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ORIGINAL RESEARCH

Amplified optical transduction of proteins derived from $Mo_6S_{9-x}I_x$ nanowires

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Abstract We demonstrate that $Mo_6S_{9-x}I_x$ nanowires (MoSI NWs) enable the detection of proteins with cytochrome *c* as a model protein using UV–vis spectrometry. The association of cytochrome *c* with the nanowires was verified by scanning electroctron microscopy, X-ray photoelectron, light scattering and micro-FTIR spectroscopies. Our results show that MoSI NWs is a promising nanostructure material for the development of ultrasensitive sensors for detecting proteins. The new MoSI NW derived amplification bioassay is expected to provide a straightforward and effective strategy for protein analysis and biosensor construction.

1. Introduction

The detection and quantification of biological and chemical species are critical to many areas of health care, from the diagnosis of diseases to the discovery and screening of new drug molecules. Central to detection is the transduction of a signal associated with the selective recognition of interesting species. The development of new methods that enable the direct, sensitive and rapid analysis of biological and chemical species is of great importance [1].

Nanostructures, such as nanowires, nanotubes and nanoparticles, offer new and sometimes unique opportunities that can be exploited for sensing [2–8]. The nanostructures provide a versatile scaffold for bio-macromolecule recognition due to their size (commensurable with proteins, DNA) and ability to tailor their surfaces with wide range of functionalities [9–14]. Currently, one main aspect of applications of the nanostructure materials are to be used for detection of biomolecules as well as studies on the interaction between nanomaterials and biomolecules, especially proteins, since the retention of protein structure and activity on

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nanoscale support is critical for sensing applications. A lot of interest has been directed on understanding how nanomaterial properties such as size and surface chemistry influence the structure activity and stability of conjugated proteins.

Inorganic nanomaterials are especially attractive because of their significant advantage of controlling the relevant physical properties by selective engineering of their geometry and composition. Among them, molybdenum–chalcogenide–halide NWs which are composed of molybdenum (Mo), sulfur (S) and iodine (I) in the form $Mo_6S_{9-x}I_x$ (MoSI) are a new class of quasi-one-dimensional objects, having two different stoichiometries $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$. An identical skeletal structure is composed of indistinguishable one dimensional polymer chains of molybdenum–sulfur–iodine clusters, strongly joined together by anions (either S or I). The individual nanowires are joined together into bundles by weak Van der Waals forces. The materials have strong anisotropy, large Young moduli along the wires, very small shear moduli, and controllable electronic properties. Compared to carbon nanotubes (CNTs), MoSI NWs have some significant advantages such as straightforward synthesis, monodisperse diameters and metallic properties [15–19]. A specific feature of these NWs is the growth of identical chains in the form of bundles. Single 0.9 nm diameter NWs are reproducibly obtained with lengths up to 100 μm by debundling and therefore can be used in solution based techniques [16,17]. Furthermore, the novel chemical structure of these materials makes them an obvious target for chemical functionalization. However, bridging of MoSI NWs with biomolecules is a relatively unexplored area [20–23].

Herein, we demonstrate that the MoSI NWs can serve as an excellent signal-intensifying nanomaterial for high sensitive, label-free detection of proteins. Using cytochrome *c* as a model protein, the highly sensitive sensing processes were transduced by UV–visible spectrophotometry (UV–vis).

2. Experimental section

Horse heart cytochrome *c* (MW 12,384, 96% purity), 2-propanol (HPLC, >99.8%) were purchased from Sigma-Aldrich. In this work, all reagents were used without further purification. Doubly distilled water was further purified with a quartz apparatus. Aqueous solutions were prepared with triple distilled water.

$Mo_6S_{9-x}I_x$ nanowires (MoSI NWs) were fabricated by direct synthesis from elemental material that had been mixed in the desired stoichiometries as described elsewhere [15]. Powders composed of aggregates of individual nanowires were obtained. In this work, all studies were carried out on $Mo_6S_3I_6$ nanowires.

