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Cadmium sulphide quantum dots with tunable electronic properties by bacterial precipitation

K. E. Marusak^a, Y. Feng^a, C. F. Eben^b, S. T. Payne^b, Y. Cao^b, L. You^b, and S. Zauscher^{a,*}

^a Department of Mechanical Engineering & Materials Science, 144 Hudson Hall, Box 90300 Durham, NC 27708, United States.

^b Department of Biomedical Engineering, Duke University, 101 Science Drive, Durham NC 27708, United States.

Abstract

We present a new method to fabricate semiconducting, transition metal nanoparticles (NPs) with tunable bandgap energies using engineered *Escherichia coli*. These bacteria overexpress the *Treponema denticola* cysteine desulphydrase gene to facilitate precipitation of cadmium sulphide (CdS) NPs. Analysis with transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy reveal that the bacterially precipitated NPs are agglomerates of mostly quantum dots, with diameters that can range from 3 to 15 nm, embedded in a carbon-rich matrix. Additionally, conditions for bacterial CdS precipitation can be tuned to produce NPs with bandgap energies that range from quantum-confined to bulk CdS. Furthermore, inducing precipitation at different stages of bacterial growth allows for control over whether the precipitation occurs intra- or extracellularly. This control can be critically important in utilizing bacterial precipitation for the environmentally-friendly fabrication of functional, electronic and catalytic materials. Notably, the measured photoelectrochemical current generated by these NPs is comparable to values reported in the literature and higher than that of synthesized chemical bath deposited CdS NPs. This suggests that bacterially precipitated CdS NPs have potential for applications ranging from photovoltaics to photocatalysis in hydrogen evolution.

1. Introduction

Escherichia coli (*E. coli*) comprise some of the most widely studied prokaryotic organisms. Extensive research efforts have been made to explore the use of bacteria for bioremediation,^{1–4} including precipitation of transition metal nanoparticles (NPs) from aqueous solutions,^{5–10} by taking advantage of inherent defensive mechanisms of bacteria to harmful ions.^{11–13} To date, however, bacterial synthesis of transition metal NPs with tunable electronic properties has not been demonstrated. The synthesis of semiconducting NPs with quantum confinement, *i.e.*, quantum dots (QDs), is important for a broad range of nanotechnology applications, including medical imaging,¹⁴ solar energy generation,^{15,16}

* zauscher@duke.edu.

†Electronic Supplementary Information (ESI) available: Selected XRD references, representative control sample TEM micrograph, image analysis explanation, additional CdS crystallite data, additional UV-vis spectra calculation data/information, supporting table, photoelectrochemical testing set-up, and the band diagram of the CdS-electrolyte interface. See DOI: 10.1039/x0xx00000x

hydrogen evolution,^{15,17} and the fabrication of light-emitting diodes.^{15,18} Additionally, when irradiated with light, some transition metal QDs act as photocatalysts that can be used to decontaminate water from organic matter.^{19–21} Due to their size-dependent semiconducting properties, QDs are especially useful for photovoltaic applications.^{22–24} One important transition metal compound used in such applications is cadmium sulphide (CdS), which is a wide-bandgap, direct semiconductor (bandgap energy of ~2.4 eV).²⁵

Chemical methods for CdS synthesis usually require high temperatures^{26–28} or non-ambient conditions,^{26,29} and produce highly concentrated cadmium waste.^{30–33} Contrarily, biological methods do not have such drawbacks, and therefore have the potential to reduce the environmental impact of CdS NP fabrication.^{34–37} Although the precipitation of NPs by microorganisms,^{38–41} including bacteria, has been reported before,^{42–50} an in-depth analysis of the size and photoelectronic properties of the resulting NPs has not yet been performed, nor has the biological system been manipulated to tune those properties through varying precursor concentrations. Additionally, the assembly of a photoactive device from bacterially precipitated CdS NPs has not been demonstrated.

