



Polyvinyl alcohol functionalized cobalt ferrite nanoparticles for biomedical applications

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ABSTRACT

In the present work, cobalt ferrite nanoparticles (CoFe₂O₄ NPs) have been synthesized by combustion method. The surface of the CoFe₂O₄ NPs was modified with biocompatible polyvinyl alcohol (PVA). To investigate effect and nature of coating on the surface of CoFe₂O₄ NPs, the NPs were characterized X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The transmission electron microscopy (TEM) and dynamic light scattering (DLS) results demonstrate the monodispersed characteristics of CoFe₂O₄ NPs after surface modification with PVA. The decrease in contact angle from 162° to 50° with PVA coating on NPs indicates the transition from hydrophobic nature to hydrophilic. The Magnetic properties measurement system (MPMS) results show that the NPs have ferromagnetic behavior with high magnetization of 75.04 and 71.02 emu/g of uncoated and coated CoFe₂O₄ NPs respectively. These PVA coated NPs exhibit less toxicity over uncoated CoFe₂O₄ NPs up to 1.8 mg mL⁻¹ when tested with mouse fibroblast L929 cell line.

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1. Introduction

MNPs because of their outstanding physical and chemical properties have received considerable attention in various fields from technology to biomedical applications [1]. The dimensions of these nanoparticles make them ideal candidates for nano engineering of surfaces and production of functional nanostructures. Such modification facilitates their use in biomedical applications for example as contrast agents for magnetic resonance imaging (MRI), for targeted drug delivery and as heating mediators in hyperthermia therapy application *etc.* [2].

Among various MNPs, spinel CoFe₂O₄ NPs are extensively studied due to their ability to form an ideal magnetic system toward understanding and controlling magnetic properties at the atomic level through chemical manipulation. CoFe₂O₄ has large anisotropy compared to other oxide ferrites [3,4]. Though they are proposed for biomedical application their use in medicine is restricted due to numerous problems such as toxicity due to the remarkable amount of cobalt release in aqueous solutions, aggregation in solution, and poor accessibility of the surface when surfactants are used. This problem can be overcome by surface coating of CoFe₂O₄ with a compatible, nontoxic, and water-stable/dispersing material [5–9].

From this point of view, encapsulating MNPs by PVA is a promising and important approach. The rich and well documented chemistry of biocompatible PVA coatings may allow practical implementation of MNPs in pharmaceutical and biomedical applications [10,11]. PVA served as the protective polymer as it has the desired solution properties in water and contains many isolated hydroxyl functional groups, which can adsorb and complex with metal ions [12]. It is assumed that PVA chain adsorbed on the surface of magnetic core of CoFe₂O₄ NPs and form a shell as shown in Fig. 1 [13].

In the present investigation, CoFe₂O₄ NPs were first synthesized by combustion method and further coated with PVA. The effect of coating on structural, morphological and magnetic properties of CoFe₂O₄ NPs was studied in detail. The attachment of PVA on the surface of CoFe₂O₄ core and stability were investigated by XRD, FTIR, TEM and DLS respectively. The biocompatibility of coated and uncoated CoFe₂O₄ NPs was tested for different concentrations (0.3–1.8 mg/mL) with mouse fibroblast L929 cell line by trypan blue assay.

2. Experimental

2.1. Materials

Analytical grade cobalt nitrate [Co(NO₃)₂·6H₂O] (99%), ferric nitrate [Fe(NO₃)₃·9H₂O] (99.9%), Glycine [CH₂NH₂COOH] (99%) and polyvinyl alcohol (–C₂H₄O)_n (99%) were purchased from LOBA

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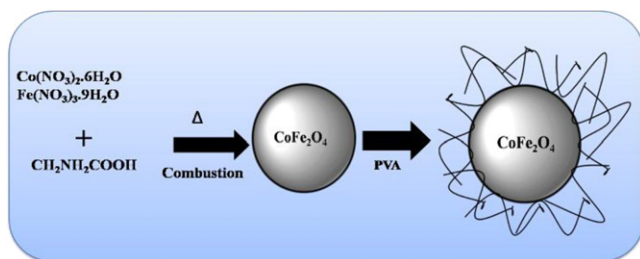


Fig. 1. Synthesis of CoFe_2O_4 NPs and layering of PVA polymers on the surface of the NPs.

CHEM, India. All chemicals listed above are water soluble and used as received.

2.2. Synthesis of CoFe_2O_4 NPs

The CoFe_2O_4 NPs (S1) were prepared by simple and inexpensive combustion method using corresponding metal nitrates and glycine. Metal nitrates were employed both as metal precursors and oxidizing agents while glycine serves as reducing agent and fuel for combustion. The stoichiometric amounts of metal nitrates and glycine were mixed in large beaker which results in slurry due to hygroscopicity of metal nitrates [14]. The obtained slurry was then introduced to hot plate preheated to 250°C . After evaporation of water content, the mixture starts frothing and ignited with flame within few seconds, giving voluminous and foamy CoFe_2O_4 powder. The detailed synthesis and reaction mechanism of CoFe_2O_4 nanoparticles was reported elsewhere [15].

