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Core–shell hybrid nanomaterial based on prussian blue and surface active maghemite nanoparticles as stable electrocatalyst



Massimiliano Magro^a, Davide Baratella^a, Gabriella Salviulo^b, Katerina Polakova^c,
Giorgio Zoppellaro^c, Jiri Tucek^c, Josef Kaslik^c, Radek Zboril^c, Fabio Vianello^{a,c,*}

^a Department of Comparative Biomedicine and Food Science, University of Padua, Italy

^b Department of Geosciences, University of Padua, Via Gradenigo 6, 35131, Padua, Italy

^c Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry and Experimental Physics, Faculty of Science, Palacky University, 17. Listopadu 1192/12, 771 46 Olomouc, Czech Republic

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ABSTRACT

A novel core–shell nanomaterial based on prussian blue (PB) coating on peculiar surface active maghemite nanoparticles (SAMNs), was developed. The synthetic process involves the direct crystallization of Fe(II)(CN)₆⁴⁻ onto the surface of SAMNs by simple incubation in water at controlled pH, demonstrating the presence of under-coordinated Fe(III) on nanoparticle surface. The coating reaction occurs in a narrow pH range and the synthetic procedure was optimized. The resulting SAMN@PB hybrid nanostructures were characterized by transmission and scanning electron microscopy, Mössbauer, UV–vis and FTIR spectroscopy and X-ray powder diffraction. The nanomaterial, characterized by high stability in alkaline media, behave as excellent electro-catalyst for hydrogen peroxide reduction. The stability of SAMN@PB hybrid has been investigated as a function of pH, showing excellent stability up to pH 9.0 and demonstrating the feasibility of SAMNs, superficially derivatized with prussian blue, to produce an efficient and extremely stable nanostructured material. This maghemite supported nanostructured prussian blue was applied to develop a sensor, based on a simple carbon paste electrode, which was able to catalyze the electro-reduction of hydrogen peroxide, in aqueous solutions, buffered at pH 7.0, at low applied potentials (0.0 V vs. SCE).

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1. Introduction

Hybrid nanomaterials, composed of different functional components and different nanoscale functionalities, have attracted increasing interest to materials scientists due to their combined physicochemical properties and great potential applications in the areas of electronics, photonics, catalysis, biotechnology, and nanotechnology (Sanchez et al., 2005; Leung et al., 2012).

In the last years, prussian blue (PB) has been studied by many research groups involved in the optimization of amperometric sensors. This growing interest was due to the peculiar characteristic of the reduced form of PB, Prussian White, to catalyze the reduction of H₂O₂ at low applied potential, minimizing the effects of the most common electrochemical interfering species on background currents and signal to noise ratio. In electroanalytical chemistry, prussian blue attracts the attention of the biosensor community (Ricci et al., 2003), because of its analogy with the

biological family of peroxidase (Gorton, 1995), responsible in nature for the reduction of hydrogen peroxide, and it has been defined as an artificial peroxidase in literature (Karyakin and Karyakina, 1999). Additionally, for its interesting electrochemical behavior, it can be used as a mediator in many biosensor systems to accelerate the electron transfer between the electrode and the enzymes (Ricci and Palleschi, 2005; Li et al., 2003). The determination of hydrogen peroxide is important in several fields (Sanderson, 2000), even if, generally, the electrochemical detection of hydrogen peroxide suffers from high overvoltage at conventional solid electrodes (Chen et al., 2012). Several attempts have been made in order to prepare chemically modified electrodes able to catalyze the oxidation or the reduction of hydrogen peroxide at very low applied potential (ideally at 0.0 V vs. SCE) and in neutral buffers. One possible approach to solve this problem would be the use of ferric ferrocyanide, namely prussian blue (PB), modified electrodes (Malinauskas et al., 2004). However, the use of PB as catalyst for H₂O₂ reduction is still a matter of concern because of its poor operational stability, limited to a range of hours, and to a very high decrease in sensitivity at neutral and alkaline pH (Moscone et al., 2001). A possible explanation could be due to the presence of hydroxyl ions at the electrode surface, as a

* Corresponding author at: Department of Comparative Biomedicine and Food safety, University of Padua, Agripolis – Viale dell'Università 16, Legnaro, 35020 PD, Italy. Tel.: +39 049 8276863; fax: +39 049 8073310.

E-mail address: fabio.vianello@unipd.it (F. Vianello).

product of the H_2O_2 reduction. These ions are known to be able to break the Fe–CN–Fe bond, hence solubilizing PB (Karyakin, 2001).

Several groups reported on the electrocatalytic properties of inorganic prussian-blue nanoparticles towards the reduction of H_2O_2 . Compared to conventional PB microparticles, or polycrystalline film, nanosized PB shows large surface-to-volume ratio and an increased surface activity, qualifying its use in catalysis and sensing (Malinauskas et al., 2004).