The *Treponema denticola* (*T. denticola*) cysteine desulphhydrase gene has been translated to and expressed in aerobic systems,^{42,51,52} where it has been shown to increase conversion of sulphur-containing amino acids, specifically cysteine, to hydrogen sulphide (H₂S).^{42,51,52} Dissolved, free sulphides can then complex with cadmium ions provided in solution to form insoluble CdS precipitates. We show that the precipitation of CdS is typically associated with the bacterial cell wall, and occurs predominantly in the periplasmic space. This suggests that harvesting CdS NPs would be greatly simplified by inducing extracellular, enzymatic precipitation. The ability to spatially control CdS precipitation has, however, not been pursued. Here, we show that the precipitation location, *i.e.*, intra- vs. extracellular, can be controlled by varying the time point of cadmium chloride (CdCl₂) precursor addition in the bacterial growth cycle. Furthermore, we show that the size, and thus the bandgap energy (E_g), of the precipitated CdS crystallites can be controlled by varying the chemical precursor concentrations in solution. Finally, through photoelectrochemical measurements, we show that bacterially precipitated CdS NPs can generate photocurrents that equal or even exceed those of chemical-bath deposited (CBD) CdS NPs.⁵³

2. Experimental

2.1 Bacterial strain

For CdS precipitation we used the *E. coli* strain DH10B, transformed with the plasmid pCysDesulf/LacI2, which has built-in carbenicillin resistance. The plasmid was received from the Keasling group at UC Berkeley and was chosen for its ability to be incorporated in aerobic bacteria and produce H₂S for NP precipitation.⁴²

2.2 Bacterial growth medium

To facilitate bacterial CdS precipitation, we developed a modified M9 medium. One litre of this medium consists of dH₂O (750 mL), 5X modified M9 salts (200 mL), 1 M MgSO₄ (2 mL), 20% glucose (20 mL), 1 M CaCl₂ (0.1 mL), 10% casamino acids (20 mL), and 5%

thiamine HCl (10 mL). The 5X modified M9 salts were composed of glycerol phosphate disodium salt hydrate (75.55 g), NaCl (2.5 g), NH₄Cl (5 g), dissolved in dH₂O (1 L). Importantly, to prevent the formation of the side product CdHPO₄, glycerol phosphate was added in place of sodium phosphate (as used in the original recipe⁴²). Unless otherwise stated, each culture was supplemented with isopropyl β -D-1-thiogalactopyranoside (IPTG) (100 μ M), K₂SO₄ (0.2 mM), cysteine (1 mM), and CdCl₂ (0.1 mM). IPTG is specifically used here to inhibit lacI, which represses the expression of cysteine desulfhydrase. Exogenous K₂SO₄ was added to drive additional endogenous production of cysteine by *E. coli*'s native serine acetyltransferase. Finally, cysteine and CdCl₂ were added as precursors for the reactions mediated by cysteine desulfhydrase. Control experiments (Fig. S1) show that CdS particle precipitation occurs only in growth media (supplemented with K₂SO₄ and IPTG) that contained all three ingredients, *E. coli*, CdCl₂, and cysteine.

2.3 Separation of NPs from *E. coli*

To harvest isolated CdS from liquid growth cultures, we first lysed the bacteria with QIAGEN Buffer P2 and removed the white, organic supernatant to leave behind a yellow pellet which was re-dispersed in aqueous solution and sonicated for 20 mins. The solution was then centrifuged and the supernatant was decanted. Finally, the NPs were re-suspended in water 3 times to further aid in contaminant removal. We note that isolated NPs differ from extracellular NPs (discussed later in Fig. 6). Isolated NPs refer to those that have been separated from the bacterial culture as described here, whereas extracellular NPs refer to those precipitated outside of the bacteria (but here are still suspended in the original culture).

2.4 Transmission electron microscopy

For Transmission electron microscopy (TEM) imaging, grown cultures were pelleted and then fixed in 4% glutaraldehyde in phosphate buffered solution, followed by sequential dehydration in acetone at 30%, 50%, 70%, 90%, two times at 95%, and three times at 100%. Next we embedded the samples in resin (Spurr's) at ratios of 1:3, 1:1, 3:1 resin:acetone, then three times in pure resin, then baked at 75 °C overnight. The samples were then thin-sectioned (Ultracut E type #701704, Fb #396756), and deposited onto Cu TEM grids for imaging. For visualization of only the nanocrystals, we did not embed or fix the bacteria, but rather lysed them (see above), washed and drop-casted the solution onto Formvar-coated, Cu TEM grids, where the sample air-dried on the grid. TEM imaging was done on a FEI CM12, available through Duke's Shared Materials Instrumentation Facility (SMiF).

