



# Potentiometric detection of chemical species by spin-assisted assembly of vanadium pentoxide nanorods

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## ABSTRACT

Vanadium pentoxide nanorods ( $V_2O_5$ -nanorods) and poly(allylamine hydrochloride) (PAH) were assembled onto gold-coated substrates via spin-assisted assembly technique and used as a chemically sensitive electrodes. PAH/ $V_2O_5$ -nanorods detected  $H^+$  ions (pH) with sensitivity between 52–61 mV/pH (close to Nernstian theoretical value). As a proof-of-concept, a urea biosensor has been developed, upon immobilization of urease enzyme on PAH/ $V_2O_5$ -nanorods electrodes. The biosensor could detect urea in a 0.05–5 mM dynamic range. The spin-assisted assembly technique enables the combination of different materials in a simple way and offers advantages for the construction of functional electrodes.

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## 1. Introduction

Metal-oxides obtained in one dimensional (1D) nanostructures, including nanowires, nanotubes and nanorods, display enhanced physical and chemical properties in comparison to their similar bulk structures [1]. Particularly, vanadium pentoxide ( $V_2O_5$ ) has emerged as a promising 1D nanostructure for ion sensing, specially  $H^+$  ions (pH-sensing), because of the  $V_2O_5$  property of either donating or accepting protons [2]. In fact, the monitoring of the pH value is very important from a biochemical point of view. Some biochemical processes are related to the pH value or result in the release or consumption of protons, as it occurs in many enzymatic reactions [3]. We compared the pH-sensing properties of different 1D  $V_2O_5 \cdot nH_2O$  nanostructures synthesized in a one-step hydrothermal route [2]. All nanostructures showed pH sensitivity close to the theoretical value expected by Nernst equation ( $59.15 \text{ mV pH}^{-1}$ ), which indicates the pH sensitivity was not dependent on the morphology and structure of 1D  $V_2O_5 \cdot nH_2O$  [2].

Unlike most metal oxides, 1D  $V_2O_5 \cdot nH_2O$  nanostructures can be dispersed in water, which enables their manipulation in the form of thin nanostructured films or composites, unusually desirable for

applications in cost-effective sensors. The spin-assisted assembly technique represents an effective methodology for the combination of various materials and formation of nanocomposites onto different types and sizes of substrates [4–6]. Moreover, the combination of alternating layers of materials enables the functionalization of substrates with appropriate functional groups in the last layer, as in the case of covalent immobilization of biomolecules [7].

This study explored the feasibility of the spin-assisted assembly technique for the construction of pH-sensitive electrodes by the combination of  $V_2O_5$  nanorods (denoted as  $V_2O_5$ -nanorods) and poly(allylamine hydrochloride) (PAH) on gold-coated substrates. As a proof-of-concept, PAH/ $V_2O_5$ -nanorod electrodes were functionalized with urease enzyme and applied as a potentiometric urea biosensor. PAH is a cationic polyelectrolyte commonly used in self-assembly. It bears amino groups suitable for the binding of biomolecules while  $V_2O_5$ -nanorods act as a pH-sensitive material. The proposed system is easy to construct and can detect pH and urea with high sensitivity in a 0.05–5 mM dynamic range.

## 2. Materials and methods

1D  $V_2O_5$  nanorods were synthesized by a hydrothermal method at  $200^\circ\text{C}$  for 24 h. The synthesis and a complete characterization of  $V_2O_5$ -nanorods is described in details elsewhere [8,9]. We denoted the as-synthesized samples as  $V_2O_5$ , without

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H<sub>2</sub>O molecules, because in this synthesis conditions, V<sub>2</sub>O<sub>5</sub>-nanorods is composed mainly of adsorbed H<sub>2</sub>O molecules [8,9]. Poly(allylamine hydrochloride) average Mw ~ 17,500 were purchased from Sigma–Aldrich.

