excited Auger (XAES) have proved to be sensitive enough for Cu oxidation state analysis, providing more unambiguous differences between Cu(+1) and Cu(0) than Cu *2p* XPS core level shifts [29]. The spectra evaluation was carried out by CasaXPS programme. The correction of charge effects was performed by fitting to position of C(1s) peak.

Electrokinetic analysis (zeta potential) of all samples was determined by SurPASS Instrument (Anton Paar GmbH, AT). Samples were studied inside the adjustable gap cell with an electrolyte of 0.001 mol l^{-1} KCl, all samples were measured eight times at constant pH = 6.3 and room temperature. For zeta potential determination the streaming current method and Helmholtz-Smoluchowski (HS) equation were used with experimental error of 5% [30].

The morphology of the prepared structures was investigated using scanning electron microscopy (SEM, Tescan Lyra dual beam microscope; Tescan, CZ). Elemental composition and mapping were performed using an energy dispersive X- ray spectroscopy (EDS, analyzer X-MaxN, 20 mm^2 SDD detector, Oxford Instruments plc, UK). The samples were attached by carbon conductive tape to avoid sample charging. SEM-EDS and SEM measurements were carried out using accelerating voltages 10 kV and 2 kV, respectively. The samples were coated by a thin layer of gold (20 nm). Exposed and analyzed area was 5×5 μm^2.

Electron – spin resonance was studied in a commercial X-band spectrometer Bruker ELEXYS II E500 (Bruker Corp., US). Each studied sample of 3.14 cm^2 area was folded and placed in a Suprasil quartz ampoule and placed in the cryostat which is located in