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Regular Article

Electrophoretic deposition of single-source precursors as a general approach for the formation of hybrid nanorod array heterostructures

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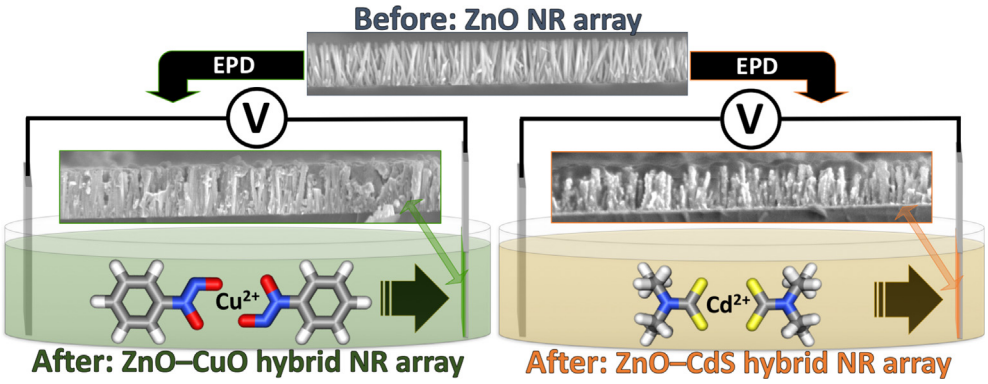
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Subjecting colloids to electric fields often results in (electrophoretic) deposition on conductive substrates. Dispersing a single-source precursor (SSP) of choice in an appropriate solvent, should allow its deposition on different substrates. The SSP-solvent interaction might play a role in the deposition (*e.g.*, direction, rate, coverage). After thermal decomposition, the SSPs convert to the designed material, thus allowing formation of thin films or hybrid nanostructures.
Experiments: Electrophoretic deposition (EPD) was applied on two representative SSPs in different solvents. These SSPs were deposited onto substrates covered with vertically-aligned ZnO nanorod (NR) arrays. After thermal decomposition, hybrid nanostructures were obtained and their morphology and interfaces were characterized by electron microscopy, X-ray diffraction, UV–vis, and electrochemistry.
Findings: Tuning the organic dispersant-SSP interaction allows control over the final film morphology, which can result in coating and filling of NRs with metal-sulfides or metal-oxides after thermal decomposition of the SSP. These findings introduce a new facile method for a fast and large-scale uniform deposition of different (nanostructured) thin film semiconductors on a variety of substrates. We discuss the influence of the dispersant medium on the deposition of metallo-organic SSPs. As an example, the formed ZnO–CdS interface supports charge transfer upon illumination.

Abbreviations: SSP, single source precursor; EPD, electrophoretic deposition; NR, nanorod; ITO, tin-doped indium oxide; $Cu(Cup)_2$, copper(II) cupferrate; $Cd(dtcEt_2)_2$, cadmium(II) bis(diethyldithiocarbamate); LSV, linear sweep voltammetry; LED, light emitting diode; SEM, scanning electron microscopy; %at, atomic percent; EDS, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; FTIR, Fourier-transform infrared; ζ-potential, zeta-potential; AN, acceptor number; DN, donor number; HRTEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy.

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1. Introduction

In 1980 Takahashi et al. used for the first time a single organometallic compound for the synthesis of CdS Films [1]. After adoption by others [2], towards the 1990's pyrolysis of single-molecule precursors became a common method for the deposition of semiconductor thin films using different gas-phase apparatus [3,4]. Pyrolysis of single-source precursors (SSP) can be performed with pure powder under inert atmosphere (in which case, the condensed volatiles are the sample of interest) [5] or *in vacuo* [6], as well as in organic solvents [5] or polymers [7]. Additional approach is the pyrolysis of the SSP left after spin-coating from a solution [8,9]. Colloidal syntheses of nanocrystals were developed using SSPs [10,11], with solventless synthesis variants existing (where the organic solvent is evaporated before the waxy precursor is thermally decomposed) [12]. Apart from the colloidal high-boiling point solvent reactions [13–15] (which can result in thin films composed of nanoparticles [16–18]), SSPs in various organic solvents are common as aerosols [19,20] for either gas- or solid/liquid-phase syntheses (aerosol-assisted chemical vapor deposition (AACVD), and spray pyrolysis, respectively) [21]. All these approaches use the SSP advantages (*e.g.*, precursor stability, precise control over the ratio of precursor atoms, no need for tuning the precursors' relative reactivities) to create nanostructures and thin films.

Various approaches to interface vertically aligned 1-D nanostructures such as nanorods (NR) with an additional material (specifically, a semiconductor which forms a radial heterojunction) have been used. The most common ones are based on gas-phase PVD [22] and CVD [23], or solution-phase methods, *e.g.*, molecular precursors dissolved in polar solvents [24,25], and casting *ex-situ* synthesized nanocrystals (dropcast [26] or spin-coat followed by a ligand exchange [27]).

