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Time, illumination and solvent dependent stability of cadmium sulfide nanoparticle suspensions

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ABSTRACT

Hypothesis: The optical properties of cadmium sulfide (CdS) nanoparticles in suspension are affected by morphology and suspending solvent. Time dependent stability of these properties is solvent dependent and is affected by illumination conditions under which the suspension is stored. Moreover, minute amounts of dissolved oxygen are sufficient in order to facilitate photodegradation.
Experiments: CdS nanoparticles were synthesized with various shapes using a single precursor, single surfactant route. Thereafter, their optical properties were measured from chloroform and toluene suspensions following periods of up to 4 months, under illumination conditions, which included dark storage, visible light and UV irradiation.
Findings: The changes in optical properties, best shown by the photoluminescence (PL), reveal an intricate behavior, which is dependent upon both the chemical environment and illumination conditions. This is mainly manifested in two ways: the first is an initial intensification of the PL, while later on gradual degradation of the particles and their optical activity are observed. Moreover, a distinct variation of surface state emission was demonstrated for each solvent. Additionally, a solvent dependent variation of the final photodegraded state was observed. Based on these observations, we describe the photodegradation route for CdS nanoparticles in chloroform suspensions.

1. Introduction

CdS is a direct band gap (2.42 eV), compound semiconductor that has a high index of refraction and intense fluorescence in the visible range. CdS has promising applications in multiple technical fields including photochemical catalysis, gas sensor, detectors for laser and infrared, solar cell, nonlinear optical materials, various luminescence devices and optoelectronic devices [1–12]. Moreover, CdS nanoparticles with defined optical spectra are commercially available and are often suspended in organic liquids such as toluene, hexanes, chloroform, dichloromethane and methanol [13,14].

Size dependent properties of CdS nanoparticles have been studied extensively [1–4,15–18], and have been shown to facilitate controllable blue shifts of absorption and luminescence larger than 100 nm, compared to bulk properties, and well into the UV range with decreased nanoparticle size. Additionally, CdS nanoparticle suspensions are known to maintain their optical properties when the nanoparticles are stored in powder form, and indeed, suspensions prepared following such storage, have been shown to do so after periods of years [18]. Moreover, toluene suspensions of CdS nanoparticles have been shown to be largely unaffected by the storage conditions for up to one month of storage [19].

However, considerable amount of studies have shown the luminescence of CdS nanoparticle suspensions to be sensitive to oxidation, photosensitive and storage sensitive [19–22]. Moreover, the optical properties of CdS nanoparticles have been shown to be affected by the choice of suspending solvent [23]. Additionally, the capping surfactant can play a key role in defining the optical spectra [24].

Standard photocorrosion of CdS has been thoroughly described [25]. The general photocorrosion reaction, regardless of the intermittent reactions, has been described as:

$$CdS + 2O_2 \xrightarrow{h\nu} Cd^{2+} + SO_4^{2-} \quad (1)$$

This reaction suggests that oxygen dissolved in the suspending liquid will facilitate the dissolution of CdS, with nanoparticles being particularly vulnerable due to their large surface-to-volume ratio. Indeed, it has been previously shown that by using a size selective photocorrosion reaction, the monodispersity of nanoparticle size can be increased [20,21]. Notably, such studies employed active saturation of the suspending liquids with oxygen, operating under the