Recently, we developed a novel wet synthesis pathway for producing a new type of superparamagnetic nanoparticles constituted of stoichiometric maghemite, $\gamma\text{-Fe}_2\text{O}_3$, revealing peculiar surface characteristics, excellent colloidal stability, reversible direct binding of organic molecules without the need of any additional organic or inorganic surface modification, unique spectroscopic properties and well-defined crystalline stoichiometric structure. We called these nanoparticles as “Surface Active Maghemite Nanoparticles” (SAMN). This nanomaterial was characterized by bulk techniques, such as in-field Mössbauer spectroscopy, magnetization measurements, x-ray powder diffractions and FTIR (Magro et al., 2010; Magro et al., 2012a). The most prominent peculiarity of these nanoparticles consists of the ability to form stable colloidal suspensions in water without any organic or inorganic coating to prevent their aggregation (Magro et al., 2012a) and, at the same time, they are able to bind specific organic molecules, leading to composite materials, which can be exploited for biotechnological applications (Magro et al., 2012b; Sinigaglia et al., 2012). Furthermore, SAMNs show remarkable electrocatalytic properties and were used for the development of an ionic liquid-modified carbon paste electrode for hydrogen peroxide detection, showing high sensitivity, low detection limit, good reproducibility and stability (Magro et al., 2013), and a biosensor for glucose detection (Baratella et al., 2013). The peculiar behavior of SAMNs, being constituted of common maghemite, must be due to their surface properties. Evidences, already reported on our previous papers (Magro et al., 2012b; Sinigaglia et al., 2012), suggested the presence of under-coordinated Fe(III) ions on SAMN surface. The presence of under-coordinated Fe(III) ions was demonstrated in our previous work (Magro et al., 2012a) by simple incubation of SAMNs in a potassium ferrocyanide solution, leading to the formation of prussian blue coated maghemite nanoparticles.

In the present work, we present an optimized procedure for the synthesis of a nanostructured SAMN@PB hybrid and its structural characterization by in-field Mössbauer spectroscopy, X-ray powder diffractions and FTIR and UV–vis spectroscopy. In particular Mössbauer analysis gave very informative results on the reactivity of under-coordinated Fe(III) on SAMNs surface, as they resulted completely available to be coordinated by $\text{Fe}(\text{CN})_6^{4-}$ at the interface between maghemite and prussian blue. Moreover, SAMN@PB hybrid was applied for the development of a sensor for hydrogen peroxide detection at low applied potential. The analytical characteristics of the sensor were investigated, toward hydrogen peroxide detection, and compared to recently published works. Interestingly, the system showed excellent stability up to pH 9.0, ease and low cost of fabrication, along with high sensitivity and renewable surface, making this type of electrode widely applicable in electroanalytical sensing.

2. Materials and instrumentation

2.1. Chemicals

Chemicals were purchased at the commercially available purity and were used without further treatment. Iron(III) chloride hexahydrate (97%), potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$), sodium borohydride (NaBH_4), and ammonia solution (35% in water) were obtained from Aldrich (Sigma-Aldrich, Italy).

2.2. Instrumentation

Optical spectroscopy was performed by a Cary 50 spectrophotometer (Varian Inc., Palo Alto, CA, USA), in quartz cuvettes (1 cm p.l.).

Scanning electron microscopy (SEM) images and X-ray energy-dispersive spectroscopy (SEM-EDX) were taken on a Hitachi 6600 FEG microscope.

Transmission electron microscope (TEM) images and selected area electron diffractions (SAED) were taken on a JEOL 2010 microscope operating at 200 kV with a point-to-point resolution of 1.9 Å.

The transmission ^{57}Fe Mössbauer spectra were recorded using a Mössbauer spectrometer in a constant acceleration mode with a $^{57}\text{Co}(\text{Rh})$ source.

X-ray powder diffraction (XRD) patterns of all solid samples were recorded on X'Pert PRO (PANalytical, The Netherlands) instrument in Bragg–Brentano geometry with iron-filtered $\text{CoK}\alpha$ radiation (40 kV, 30 mA, $\lambda=0.178901$ nm) equipped with an X'Celerator detector and programmable divergence and diffracted beam antiscatter slits.

Fourier transform infrared (FT-IR) spectra of the dried samples were recorded on a Nexus 670 FTIR spectrometer (Thermo Nicolet) using a Smart Orbit diamond ATR technique ($400\text{--}3600\text{ cm}^{-1}$).

Voltammetric experiments were carried out by a computer-controlled electrochemical system (PGSTAT 10, EcoChemie, The Netherlands).

3. Results

3.1. Surface coating of SAMNs with ferrocyanide

As prepared maghemite nanoparticles can easily form colloidal dispersions when treated in an ultrasonic bath, as described in Methods. Furthermore, as a colloidal suspension, SAMNs can be superficially modified by simple incubation in the presence of $\text{K}_4\text{Fe}(\text{CN})_6$, forming the SAMN@PrussianBlue (SAMN@PB) complex.

The derivatization of bare maghemite nanoparticle suspensions (500 mg/L SAMNs, 50 mL) was tested in the presence of 0.10 mol/L $\text{K}_4\text{Fe}(\text{CN})_6$ as a function of pH, in the range 1.5–4.0, by HCl additions (see Fig. 1). In particular, when the coating reaction is carried out at pH values below 2.0, pure prussian blue is formed, as confirmed by XRD and Mössbauer spectroscopy of the resulting material. Conversely, when the coating reaction is carried out at pH values above 3.0, it simply does not occur, and reactants (SAMNs and potassium ferrocyanide) remained unaltered. Whereas, in the narrow 2.0–2.5 pH range, SAMNs and potassium ferrocyanide mixture turns to blue in few seconds, forming a colored nanomaterial, which can be magnetically isolated (Fig. 1). This magnetic material appears to maintain the magnetic properties of maghemite and the prussian blue appearance. In Fig. 1, the typical appearance of unmodified SAMNs, of pure prussian blue formed at pH below 2.0 and of magnetic prussian blue modified SAMNs (SAMN@PB), are presented. Furthermore, both SAMNs and SAMN@PB showed same stability in water, as colloidal suspensions, up to a concentration of 1 gL^{-1} .

3.2. Mössbauer characterization of SAMNs and SAMN@PB

The most important issue in the development of a synthetic method for the generation of novel nanostructures, is the need to address the simultaneous control over dimensions, morphology (or shape), and size distribution. Another crucial point, in particular for electrochemical applications, is to obtain nanomaterials with controlled crystallinity, because of the conductance of metal

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