2.5 Film deposition

X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and UV-vis measurements were performed on dry NP films, deposited onto clean glass slides. After separation of the NPs from the *E. coli* (see above), the NPs were drop casted from concentrated solution (~50 μ L) onto a glass slide. The resulting NP thin film was left to air-dry overnight, and covered with aluminium foil to avoid contamination and photodegradation.

2.6 X-ray photoelectron spectroscopy

XPS measurements were carried out with a Kratos Axis Ultra X-ray Photoemission Spectrometer, available at SMiF. We performed 3 sweeps for each high-resolution scan, with a step size of 1 eV, a dwell time of 2000 ms, and pass energy set to 20 kV. For deconvolution, peak positions were set to 404.62 eV and 405.18 eV for CdO and CdS, respectively. Peak spacing for deconvolution was set to 6.74 eV for each compound and area ratios were set to 3:2, according to d subshell fitting rules.

2.7 X-ray diffraction

For diffraction experiments, the deposited NPs were heat-treated to remove residual organics at 450 °C for 15 mins. We used a Panalytical X'Pert PRO MRD HR X-Ray Diffraction System (Cu K α (1.5405 Å)), available through SMiF. We used a scan step size of 0.02°, a time/step of 0.75 sec, a pre-set count of 10,000, and the number of steps set to 2,000.

2.8 UV-vis spectroscopy

UV-vis absorbance spectra were recorded with a Shimadzu UV-3600 Spectrophotometer, available at SMiF. The scan speed was set to medium using a sampling interval of 1 nm, and a slit width of 5 nm. Each sample was scanned 5 times at various locations on the slide and each spectra was normalized.

2.9 Determination of the UV-vis absorbance onset

A custom MATLAB code was developed to determine the onset of UV-vis absorbance (Fig. S2). This was done by fitting two straight lines to the normalized UV-vis absorbance spectra (representative spectra shown in Fig. S3); one to the absorption edge and one to the drop-off region. The intercept of these two lines was calculated, and the corresponding wavelength recorded as the absorption onset.

2.10 Calculations of bandgap and diameters

The E_g of a sample was calculated by the Planck Relation (Fig. S2). We used this bandgap energy along with the values 0.18, 0.53, and 5.23 for m_e^*/m_e , m_h^*/m_h , and ϵ ,⁵⁴ respectively, to calculate the average crystallite diameters of each sample.⁵⁵ We used 2.39 eV for $E_g(\text{bulk})$ measured on our own bulk CdS produced by CBD. Error estimates were obtained by error propagation starting with the calculation of the bandgap energy and carried through for the crystallite diameter calculation.

2.11 Photoelectrochemical measurements

The bacterially precipitated CdS and the CBD CdS NPs were dispersed in dH₂O. CdS NPs were drop-casted onto cleaned (1.27 cm by 1.27 cm) indium tin oxide (ITO) glass slides (703192 Aldrich). After the water evaporated at room temperature, the CdS coated ITO glass slides were connected to copper wires with Gallium-Indium (liquid metal), and the edges and the backside of these ITO slides were covered with Epoxy adhesive to firmly connect the wires to the films. Glass tubes were used to insulate the copper wires from the electrolyte. A 150 W xenon lamp (Oriel-66001, with 68805 universal power supply) was used as the light source, and filtered to simulate the solar spectrum. The counter electrode

was a platinum wire (012961 Peixin), the reference electrode was Ag/AgCl (012167 Peixin), and Na₂SO₄ (0.5 M) was used as the electrolyte (see Fig. S4). Before measurement, the electrolyte was purged with N₂ for 20 mins, and continued throughout the measurements. The potential bias applied while measuring the transient photocurrent response was + 0.5 V vs. Ag/AgCl (see Fig. S5).

