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Organophosphorous modifications of multifunctional magnetic nanowires

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ABSTRACT

In the presented study, efforts have been undertaken to obtain the magnetic nanowires of multisegmental internal structure by AC and DC electrodeposition methods. The core–shell nanowires were obtained by wetting chemical deposition followed by thermal crystallization and electrodeposition. Such nanowires were tested to obtain functionalization by organophosphorous compounds and finally immobilize enzymes like trypsin. All obtained nanostructures were tested by X-ray diffraction, infrared spectroscopy and transmission electron microscopy.

1. Introduction

It has been found out that superparamagnetic nanowires and nanotubes can be used in many areas of human life [1]. Magnetic properties allow to use them for site-specific targeting and delivery through external magnetic field in various applications of human activity [2]. Proper size nanoparticles can be used in medicine as magnetic resonance imaging medium, drug delivery medium or tissue repair, cell separation, and test of genome sequencing [3]. Nanomaterials characterized by small diameters and relatively large length become especially interesting. A high aspect ratio causes that such structures posses unique optical and electrical properties different from bulk materials. Many applications are possible because of unusual magnetic properties of core–shell nanostructures. Besides specific properties of core material, important issues are connected with the structure and properties of most outer shell. Then, in the fabrication of useable nanoparticles with active surface, the main and most crucial step is its functionalization. This process can be done by bonding to naked surface compounds of structures which have amino, hydroxide, carboxylate or phosphate functional groups. Those functional materials can be attached to the surface by electrostatic or Van der Waals forces, or can be bound by covalent by ionic bands. In latter treatments it allows to immobilize biological compounds, for example proteins, enzymes or antibodies on the surface of a modified particle. Especially interesting candidates for surface modification are organophosphorus compounds [4]. The reason why the phosphate functional groups are particularly interesting is the presence of strong M—O—P bonds via which particles can be connected [2]. Bonding organophosphorous molecules to inorganic phase results in the formation of strong M—O—P bonds (coupling of organic components (P) to metal (M) via oxides (O)) [2]. It has been shown that M—O—P bonds are very stable over a wide range of pH, which causes that such functionalization becomes particularly interesting for bioapplications [5]. The phosphonate group might be functionalized by the reaction with metal or contain functional groups beforehand to the reaction with metal. This creates many opportunities to draft compounds with specific properties. Compounds containing phosphonate group react specifically with metal–oxide surfaces and participate only in a monolayer form [2]. Moreover, the phosphate and phosphonate alkyls can be used for obtaining thermodynamically stable dispersions of magnetic nanoparticles [6]. The research shows that these ligands exhibit good biocompatibility, which can increase the utilization of magnetic nanoparticles in many medical applications [6]. Another research demonstrates that the use of alkyl phosphonates helps to avoid the formation of bulk phases titanium oxide nanoparticles [7]. All these reasons open new possibilities for nanoparticles functionalized with organophosphorus compounds and make this topic a very attractive area for future studies.

In this paper magnetic elongated nanomaterials like Fe, Fe/Au, Fe/Ag nanowires and CoO, $NiFe_2O_4$, Ag, Au nanotubes were functionalized with organophosphorus acids and then attempted to connect with enzymes like trypsin. Obtained structures were

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Table 1
Processes parameters for the preparation of nanowires.

	Fe nanowires	Fe/Au nanowires	Au nanotubes	Ag nanotubes	CoO nanotubes	$NiFe_2O_4$ nanotubes
Method	DC deposition	AC deposition			Crystallization	
Main parameter	I = 0.01 A	U = 10 V			T = 60/550 °C	
Time	10 min	16 min (2 min for each segment)			3 h/20 h/3 h*	
Solution	0.43 M $FeSO_4 \cdot 7H_2O$ 0.73 M H_3BO_3 0.0043 M $FeCl_3$ ascorbic acid	0.3 M $FeSO_4 \cdot 7H_2O$ 0.5 M $AuCl_3 \cdot HCl$	0.5 M $AuCl_3 \cdot HCl$	0.5 M $AgNO_3$	0.15 M $Co(NO_3)_3 \cdot 6H_2O$	$Ni(NO_3)_2$-$6H_2O$-$Fe(NO_3)_2$-$6H_2O$

* Three hours bath of matrices in the solution/20 h crystallization in an oven at 60 °C/3 h crystallization in an oven at 550 °C.

examined by transmission electron microscopy (TEM) imaging, X-ray diffraction (XRD) and infrared (IR) spectroscopy.