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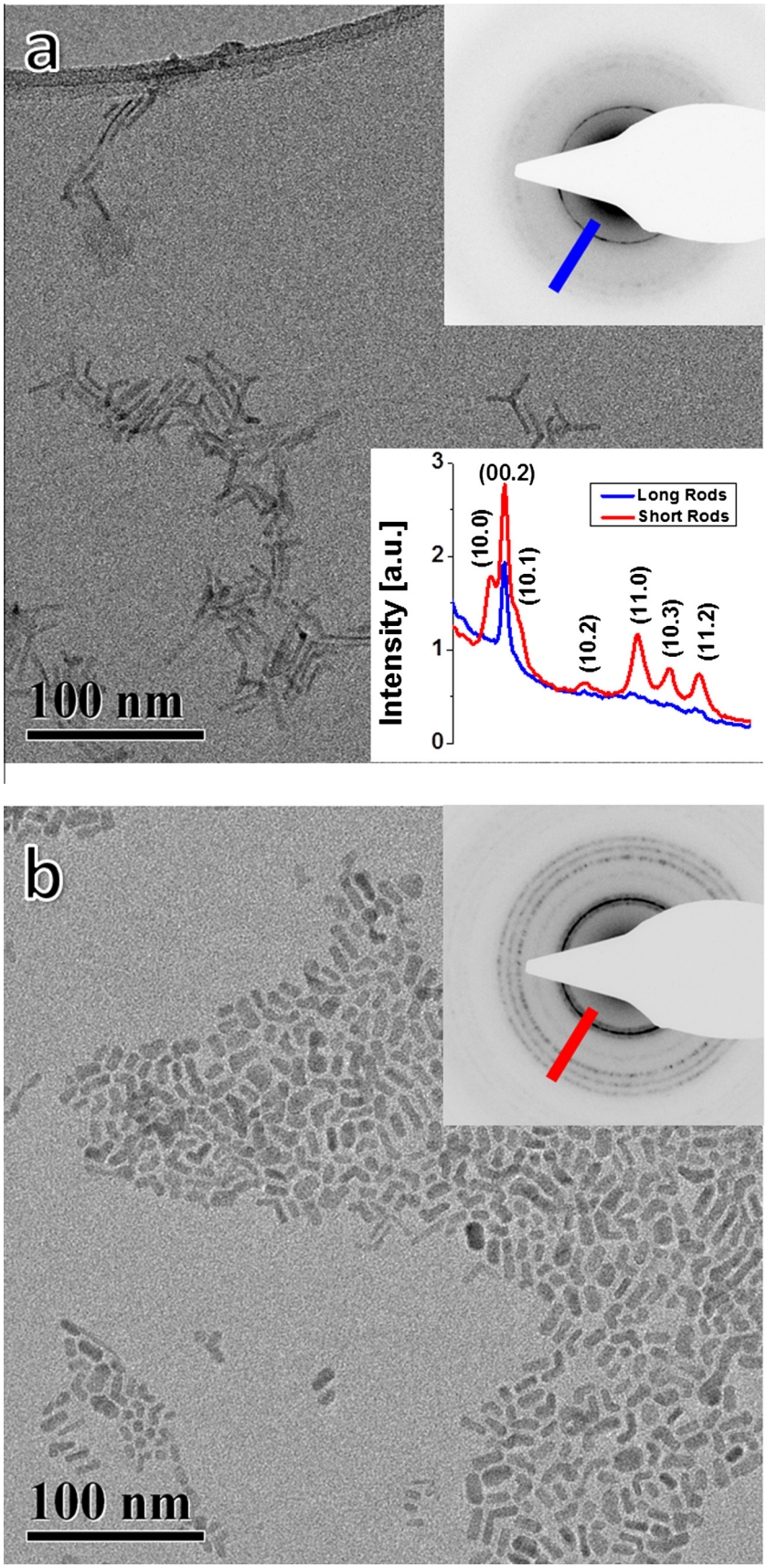

Fig. 1. BF-TEM images of the nanoparticles chosen for this study. (a) Long nanorods with a tendency to form multipods as a significant minority. Top right inset is the selected area electron diffraction (SAED) pattern, with the region digitized for intensity profile marked in blue. Bottom right inset is a comparative SAED intensity profile for long and short rods, marked in blue and red respectively. (b) Short nanorods with a wider diameter and significant multipod minority. Inset is the SAED pattern, with the region digitized for intensity profile marked in red.