2.12 Image analysis

A routine from the image processing toolbox in MATLAB was used to locate the NPs in a TEM image and to measure their diameters. Ten images per sample were analysed. Images of samples at the lowest CdCl₂ and cysteine concentrations were measured manually as there were only very few, small NPs visible in the images. The analysis of the high-resolution TEM images was carried out manually. To avoid bias, the images were de-identified prior to analysis. For each experimental condition, we measured the crystallite diameters in ten images (ImageJ). After averaging each set, the samples were relabelled with their correct sample number.

2.13 Chemical bath deposition

CBD was done in aqueous solution containing CdSO₄ (0.06 M), thiourea (0.12 M), and NH₄OH (1.74 M) brought to 80°C.^{31,53} A magnetic stir bar was added and the solution was stirred at 80°C for one hour. After completion, the hot plate was turned off, and the solution cooled to room temperature. Subsequently, the NPs were centrifuged out of suspension, and rinsed several times by resuspension and centrifugation in water.

3. Results and discussion

This work, at the interface between materials science and bioengineering, explores the potential of genetically programmed bacteria to synthesize size-controlled transition metal NPs (here CdS) with technologically relevant properties. Specifically, we overexpress the desulphydrase gene of *T. denticola* in *E. coli* to aid in the precipitation of CdS NPs, and go on to show that by varying the precipitation conditions, we can control the size and thus the electronic properties of the CdS crystallites contained within the NPs. Finally, we show the application of the CdS precipitates in a prototypical, photovoltaic device. Our research is motivated by the need to produce industrially useful materials with reduced environmental impact, using biosynthetic routes.

3.1 CdS nanoparticle characterization

Through several characterization methods we established that our bacterial NP precipitates contain CdS. TEM images of microtomed sections of fixed, embedded bacterial samples show electron-dense NPs ranging from 20 to 80 nm in diameter associated with the bacterial cell wall. Fig. 1a shows that membrane-associated precipitates typically occur in the periplasmic space. Importantly, high-resolution TEM images (Fig. 1b) reveal that the NP precipitates contain single crystals that have agglomerated into larger clusters which are embedded in an amorphous, organic matrix. In the particular example shown, the crystallites are about 6–9 nm in diameter (Fig. 1c), commensurate with the size of technologically relevant QDs.

To assess the surface composition of the NPs we used XPS (Fig. 2a), and to determine the identity of the crystallites within them we used XRD (Fig. 2b). The XPS measurements established the presence of a small amount of cadmium (1.1 at%) and sulphur (2.2 at%) on the surface of the NPs, and the deconvolution of the high-resolution cadmium doublet peaks ($\text{Cd } 3d_{5/2}$ and $3d_{3/2}$) suggested that the cadmium on the surface is mostly bound to oxygen (62:38 atomic percent $\text{CdO}:\text{CdS}$, calculated binding percentages from peak deconvolution), likely due to oxidation of cadmium during sample preparation. Additional XPS data, including the survey scan and the high resolution scan of the oxygen peak can be found in Fig. S6. The XRD spectrum of the NPs is largely consistent with the face-centred cubic (fcc) crystal structure of CdS. However, due to the relatively broad peaks, an unequivocal assignment to fcc is not possible, as several peak positions for the hcp structure of CdS lie in close proximity to those of fcc (Fig. S7). Further analysis of the XRD data confirmed that the oxidation shown in the XPS data only occurs on the surface and not throughout the sample, as the measured XRD peak positions are not consistent with those of the cadmium oxide reference spectrum (Fig. S7). Taken together, these results establish that bacterially precipitated NPs contain nanoscale fcc/hcp CdS crystallites, embedded in an amorphous, organic matrix.

