



A novel method for preparation of bare and poly(vinylpyrrolidone) coated superparamagnetic iron oxide nanoparticles for biomedical applications



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ABSTRACT

Pure crystalline superparamagnetic iron oxide nanoparticles (SPIONs) of magnetite (Fe₃O₄) were prepared from an additive-free aqueous solution of iron(III) nitrate salt *though* a novel one-pot electro-deposition method. The prepared nanoparticles were characterized by XRD, IR and TEM. The SPIONs were further coated by poly(N-vinyl-2-pyrrolidone) during their deposition process. The coating of PVP on SPIONs was confirmed by FT-IR, DSC-TGA and DLS analyses. The proposed electrochemical route can be concluded as a great routine for the preparation of polymer-coated SPIONs for biomedical applications.

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1. Introduction

Preparation and surface engineering of superparamagnetic iron oxide nanoparticles (SPIONs) have been subject of many recent studies due to the wide range of promising applications such species can have as MRI contrast and tissue repair agents, as well as, in immunoassays, detoxification of biological fluids, hyperthermia, drug delivery, and cell separation [1]. At present, various wet chemical processes like pyrolysis [2], solvothermal [3], hydrothermal [4], precipitation [5] and thermal decomposition [6] routes have been applied for synthesizing of SPIONs. Although, these methods have been improved in the recent years, controlling particle size and distribution is still a serious issue. Electrochemical methods, on the other hand, can be considered as promising alternative techniques for the preparation of SPIONs, since they can help control the crystallinity, purity, particle size and

properties of the deposit through manipulating or adjusting the deposition conditions [7,8]. So far, both anodic and cathodic electro-deposition procedures have been used for the preparation of SPIONs. Anodic electro-deposition of SPIONs, has been extensively evaluated as reflected by the literature [9–14], and has been found to require high voltage values (40–62 V) [11], a critical distance between anode and cathode (< 5 cm) [12], as well as the presence of supporting electrolytes and/or surfactants [9], which can complicate the conditions. As an alternative route, cathodic deposition seems that could avoid suffers of anodic deposition disadvantages. The approach, has however, not been thoroughly evaluated, especially in terms of its application for the preparation of SPIONs and even the few reports in this area [15–17] have been focused on the synthesis of pure magnetite from ethanol media. In short one can conclude that the preparation of SPIONs from aqueous solutions and their surface engineering through cathodic electro-deposition is an attractive yet unexplored area of research. Based on the above explanations the current work focuses on the specification of the optimal conditions for the preparation of well-dispersed Fe₃O₄ NPs from aqueous media, and also developing a

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parallel in situ approach for polymer coating the SPIONs through with poly(vinylpyrrolidone) (PVP). A review of the literature indicates that such a one-step electrochemical preparation of PVP coated SPIONs has not been reported so far.

2. Experimental procedure

2.1. Sample preparation

All chemicals including iron(II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.95%) and poly(vinylpyrrolidone) (PVP, $M_w=4000$) were purchased from Sigma-Aldrich. The deposition experiments were conducted using an electrochemical workstation system (Potentiostat/Galvanostat, Model: NCF-PGS 2012, Iran) and a two-electrode electrochemical cell stainless-steel cathode and graphite anode was applied in the electrodeposition experiments. A .01 M aqueous solution of $[\text{FeCl}_2 + \text{Fe}(\text{NO}_3)_3]$ with a 1:2 M ratio was used. The bare Fe_3O_4 NPs were prepared through galvanostatic electrodeposition ($I=10 \text{ mA cm}^{-2}$, $T=25^\circ\text{C}$ and $t=30 \text{ min}$). The PVP coated NPs were prepared under the same electrochemical conditions composition and the only difference was the addition of 1 g L^{-1} of PVP to the electrolyte solution. After the deposition, the prepared powder was repeatedly rinsed with distilled water and centrifuged at 3000 rpm for 10 min to remove the weekly bonded PVP to the surface of SPIONs. For better purification, the prepared SPIONs were washed several times with ethanol solution and separated with magnet, and they were again dispersed in ethanol and centrifuged at 6000 rpm for 30 min to remove the weekly bounded PVP on the surface of NPs. Then the SPIONs were separated from the solution by magnet. Finally, the obtained black powder was evaluated by characterization analyses.

2.2. Sample characterization

The size and morphology of the prepared NPs were monitored using a transmission electron microscopy (TEM, Phillips EM 208 with an accelerating voltage of 100 kV); their crystal phase and structure were determined by XRD, model Phillips PW-1800 diffractometer with $\text{Co K}\alpha$ radiation ($\lambda=1.789 \text{ \AA}$); and the hydrodynamic diameter was determined by dynamic light scattering (DLS, 4700 Malvern Instruments, UK). FTIR spectra were recorded using a Bruker Vector 22 Fourier transformed infrared spectroscope. The thermal behavior analyses were carried out in an N_2 atmosphere between room temperature and 600°C at a heating rate of 5°C min^{-1} using a thermo-analyzer (STA-1500). The magnetic properties of NPs were measured from $-20,000$ to $20,000 \text{ Oe}$ at room temperature using a Lakeshore model 7410 vibrational sample magnetometer (VSM).