1 mg mL^{-1} MoSI dispersions in isopropanol were prepared according to the procedure described elsewhere [15], that is, the dispersions were initially sonicated for 2 min using a high power ultrasonic tip (120 W, 60 kHz), followed by a low power ultrasonic bath for 2 h. Before use, the dispersions were re-sonicated for 20 min to obtain uniform suspension, which was denoted as MoSI NWs suspension. Some of these dispersions were placed at rest for 24 h, and then the upper solution was decanted and centrifuged at 4500 rpm for 30 min. Soluble phase of MoSI NWs in isopropanol denoted as MoSI NWs solute was obtained by getting rid of sediment, and used for spectrometric investigation.

UV–visible spectrophotometric (UV–vis) detection was carried out using a PerkinElmer Lambda 11 spectrophotometer on 1 cm path length quartz cells. The Light Scattering (LS) measurements were performed with an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The LS spectrum was recorded by scanning simultaneously the excitation and emission monochromators from 210 to 750 nm (namely, $\Delta\lambda = 0$ nm) with a 5.0 nm slit width of the excitation and the emission of the spectrofluorometer, and the LS intensity was measured at the maximum LS peak.

The transmission electron microscopy (TEM) images, selected-area electron diffraction patterns, and energy spectra were taken using a JEOL JEM-200CX electron microscope operated at 150 kV. The samples for TEM characterization were prepared by dropping MoSI NWs solute in the absence and the presence of 2.0×10^{-6} mol L^{-1} cytochrome *c* on copper grids and allowed dry on air and rinsed with water. Scanning electron microscope (SEM) images were obtained with a JEOL JSM-6700F (operating voltage 15 kV). The samples for SEM characterization were prepared by using the same method employing a clean gold coated silicon substrate.

The Micro-FTIR spectra in the range between 4000 and 650 cm^{-1} were recorded on Nicolet Magna-IR750 (USA) instrument at a 2 cm^{-1} resolution. The samples were dropped on glass sheets and dried on air, then scrapped to be detected. The mixture of cytochrome *c* and MoSI nanowires was obtained by volatilizing the solvent of cytochrome *c* and MoSI nanowires solute which was deposited in air.

XPS analysis was performed with an Axis Ultra spectrometer (Kratos, UK). Using Mono Al K α (1486.6 eV) radiation at a power of 225 W (15 mA, 15 kV). To compensate for surface charge effects, binding energies were calibrated using C1s hydrocarbon peak at 284.8 eV.

3. Results and discussion

We demonstrated the optical detection of cytochrome *c* in a solution containing NWs through UV–vis and light scattering (LS) signal amplification effects. This is the first work to optically detect the presence of proteins directly based on soluble MoSI nanowires and therefore opens possibilities for new types of nanowire based sensors and probes that do not require analyte labeling. MoSI NWs were dispersed in isopropanol using a method outlined previously to obtain a MoSI NWs solute [16,17]. The absorption spectra of cytochrome *c* in the absence of MoSI NWs solute displayed a characteristic absorption

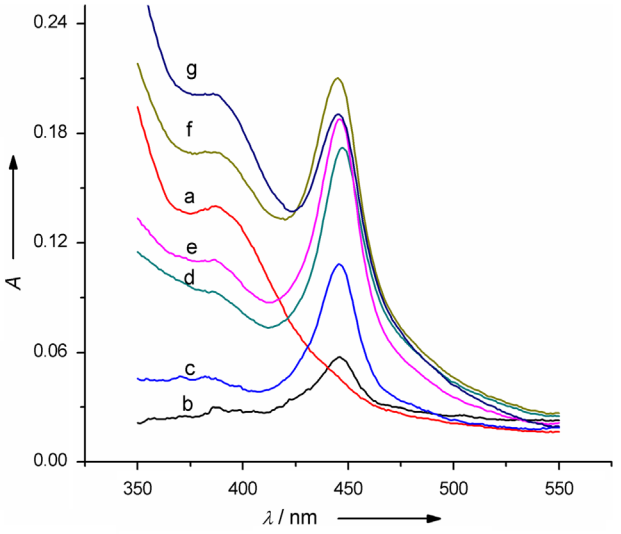

Fig. 1 UV–vis spectra of MoSI NWs solute (a), 1.3×10^{-6} mol L^{-1} cytochrome *c* with addition of different volumes of MoSI NWs solute: 0 mL (b), 0.05 mL (c), 0.1 mL (d), 0.5 mL (e), 1 mL (f), 1.5 mL (g) in propanol (The total volumes of all the solutions are 1.5 mL).