3.2 Reaction engineering of the precipitation conditions

The exciting discovery of CdS single crystals or QDs in the NPs prompted a detailed study of whether crystallite size, and in turn photoelectronic properties, could be tuned through bacterial culturing conditions. To understand the effects of the concentration of the precursors (CdCl_2 and cysteine), and of the protein expression inducer IPTG, on the precipitate and crystalline size, we examined bacterially mediated CdS precipitation for a range of concentrations of each chemical (Fig. 3, control shown in Fig. S8). Fig. 3 shows that the extent of NP precipitation increases with increasing CdCl_2 and cysteine concentrations (*i.e.*, the cadmium and sulphur sources, respectively), and that NP size is largely independent of IPTG concentration (Fig. S9). Although Fig. 3 might suggest that there was less NP precipitation at the lower IPTG concentrations, examination of many TEM images does not substantiate this impression. The latter observation suggests that even the lowest IPTG concentration can induce the cysteine desulphydrase gene expression and is sufficient to cause CdS precipitation, while not affecting NP growth. The median size of the NP precipitates is relatively independent of the precursor concentrations for all but the smallest concentrations (Fig. S9). We note, however, that the size of precipitates outside the 90th percentile (*i.e.*, large outliers) increases with increasing CdCl_2 concentration and at the lower concentrations of cysteine (Fig. S9 and discussion).

We also determined the effect of precursor and inducer concentration on the size of the CdS crystallites embedded within the NP precipitates. Analysis of high-resolution TEM images of crystallites isolated from lysed bacterial cultures, shows that the crystallite diameter (measured manually) and the diameter dispersity increase with increasing concentrations of CdCl_2 and cysteine, while IPTG concentration has no significant effect (Fig. 4). The lower concentrations of CdCl_2 and cysteine are particularly interesting as under these conditions the diameter range of the crystallites is fairly monodisperse and commensurate with that of QDs. Representative high-resolution TEM images for each experimental condition are

shown in Fig. S10 and box plots of diameters of the isolated crystallites are shown in Fig. S11. The lowest concentration of CdCl₂ had no apparent NPs/crystallites and therefore could not be measured.

To establish whether the bacterially precipitated NPs contain CdS crystallites with quantum confinement properties, and whether the bandgap energy can be manipulated by varying the precursor and inducer concentrations, we determined the bandgap energies of the CdS crystallites from UV-vis absorption spectra (Fig. S3). Briefly, we extracted precipitated NPs from the bacterial cultures and determined the bandgap energy from the wavelength at the onset of the absorption transition (see Fig. S2). Furthermore, we calculated the crystallite diameters, *D*, that give rise to the measured bandgap energies, *E_g*(QD), using Equation (1),⁵⁵ where we used 0.18, 0.53, and 5.23 for *m_e*^{*}/*m_e*, *m_h*^{*}/*m_h*, and *ε*,⁵⁴ respectively, *i.e.*, standard values for CdS.

$$E_g(QD) = E_g(\text{bulk}) + \frac{h^2}{2D^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8c^2}{2\pi\epsilon_0 \epsilon D} \quad (1)$$

The reported bandgap energy (*E_g*(bulk)), for chemically synthesized, bulk CdS, ranges between 2.39 and 2.42 eV.^{25,53,56} Rather than selecting the average of these values, we used a bandgap of 2.39 eV, measured for our CBD CdS, and used it in Equation 1. As shown in Fig. 5 and summarized in Table S1, the bandgap energy decreases and the crystallite size increases with increasing precursor concentrations, whereas IPTG concentration has little effect on either, at the higher concentrations. The bandgap values calculated from Equation 1 ranged between 2.67 eV and 2.36 eV, and are therefore commensurate with a transition from quantum confinement to bulk behaviour, and compare favourably with values reported for wet chemical synthesized CdS NPs.⁵⁶ The calculated crystallite diameters agree well with those measured from high-resolution TEM images of isolated crystallites (compare Fig. 4 and 5). We note, however, that there is a systematic difference in the average diameter, which we attribute to the limitations in detecting very small crystallites (< 2 nm) in the high-resolution TEM images. This also would explain the dependence of calculated crystallite size on IPTG concentration at low concentrations. Additionally, the lowest concentrations of both CdCl₂ and cysteine (0.01 mM and 0.1 mM, respectively) show “Bandgap” and “Calculated Diameter” values very similar to those calculated for control samples that did not contain CdCl₂ or cysteine. We thus believe that the absorbance signal for these samples arises largely from the organic components in the system and are not representative of CdS NPs. In summary, the data suggest that crystallite size—and thus bandgap energy—can be manipulated through the concentrations of the cadmium and sulphur precursors, which could prove useful in the application of NPs to functional devices. The biological method presented here is the first demonstration that CdS crystallite size can be controlled through the concentration of reactants in the bacterial precipitation system, with excellent crystallite monodispersity at lower precursor concentrations.