3. Results and discussion

The crystalline properties of the SPIONs were analyzed through XRD as shown in Fig. 1(a). For both samples, all observed peaks were completely coincident with spinal structure of magnetite (JCPDS card No. 01-088-0315). Notably, it is possible that the surfaces of the particles have been oxidized to maghemite due to deposition from aqueous solution. Using the Debye-Scherrer equation ($D=K\lambda/\beta\cos\theta$), the average crystallite size was calculated to be about 10.1 and 14.7 nm for bare and PVP coated SPIONs, respectively. In the FTIR spectra (Fig. 1(b)), the broad band at $\sim 3430 \text{ cm}^{-1}$ is caused by the stretching vibration of the OH group

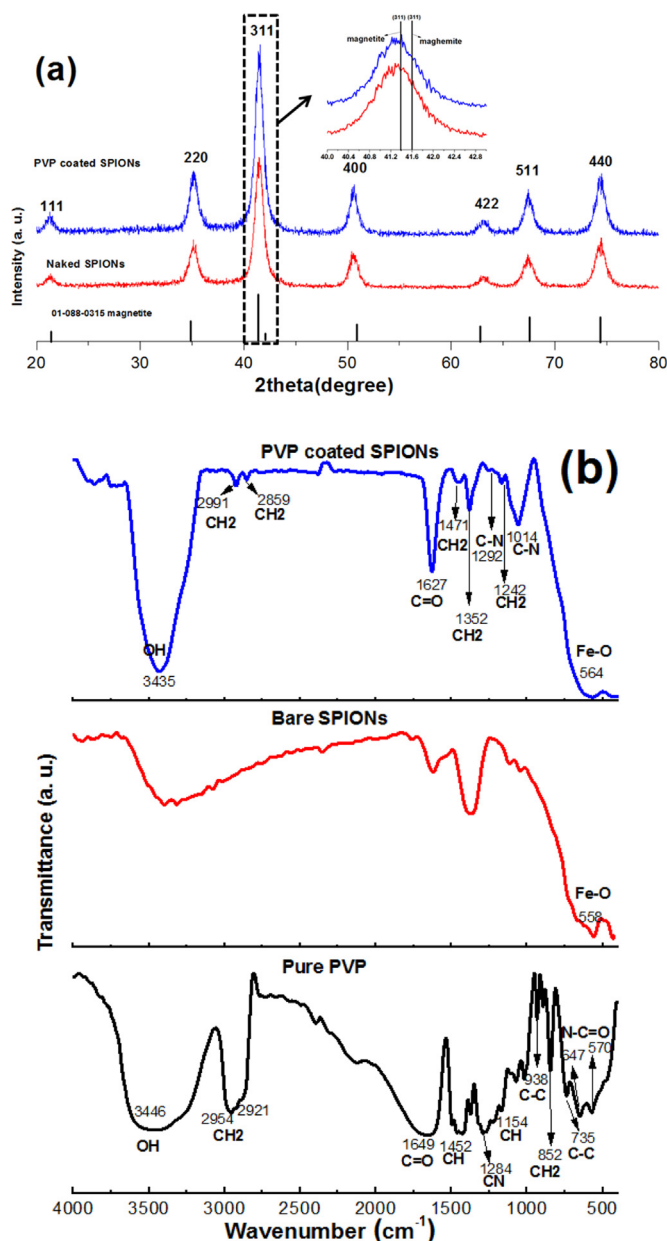


Fig. 1. (a) XRD patterns and (b) IR spectra of bare and PVP coated SPIONs.

in water molecules adsorbed on the SPIONs surface. The Fe–O stretching mode is observed at 556 and 564 cm^{-1} for bare and PVP coated SPIONs, respectively, which indicates the formation of Fe_3O_4 during the electrodeposition. The spectra of the PVP coated SPIONs include all the characteristic peaks of PVP including CH_2 groups vibration modes (at 2922, 2859, 1471, 1352 and 1242 cm^{-1}), C–N stretching mode (at 1292 and 1014 cm^{-1}) and C=O group vibration (at 1627 cm^{-1}). Notably, the C=O vibration is seen at about 1649 cm^{-1} for pure PVP. The C=O band shifted from 1649 cm^{-1} to 1627 cm^{-1} indicated the chemical interaction between C=O groups and the Fe_3O_4 nanoparticles.

These results completely confirmed the presence of PVP layer on the surface of the electrodeposited NPs. Notably, the C=O vibration is reportedly observed at 1661 cm^{-1} for pure PVP [2,9,18]. The shift of the vibrational band of the C=O from 1661 cm^{-1} to 1647 cm^{-1} in the case of this work, suggests that PVP is connected to the surface of the SPIONs via through its carbonyl group.

The thermal properties of the prepared SPIONs were specified by DSC–TG results in Fig. 2. The bare SPIONs exhibited only a 2.01%

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