

Towards thiol functionalization of vanadium pentoxide nanotubes using gold nanoparticles

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Abstract

Template-directed synthesis is a promising route to realize vanadate-based 1-D nanostructures, an example of which is the formation of vanadium pentoxide nanotubes and associated nanostructures. In this work, we report the interchange of long-chained alkyl amines with alkyl thiols. This reaction was followed using gold nanoparticles prepared by the Chemical Liquid Deposition (CLD) method with an average diameter of ~ 0.9 nm and a stability of ~ 85 days. V_2O_5 nanotubes (VOx-NTs) with lengths of ~ 2 μm and internal hollow diameters of 20–100 nm were synthesized and functionalized in a Au-acetone colloid with a nominal concentration of $\sim 4 \times 10^{-3}$ mol dm^{-3} . The interchange reaction with dodecylamine is found only to occur in polar solvents and incorporation of the gold nanoparticles is not observed in the presence of *n*-decane.

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1. Introduction

The template-directed synthesis is a promising route to realize 1-D nanostructures, because it offers the possibility to design and create nanotubes, nanowires and other associated nanostructures, with specific electronic and optical properties [1]. This is demonstrated by the increasing body of work describing the formation and morphology of nanotubes prepared using this approach [2–8]. An pertinent example is the work of Nesper and co-workers [2,3] who reported the formation of vanadium pentoxide nanotubes (VOx-NTs) using long alkyl primary amines and other varieties of amines [1] as direct structural agents. One of the current applications of vanadate-based nanocomposites is their incorporation in secondary Li-batteries [1,3] following several reports of metal cation insertion in vanadate-based compounds [1,5,7,8].

A new direction for the application of nanostructure research is their employment as optical materials. Indeed, vanadium oxide nanotubes are already becoming an important optoelectronic material [1] for non-linear optics and have been found to exhibit unique anisotropic properties [3,6]. These can exhibit intensity dependent transmission and

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are of central interest in the field of non-linear optics and optoelectronics because of their potential application in a wide variety of optical systems. In particular, optically active nanoparticles have gained tremendous importance in this field because they exhibit very little Rayleigh scattering in the visible spectrum and thus exhibit optical limiting characteristics [9]. The drive to incorporate metal nanoparticles in nanostructured systems [9] in order to observe the relation between the suitability/compatibility of these systems and biological molecules [10], has opened a new direction for functionalized nanotube research with promising potential applications. The incorporation of nanoparticles in carbon nanotubes has been reported [10] and the attachment of biological molecules to these nanotubes by different methods has also been realized [10,11].

Nanoparticle incorporation in vanadium oxide nanocomposites, in particular VO_x-NTs, has not yet been realized and this work reports the first successful functionalization of V₂O₅ nanostructures with Au nanoparticles. While metallic colloids are well known, non-aqueous systems enjoy more recent attention because their properties are different to the bulk material and at the same time different to the atomic state with intermediate electronic properties [12]. Another important property is that nanometric particles possess a large fraction of atoms localized on the surface, producing unique and unusual properties; indeed we previously reported [13] the preparation and formation of stable metallic colloids in organic solvents at low temperature. The colloidal particles thus obtained are not only stable at room temperature but in addition, they are also free of impurities [14].

In this paper, we report the first observation of successful thiol functionalization of vanadium pentoxide nanotubes using a new method of functionalization by means of Au nanoparticles with an average diameter of 0.9 nm. Using the Chemical Liquid Deposition method, the reaction was amenable to in situ observation and such a new technique is critical for the successful functionalization of the next generation of nanotubular materials with unique optical and electrical properties.

2. Experimental

2.1. Synthesis of vanadium pentoxide nanotubes

The method employed for the synthesis of vanadium pentoxide was essentially the one described in Refs. [1–6] with some variations. A mixture of *t*-butyl alcohol and orthorhombic V₂O₅ was refluxed for 6 h to form the xerogel [6,15]. Water was added to the resulting dark yellow solid and the remaining *t*-butyl alcohol was removed with excess water in vacuum. Water was then added to yield a suspension. The material was aged at room temperature yielding a red-brown colloidal V₂O₅. The xerogel and a primary amine, dodecylamine (DDA), mixed in a molar ratio of 1:2 were stirred in ethanol for 2 h and left to age for 2 days. The composite was transferred into a Teflon-lined autoclave and held at 180 °C for 3 days under auto-generated pressure in a sand bath. The product was washed with deionized water and alcohol several times and dried under vacuum.

2.2. Preparation of the Au-acetone colloid

The metal atom reactor (3 L) used was described elsewhere [12–14]. As a typical example of preparation, 70 mg of Au metal was placed into the alumina-tungsten crucible. Dry acetone was placed in a ligand inlet tube and freeze–pump–thaw degassed in several cycles. The reactor was pumped down to 4–5 mm Hg, while the crucible was warmed to red heat. The surrounding vessel was cooled with liquid nitrogen and Au and acetone (100 ml) were deposited for a period of 1 h. The matrix was allowed to warm under vacuum for 1 h; upon meltdown and subsequent cooling down to room temperature, a purple colloid was obtained. Subsequently, upon the addition of nitrogen up to 1 atm, the colloid was allowed to warm for another 0.5 h up to room temperature. The solution was siphoned into a flask cooled in a nitrogen atmosphere from the acetone inlet. The molarity of the metal-containing solution is typically $\sim 10^{-3}$ mol dm⁻³. During the warm-up to room temperature, clustering of metal atoms developed slowly [12,16].

2.3. Incorporation of gold nanoparticles in VO_x-NTs

Six milligrams of the V₂O₅(DDA)_{0.34} (VO_x-NTs) was refluxed with 3 ml of *n*-dodecanthiol in 15 ml of anhydrous ethanol (fraction distillation in ethanol 98% in CaCl₂) for 2 h. After that, the colloidal solution with gold nanoparticles (Au-NPs) was added to acetone (average of the size of particles ~ 0.9 nm). The system was then agitated for 12 h.

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