Herein, we deposit CuO and CdS materials on pre-grown ZnO NR arrays *via* electrophoretic deposition (EPD) of SSPs followed by a thermal decomposition process. This facile, general, and large-scale approach allows achieving coating and filling of vertically aligned NR arrays. EPD is a well-established technique used for the assembly of different structures using a DC field from organic media. Successful thin film deposition examples include semiconductor [28] and metal [29] nanoparticles, nanoplates [30], oriented nanorods [31], carbon based nanomaterials [32–34], and composites [35].

Recently, ter Horst and co-workers have shown that applying high voltage on a suspension of various organic molecules in 1,4-dioxan enhances the crystallization, which is ascribed to dielectrophoretic or electrophoretic phenomena [36]. In this work, metallo-organic SSPs are subjected to an electric field to interface semiconductors on the nanoscale for the first time. We discuss the influence of the dispersant medium (*e.g.*, SSP-solvent interactions) on the film morphology and show the suitability of this method for deposition of uniform semiconductors in hybrid nanostructures.

2. Materials and methods

The complete experimental procedures are detailed in the SI. Briefly, tin-doped indium oxide (ITO)-covered glass (Delta Technologies; R_s = 15–25 Ω) or single-side polished Si(1 0 0) (p type, boron doped, resistivity 0–100 Ω cm) were cut to 2.5 × 0.8 cm^2 dimensions. After cleaning, the substrates underwent a two-step procedure for the growth of vertically aligned ZnO NR arrays as was previously published [37]. These substrates served as the electrodes in the EPD setup. ITO electrodes were used for UV–vis measurements and p-type Si(1 0 0) electrodes were used for SEM imagery.

2.1. Preparation of the deposition suspensions

$Cu(Cup)_2$ and $Cd(dtcEt_2)_2$ SSPs were synthesized according to previously published procedures [11,38]. The suspensions were prepared by adding the solvent of choice to the SSP powder, reaching nominal concentrations in the 3–30 mM range. The vials were sonicated for 15 min in all cases except with pyridine. When the suspensions were not stable (heptane and toluene solvents), they were vigorously stirred prior to deposition.

2.2. Electrophoretic deposition of the SSPs

EPD was performed by connecting two vertically placed electrodes with 3 mm separation to Spellman SL2PN10 power supply. The suspensions were then poured into the vial with the electrodes and the voltage (100–300 V) was immediately turned-on. At the end of the deposition, the suspension vial was quickly lowered to avoid dip-coating, and the substrates were left horizontally to dry for ~15 min. As a subsequent step, the deposited SSP films were thermally decomposed in a tube furnace: for CuO, $Cu(Cup)_2$ coated substrates were heated in an open-to-air tube; for CdS, $Cd(dtcEt_2)_2$ coated substrates were heated under inert atmosphere (constant Ar flow). The standard decomposition temperature was 500 °C for 60–90 min.

2.3. Photoelectrochemical characterization

An ITO covered with the characterized materials (ITO/ZnO NR–CdS) acted as the working electrode in a three-electrode configuration system using PalmSens^3 potentiostat. The photoelectrode was dipped in an aqueous solution of 0.3 M K_2SO_4, with a Pt wire acting as a counter-electrode, and Ag/AgCl in saturated KCl as the reference electrode. Linear sweep voltammetry (LSV) was conducted by scanning at a rate of 0.05 V s^{-1}, from −0.6 to 0.3 under illumination through a quartz window. A 365 nm light-emitting diode (LED), ~22 mW cm^{-2}, was used as the illumination source.

3. Results and discussion

We have used two common SSP families, where the metal is coordinated by bidentate oxygen-containing cupferrates (*N*-nitroso-*N*-phenylhydroxylamine) or sulfur-containing dialkyldithiocarbamates (R_2NCS_2). Specifically, copper(II) cupferrate [$Cu(Cup)_2$] and cadmium(II) bis(diethyldithiocarbamate) [$Cd(dtcEt_2)_2$] were used as precursors for interfacing vertically aligned ZnO NR arrays with CuO and CdS, respectively. A schematic illustration of the EPD setup (a), the two SSP molecular structures (b), and the two-step process (c), are presented in Scheme 1.

We have chosen these two SSP families as a case study since they are easy to prepare, stable at ambient conditions, and their structure, properties, as well as decomposition mechanisms are well established [39–43]. Herein, we report that subjecting a SSP suspension in toluene to an electric field by immersing two electrodes in parallel-capacitor configuration results in deposition on the negatively biased electrode. Therefore, we used this method to achieve controlled filling and coating of vertically aligned ZnO NR arrays. When the negative-biased electrode is a conductive substrate (*e.g.*, ITO) covered with an array of ZnO NRs, EPD of [$Cu(Cup)_2$] and [$Cd(dtcEt_2)_2$] followed by thermal decomposition at 500 °C yields ZnO–CuO (Fig. 1a–b) and ZnO–CdS (Fig. 1c–d) hybrid nanostructures, respectively.