



Point of zero charge of maghemite decorated multiwalled carbon nanotubes fabricated by chemical precipitation method



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ABSTRACT

In this research paper, maghemite decorated multiwalled carbon nanotubes (maghemite/MWCNTs) were synthesized using a low temperature (50 °C) co-precipitation method. Synergistic effects due to the combination of unique surface characteristics of MWCNTs with magnetic properties of iron oxide nanoparticles were achieved using this versatile and easy chemical method. Synthesized nanocomposites were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, Field emission scanning electron microscopy (FESEM), Energy dispersive spectroscopy (EDS), Transmission electron microscopy (TEM) and Vibrating sample magnetometer (VSM). In addition, changes in point of zero charge (pH_{PZC}) value of nanostructures were investigated in chronological order of sample preparation using pH drift method. The measured pH_{PZC} values were 5.43, 2.66, 3.63 and 3.89 for raw MWCNTs, oxidized MWCNTs, maghemite/MWCNTs with Iron salt/MWCNT ratio of 2:1 and 4:1, respectively. It is demonstrated that introducing maghemite nanoparticles on the surface of oxidized MWCNTs slightly increased pH_{PZC} values of nanocomposites making them promising candidates for many technological applications.

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1. Introduction

Due to desirable mechanical, thermal and outstanding electrical properties [1,2], high aspect ratio, and tunable surface chemistry [3,4], carbon nanotubes (CNTs) have widely attracted attention from many researchers all around the world. Their unique structure [5] have made them ideally suited candidates for a wide range of potential applications including field emission [6], scanning probe sensors [7], nanoelectronics [8], solar cells [9], biological treatments [10] and water remediation agents [11–13]. However, these characteristics of CNTs can be vastly enhanced by surface modifications with selected organic, inorganic and biological species. For instance, decoration of multiwalled carbon nanotubes (MWCNTs) by spinel ferrite nanoparticles MFe_2O_4 ($M = Mn, Co, Ni, Mg, \text{ or } Zn$) has been extensively reported to improve adsorption properties of MWCNTs [14–18]. In other words, these magnetic nanocomposites are classified as an important group of inorganic adsorbents to remove toxic metal ions from water for human health concern [19]. Therefore, in any adsorption system, it is of great significance to determine their pH dependent surface charge characteristics in order to be in pH conditions favoring the desired pre-concentration and adsorption applications. In this sense, point of

zero charge (pH_{PZC}) is a substantial property of nanocomposite–water interface to be evaluated in technological issues. pH_{PZC} is the pH value at which the sum of surface positive charges balances the sum of surface negative charges. In addition, the surface is positively charged at pH values below pH_{PZC} and negatively charged at pH values above pH_{PZC} [20–23].

Different values of pH_{PZC} for simple and mixed oxide nanostructures have been reported in literature [24–27]. The diversity actually stems from the fact that pH_{PZC} depends on materials synthesis method, size distribution and any heat treatment processes which control the hydration ratio of materials [26,27]. For instance, Ji and co-workers [28] reported pH_{PZC} value for MWCNT/ Fe_3O_4 nanocomposite fabricated through thermal decomposition method as 4.9. Ai et al. [29] evaluated pH_{PZC} value of 6.5 for magnetite coated MWCNTs prepared by one-pot solvothermal route. In other research papers conducted by Ntim et al. [30] and Kerkez et al. [31], pH_{PZC} values of iron oxide decorated MWCNTs synthesized using a chemical co-precipitation method were reported as 7.35 and 6.8, respectively which were in consistence with previous research works [32,33]. According to reported literature, choice of nanocomposite preparation method and effective parameters in the preparation process seems extremely vital in optimization of pH dependent surface characteristics. Among various chemical methods, co-precipitation is considered as one of the most versatile, conventional and economical routes for preparing nanoparticles in which process parameters can be manipulated in order to achieve desired properties

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favoring the intended applications including adsorption of metal ions [34,35]. In this regard, optimization of process parameters could lead to the formation of nanocomposites with unique surface characteristics and magnetic properties possessing an expanded range of surface negative charges (low pH_{PZC} values) which indeed has valuable potential applications in water remediation of metal ions.

In this study, we applied a low temperature (50 °C) and in-situ co-precipitation method to decorate MWCNTs with maghemite nanoparticles with varied iron salt precursor to MWCNTs ratio. Effect of different modification steps including iron salt/MWCNTs ratio on pH_{PZC} value of MWCNTs were determined in chronological order of sample preparation using pH drift method. Morphology, structural and magnetic properties of nanocomposites were investigated using Field emission scanning electron microscopy (FESEM), Energy Dispersive spectroscopy (EDS), Transmission electron microscopy (TEM), X-Ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Vibrating sample magnetometer (VSM).

2. Experimental procedure

2.1. Materials

MWCNTs with outer diameters of 5–15 nm and length of approximately 50 μm were purchased from US Research Nanomaterials, Inc. with purity of more than 95% and 97.46% carbon content. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Sigma-Aldrich and used without further purification. NaCl (99.5%), NaOH (97%), Ammonia solution (25%), Nitric Acid (69%) and HCl stock solution (37%) were supplied by Merck-Millipore. All the solutions were prepared using deionized water.