As previously introduced by Cho and Chiarelli, the assembly technique used to build up PAH/V<sub>2</sub>O<sub>5</sub>-nanorods was based on the alternating deposition of PAH and V<sub>2</sub>O<sub>5</sub>-nanorods using a spin coater [4,5]. Fifty microliters of PAH (0.5 mg mL<sup>-1</sup>) and V<sub>2</sub>O<sub>5</sub>-nanorods (1 mg mL<sup>-1</sup>) aqueous solutions were alternately deposited onto gold-covered substrates with approximately 23 mm<sup>2</sup> of active area (Fig. S1). The solutions were prepared using ultra-pure water (Milli-Q source, 18.3 MΩ cm) without pH adjustment and with no addition of salt or additive compounds. In these conditions, the pH of both solutions was ca. 5. The deposited layers were allowed to dry for 1 min at 3000 rpm. This procedure was repeated for a desired number of layers, that varied from 1 to 5 layers of PAH and V<sub>2</sub>O<sub>5</sub> nanorods. The assembly of the PAH/V<sub>2</sub>O<sub>5</sub>-nanorods was monitored via UV–vis absorbance (Hitachi U-2001 spectrophotometer) after the materials had been deposited onto quartz slides.

Urease (EC 3.5.1.5, 109 U/mg) from Jack beans, serum bovine albumin (BSA), glutaraldehyde (GA) and urea were purchased from Sigma–Aldrich and used without purification. The enzyme immobilization method involved the cross linkage of urease on three bilayers of PAH/V<sub>2</sub>O<sub>5</sub>-nanorods. The last layer was formed by PAH and contained exposed amine groups. Ten microliters of a mixture containing urease (50 μL, 40 mg mL<sup>-1</sup>), BSA (50 μL, 20 mg mL<sup>-1</sup>) and GA (18 μL, 2.5% in phosphate buffer (pH 7.4)) were dropped on the PAH/V<sub>2</sub>O<sub>5</sub>-nanorods [7].

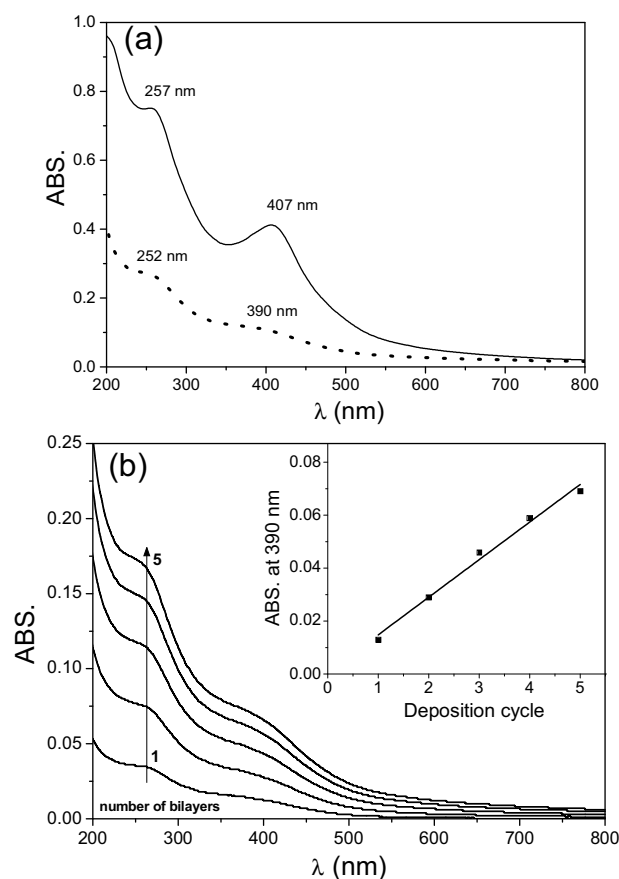
We have constructed an easy and cheap potentiometer read-out circuit based on an instrumentation amplifier operating as a unity gain buffer. The system can measure the open circuit potential between a work electrode and a reference electrode [2,7]. PAH/V<sub>2</sub>O<sub>5</sub>-nanorods were connected to the input pin of the amplifier and an Ag/AgCl electrode was utilized as a reference electrode. The schematic diagram of the sensor/biosensor is shown in Fig. S2 and the complete circuit configuration can be seen in details in our previous papers [2,7]. All pH or urea sensing measurements were performed at 25 °C.

Scanning electron microscopy (SEM) images were obtained in the Inspect F50 equipment (Fei, The Netherlands).