2.3. Surface coating of CoFe_2O_4 nanoparticles

The mixture of CoFe_2O_4 nanoparticles and water was vigorously stirred for 10 min by dispersing the nanoparticles in double distilled water (DDW). PVA solution was prepared by dissolving 0.6 M PVA in 40 mL water. PVA solution was added to above mixture and stirred further for 30 min. The obtained mixture was kept overnight at room temperature, then supernatant was discarded and PVA coated CoFe_2O_4 nanoparticles were collected. Surface modified CoFe_2O_4 NPs (S2) are easily dispersible in DDW after 10 min sonication.

2.4. Characterizations

Structure and phase of as synthesized and PVA coated CoFe_2O_4 NPs was studied by XRD (Philips-3710) with $\text{Cu-K}\alpha$ radiation ($\lambda = 2.2897 \text{ \AA}$) in the 2θ range from 20 to 100° . The patterns were evaluated by Panalytical X'pert high score software and compared with standard JCPDS (card no. 22-1086). Presence of the magnetic core and polymer coating of the MNPs was confirmed by FTIR spectroscopy (Perkin Elmer spectrometer model no. 783, USA). Elemental composition of the MNPs was determined by TGA with Trans analytical instruments (SDT 2960) operated in temperature from 35°C to 1000°C with heating rate of $10^\circ\text{C}/\text{min}$ in flowing nitrogen ambiance. The particle size of coated and uncoated CoFe_2O_4 NPs was measured with TEM (Philips CM 200 model, operating voltage $20\text{--}200 \text{ kV}$, resolution 2.4 \AA). Water contact angles of coated and uncoated MNPs were measured using the sessile drop method by deposition of $4\text{--}6 \mu\text{L}$ droplets of DI water on a horizontal surface and their observation in cross-section. Each drop was observed directly with an Olympus BX-41 microscope objective lens, whereas its image was digitally captured using a 1.4 megapixel computer-controlled digital CCD camera. The values reported are averages of more than 20 measurements performed in different areas of each sample surface. DLS measurements were carried out

using a PSS/NICOMP 380 ZLS (Particle Sizing System, Santa Barbara, CA, USA). The light source was He-Ne laser operated at 632.8 \AA . All measurements were carried out at $25.0 \pm 0.1^\circ\text{C}$ using a circulating water bath. Cylindrical cells of 10 mm diameter were used in all of the light scattering experiments. The autocorrelation function was obtained using a 192-channel photon correlator. For reproducibility, at least three measurements were conducted for each reading. Magnetic properties of the NPs were measured by the MPMS XL.

2.5. Cytotoxicity study

2.5.1. Cell culture

In vitro cell viability of coated and uncoated CoFe_2O_4 MNPs was studied using mouse fibroblast L929 cell line purchased from National Center for Cell Science (NCCS), Pune, India.

L929 cells were grown in minimal essential medium supplemented with 10% (v/v) FBS (fetal bovine serum), kanamycin (0.1 mg/mL), penicillin G (100 U/mL), and sodium bicarbonate (1.5 mg/mL) at 37°C in a 5% CO_2 atmosphere. In brief, cells ($1 \times 10^5 \text{ cells/mL}$) were grown for 24 h. After 24 h, the old media was replaced by fresh media and different particle concentrations ($0.3, 0.6, 1.2$ and 1.8 mg/mL) of uncoated and coated CoFe_2O_4 NPs.

2.5.2. Cell viability by trypan blue dye exclusion assay

For this experiment, L929 cells were seeded at a density of $1 \times 10^5 \text{ cells/mL}$ in a culture plate. After 24 h of incubation, the old media was replaced with a media containing different concentrations of MNPs. And the cells were exposed for 48 h incubation time. Then, the dishes were washed thrice with PBS to remove the MNPs. Both the attached and unattached cells were harvested and combined after trypsinization (0.025% trypsin, 10 min). The cells were then stained with trypan blue dye and counted with a hemocytometer. The experiments were replicated three times and the data was graphically presented as mean. The total amount of cells, stained and unstained is counted. The calculated percentage of unstained cells will represent the percentage of viable cells.

3. Results and discussion

3.1. Effect of surface coating on structural properties

3.1.1. XRD analysis

The formation of uncoated and PVA coated CoFe_2O_4 NPs was confirmed from XRD pattern (Fig. 2(a)). CoFe_2O_4 nanoparticles display several relatively strong reflection peak in the 2θ region of $20\text{--}100^\circ$, which is quite similar to the other groups, confirming that prepared NPs are CoFe_2O_4 with spinel cubic structure having $\text{Fd}\bar{3}m$ space group [16,17]. The obtained peaks are well matched with standard JCPDS card no. 22-1086. The determination of crystallite size (D) of CoFe_2O_4 powder was based on X-ray diffraction line broadening and calculated by using Scherrer formula [18],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is the full-width at half maxima of the strongest intensity diffraction peak ($3\ 1\ 1$), λ is the wavelength of radiation and θ is the angle of strongest characteristic peak. From Fig. 2(a) it can be revealed that all resultant NPs are pure CoFe_2O_4 with an inverse spinel structure. No change in phase was observed in case of particles coated with PVA while slight suppression of diffraction peaks can be clearly observed. There is no pronounced change in the lattice constant however crystallite size varies slightly after surface modification. The calculated crystallite size (D) for uncoated and coated CoFe_2O_4 NPs are 38 nm and 35 nm respectively.

The corresponding selected area electron diffraction (SAED) pattern of coated CoFe_2O_4 is shown in Fig. 2(b). Figure shows spotty

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