2. Experimental

2.1. Materials and used apparatus

$FeSO_47H_2O$, $FeCl_2$ $4H_2O$, H_3BO_3, $AgNO_3$, $Co(NO_3)_3$ $6H_2O$, $Ni(NO_3)_2$ $6H_2O$, $Fe(NO_3)_2$ $6H_2O$, NaOH, $CoSO_47H_2O$ were obtained from POCH. $HAuCl_4$, Tris–HCl (pH = 7.4), 3-phosphonopropionic acid, 16-phosphonohexadecanoic acid, Trypsin (10× solution), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), dichloromethane, N- hydroxysuccinimide (NHS), acetonitrile, phosphate buffer saline (PBS) (C = 0.1 M, pH = 7.4) were purchased from Aldrich.

For the surfaces chemical modulation analysis Infrared spectrometer Nicolet 6700 working in reflection mode was used. The wires structure was obtained with use of TEM microscope Tecnai GZ X-TWIN. The crystalline analysis was done by Agilent Technologies SuperNova X-ray diffractometer equipped with microfocus Mo source ($k_{\alpha 2}$ = 0.713607 Å).

2.2. Preparation of nanowires which contain noble metal

The basic structures used for modification were Fe nanowires, multilayered Fe/Au nanowires and core–shell Au and Ag nanowires shells filled with Fe as a core material. All kinds of nanostructures were obtained in AAO matrices with a pore diameter below 200 nm [8]. Two different methods for nanostructures preparation were applied.

The core–shell nanowires were obtained by wetting chemical deposition followed by thermal crystallization (during this process empty inside nanotubes were formed). In the following step, electrodeposition of core material was proceeded. In such a manner, Fe was deposited inside previously prepared tubes.

Multisegment Fe/Au nanowires were fabricated by deposition of Fe and Au in sequence (repeated few times). All these structures were fabricated in aqueous solutions. Main process parameters are collected in Table 1.

As a reference, pure Fe nanowires were obtained in the same way as described previously [8].

To isolate nanostructures from the templates, they were bathed in 1 M NaOH solution. After that the wires were cleaned with distilled water several times, once with acetone, and finally left for a night to evaporate the rest of solvents and to get dry. The nanostructures fabricated in this way were the basis to carry out modification of their surfaces.

2.3. Modification of nanowires by 3-phosphonopropionic acid

All described structures (Fe wires, Fe/Au multisegment nanowires, tubes Au and Ag filled with Fe) were sequentially cleaned in acetone and ethanol, 3 min in each, and mixed in sonication bath. After that, to every sample 1 ml of 1 mM 3-phosphonopropionic acid was added. The probes were exposed to sonication bath for a while and then left on a permanent magnet for 18 h incubation time. The last step of the modification was washing the nanowires in the solution of acid with PBS and leaving the residual solvent for evaporation (Fig. 1).

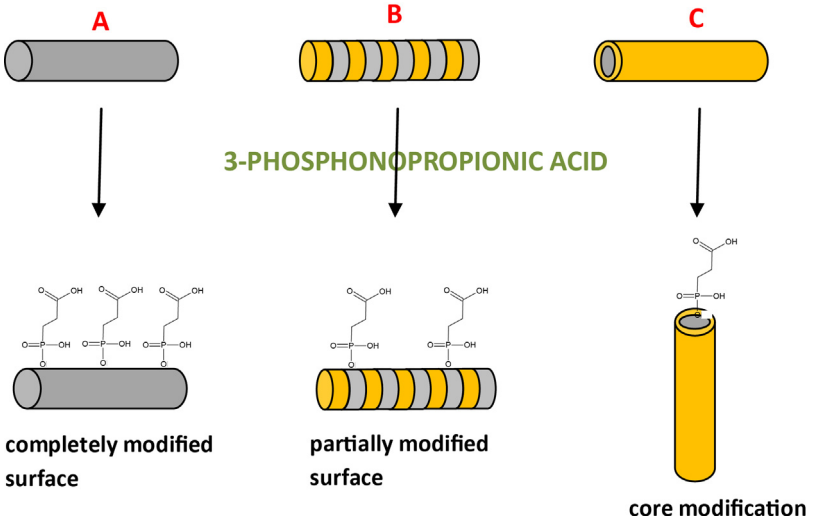

Fig. 1. Schematic illustration of surface modification: (A) Fe nanowire, (B) Fe/Au multisegment nanowire, and (C) Au tube filled with Fe.