### 3. Results and discussion

#### 3.1. Characterization of the PAH/V<sub>2</sub>O<sub>5</sub>-nanorods assembly

Fig. 1a shows a comparison of the normalized absorbance spectra of an aqueous solution containing only V<sub>2</sub>O<sub>5</sub>-nanorods and the as-prepared PAH/V<sub>2</sub>O<sub>5</sub>-nanorods formed by five layers of each material. The two bands observed around 407 nm and 257 nm for the V<sub>2</sub>O<sub>5</sub>-nanorods solution are associated with charge transfer transitions of an electron from the  $\pi$  orbital of the oxygen atom to the d level of vanadium for the vanadium electronic configuration in the oxidized state [10,11]. The PAH/V<sub>2</sub>O<sub>5</sub>-nanorods spectrum shows a small blue shift, which may be related to environmental effects due to the formation of a nanocomposite, i.e., interaction of V<sub>2</sub>O<sub>5</sub>-nanorods with PAH [12]. Fig. 1b shows the absorbance spectra of each deposition cycle of the PAH/V<sub>2</sub>O<sub>5</sub>-nanorods. The linear dependence (inset of Fig. 1b) of the absorbance indicates that a same amount of V<sub>2</sub>O<sub>5</sub>-nanorods is deposited at each deposition cycle. The regular deposition of the film may be related to electrostatic interactions between NH<sub>3</sub><sup>+</sup> terminal groups from PAH and OH<sup>-</sup> from V<sub>2</sub>O<sub>5</sub>-nanorods. However, a contribution of H-bonding for the formation of the PAH/V<sub>2</sub>O<sub>5</sub>-nanorod layers, as reported by



**Fig. 1.** (a) Absorbance spectra of an aqueous solution of V<sub>2</sub>O<sub>5</sub> nanorods (0.01 mg mL<sup>-1</sup>) (solid line) and a PAH/V<sub>2</sub>O<sub>5</sub>-nanorods assembly (dotted line). (b) Relationship between film absorbance at 390 nm and number of deposition cycles of PAH/V<sub>2</sub>O<sub>5</sub>-nanorod bilayers.

Ferreira et. al., in the multilayered films of V<sub>2</sub>O<sub>5</sub> and a conducting polymer that also has terminal amino groups is expected [12].

Fig. S3 shows the scanning electron microscopy (SEM) images of the samples containing 3 and 5 bilayers of PAH/V<sub>2</sub>O<sub>5</sub>. Due to morphologic characteristics of V<sub>2</sub>O<sub>5</sub> sample, i.e., nanorods, it is not expected a preferential orientation of the nanoparticles after deposition onto the PAH film. As it can be seen on Fig. S3, V<sub>2</sub>O<sub>5</sub> nanorods are well dispersed onto the PAH surface. The V<sub>2</sub>O<sub>5</sub> nanorods presented a diameter around 55 nm and a length varying from 1 to 5 μm. From electron microscope images, we estimated that the thickness of each deposited bilayer was around 150 nm.

#### 3.2. PAH/V<sub>2</sub>O<sub>5</sub>-nanorods as a pH sensor

The pH-sensitivity of PAH/V<sub>2</sub>O<sub>5</sub>-nanorods electrode was analyzed through the immersion of the nanocomposite grown in Au into different buffer solutions (from pH 2 to 12) and the time-dependent output potential of the system was measured along time. The typical dynamic pH-response of PAH/V<sub>2</sub>O<sub>5</sub>-nanorods, shown in Fig. 2, is similar to that observed for V<sub>2</sub>O<sub>5</sub>-nanorods deposited directly onto Au-coated substrates and addressed in our previous paper [2]. It is important to note that there is a drift in output voltage. As shown in Fig. 2, the drift was: 38 mV; -16 mV, -21 mV, -25 mV, -29 mV; -24 mV; and 17 mV for pH values of: 2; 4; 6; 7; 8; 10 and 12, respectively. Drift voltage is a very common behavior and is inherent for pH sensitive electrodes composed of metal oxides, such as V<sub>2</sub>O<sub>5</sub>-nanorods, because metal oxides participate in redox reactions with the ions in the electrolyte [13]. The

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