2.2. Characterization instruments

Crystalline structure of samples was revealed with the aid of X-ray diffraction (XRD) measurement on X'pert MPD, Philips ($\text{CuK}\alpha$, wavelength of 1.54 Å) system. XRD patterns were collected from $2\theta = 5^\circ$ to 80° with step size of 0.02° and working voltage of 40 kV. Spectroscopic analysis of samples was performed using Fourier Transform Infrared Spectroscopy (FTIR) on Bruker-Tensor 27 IR equipment in 400–4000 cm^{-1} range with 2 cm^{-1} resolution at 14 s and 10 kHz scan speed. Sampling method was a KBr pellet method. Raman spectra were acquired using an Almega Thermo Nicolet Dispersive Raman Spectrometer in spectral range between 100 and 4200 cm^{-1} . The excitation source was a second harmonic Nd:YLF laser emitting at 532 nm with power of 30 mW and resolution of 4 cm^{-1} . 32 scans within 3 min were performed for each sample. Morphology and elemental analysis of synthesized nanocomposites were analyzed using MIRA3 TESCAN field emission scanning electron microscopy with voltage of 5 kV equipped with an EDS analyzer (SAMx company, France). TEM images were performed using Zeiss-EM10C Transmission Electron Microscope with an accelerating voltage of 80 kV. To prepare samples for TEM analysis, small amount of each sample was dispersed in deionized water using Misonix-S3000 ultrasonicator for 5 min, and then a drop of dispersion was deposited on a carbon coated grid (Cu Mesh 300) and placed in specimen chamber. Magnetic hysteresis measurements were collected by MDKFD (Meghnatis Daghig Kavir. Co, Iran) vibrating sample magnetometer at room temperature.

2.3. Oxidation of MWCNTs

Oxidized MWCNTs (Ox-MWCNTs) were prepared by dispersing 1 g of MWCNTs in diluted (7 M) nitric acid under refluxing conditions at 85 °C. The time was set after the first condensed drop appeared on the round bottom flask. After 6 h, the Ox-MWCNTs were left to reach room temperature. Then, three cycles of 10 min centrifugation at 6000 rpm were performed to wash Ox-MWCNTs reaching an

approximate pH value of 5. These nanotubes were then vacuum filtered using a 0.45 μm PTFE membrane to reach the final pH equal to that of deionized water. The samples were then dried in an oven at 75 °C for 3 h.

2.4. Preparation of maghemite decorated MWCNTs

To decorate Ox-MWCNTs with maghemite nanoparticles, an in-situ modified co-precipitation method was used in which, iron chloride salts were reduced in the presence of Ox-MWCNTs. Following this process, solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 0.5 M HCl were prepared with a molar ratio of $\text{Fe}^{3+} : \text{Fe}^{2+} = 2 : 1$. Furthermore, 200 mg of Ox-MWCNTs were dispersed in deionized water with the aid of ultrasonication for 20 min. Iron solutions were slowly added to Ox-MWCNTs dispersion. In the next step, 2 M ammonia solution was added dropwise (with a rate of 1.5 ml min^{-1}) to the suspension containing Ox-MWCNTs and iron precursors until pH reached 10. Then, samples were mechanically stirred for 1 h at 50 °C to ensure completeness of the reaction. Finally, samples were repeatedly washed with absolute ethanol and deionized water to reach neutral pH and then dried in an oven for 48 h at 45 °C. The schematic diagram of sequential co-precipitation process in which maghemite nanoparticles were introduced on MWCNTs is shown in Fig. 1. In nanocomposite preparation experiments, two different ratios of iron salt precursor to MWCNTs were considered, 2:1 and 4:1. The corresponding samples were labeled Fe-CNT-21 and Fe-CNT-41, respectively.

2.5. pH_{PZC} determination

To measure pH_{PZC} values in sequential order of co-precipitation process after each surface modification, pH drift method was applied. pH drift is preferred over other conventional methods such as titrations because it is less time consuming, results can be obtained in few steps using common laboratory apparatuses which indeed lowers the overall expenditure of the experiment and the results are perfectly in accordance with the ones obtained from other applied methods [23,36]. According to this method, solutions of 0.01 mol L^{-1} NaCl in 10 ml test tubes were adjusted to pH values of 2 to 8 ($\text{pH}_{\text{initial}}$) using 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl. Then, 30 mg of raw-MWCNTs, Ox-MWCNTs, maghemite decorated MWCNTs (ratios of 2:1 and 4:1) were added to test tubes and shaken at 250 rpm at 25 °C. After 48 h the final pH (pH_{final}) of samples were measured using a microprocessor pH meter (pH 211, Hanna Instruments, Inc.) and plotted against initial pH. Intersection point of the resulting curve with the line passing origin ($\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$) gives pH_{PZC} [32].

3. Results and discussion

Iron oxide nanoparticles were coated on Ox-MWCNTs via an in-situ co-precipitation method. In this process, oxidation of MWCNTs is considered as a crucial step in the decoration of iron nanoparticles on MWCNTs. Chemical surface tuning of MWCNTs using acid oxidation provides stable dispersions of MWCNTs in aqueous media which can then act as parent solution for iron precursor reduction [4]. In order to initiate reduction reaction which leads to metal hydroxide precipitation, a base should be used [34]. NH_4OH is one of the common bases which can be added as reducing agent in precipitation processes [35,37]. In fact, the use of a base is vital for co-precipitation of Fe^{2+} and Fe^{3+} in their mixed solutions. It is important to note that precipitation of Fe^{3+} occurs at pH 3–4, whereas Fe^{2+} gets precipitated at pH 8–9 [38]. Therefore, adequate concentration of OH^- ions is required for co-precipitation of both Fe^{3+} and Fe^{2+} ions. In other words, if pH is not optimum, Fe^{3+} ions get preferentially precipitated over Fe^{2+} and more FeOOH phase will be formed. Thus the role of bases is to provide hydroxyl ions for metallic hydroxides. Elimination of water from metallic hydroxides leads to oxides, often by heating [38–40].

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