Transition metal NPs produced by a bacterial precipitation system will naturally contain organic contaminants. Such contamination will likely interfere with the performance of functional electronic devices fabricated using such NPs. This issue could be alleviated if NP

precipitation occurred in the extracellular environment, as this would enable relatively easy NP harvest and purification. To this end, we examined how timing of CdCl₂ addition during bacterial culture growth would affect the location and extent of CdS NP precipitation.⁵⁷ We found that precipitation was minimal in a culture that is fully grown before CdCl₂ addition (Fig. 6a). This result suggests that the culture no longer produces or contains sufficient H₂S. The extent of precipitation in an *E. coli* culture that is grown with CdCl₂ in solution from the start (Fig. 6c) was similar to that of a culture to which CdCl₂ was added after an initial 10-hour growth period (Fig. 6b). However, the latter shows mostly extracellular precipitation, which is likely due to the presence of a sufficiently high, extracellular H₂S concentration coming into contact with the transition metal ions in solution. We note that while these observations are qualitative, these trends in precipitation concentration and location were consistently observed in our experiments. This important discovery suggests that timing of CdCl₂ addition can be used to localize CdS NP precipitation in the extracellular space. In future experiments, we will use extracellular precipitation conditions to aid in particle extraction and purification. To show the feasibility of scale-up, we synthesized bacterially precipitated CdS nanoparticles using a 1 litre culture (Fig. S12). The successful experiment suggests that scale-up to even larger bioreactors should be readily possible.

3.3 Photoelectronic properties of bacterially precipitated CdS nanoparticles

To show the technological potential of our bacterially precipitated CdS NPs, we built a prototypical device by depositing CdS NPs onto a conducting, ITO thin film, and then measuring the photocurrent produced by this device in an aqueous electrolyte (Fig. S4). Fig. 7 shows that bacterially precipitated CdS NP are photoactive, given the fact that the photocurrent generated by them is much larger than that of the bare ITO thin film (control). Furthermore, bacterially precipitated CdS NPs react instantly when irradiated with visible light, and their transient photocurrent response is larger than that of our CBD CdS NPs. This difference in photocurrent response may be due to differences in the thickness of the CdS NP layer, differences in the overall series resistance of the device, or a higher light absorbance of the bacterially precipitated CdS NPs caused by their organic matrix.⁵⁸ We note that the photocurrent of the bacterially precipitated CdS NPs did not drop back uniformly to the base level. As seen in Fig. 7, there was an initial fast drop when the light was blocked, and then the drop rate slowed. This can be explained by the accumulation of photogenerated holes which occurs at a positive bias voltage at the CdS-electrolyte interface, and causes a slower current density drop when the light is removed.⁵⁹ Refer to the Supporting Information for a schematic depiction and discussion of the band diagram of the CdS-electrolyte interface (Fig. S5).⁶⁰

4. Conclusions

We showed that our genetically engineered *E. coli* are able to precipitate semiconducting CdS NPs with control over crystallites size. We found that the NP precipitates contain clusters of CdS single crystals, embedded in a carbon-rich matrix. While the NP size ranges from ~10 to 80 nm, the sizes of the embedded crystallites range from ~3.5 to 15 nm, suggesting QD properties (or quantum confinement) for the smaller crystallite sizes. We showed that we can manipulate the bandgap energy of the NPs by controlling their size

through varying the precursor concentrations. Our calculated bandgap energies ranged between 2.67 eV (*i.e.*, quantum confined CdS) to 2.36 eV (*i.e.*, bulk CdS). By adding the CdCl₂ precursor at a specific stage of the bacterial growth cycle, we were able to induce extracellular CdS NP precipitation. This control over the precipitation location aids in the extraction of the NPs from the biomass and is important for harvesting NPs for technologically relevant application or situations where deposition onto a solid substrate (such as a membrane) is desired. We tested our bacterially precipitated NPs for photoelectrochemical current generation by depositing them onto an ITO thin film and irradiating them with simulated sunlight. We showed that bacterially CdS NPs generate almost four times more current than the control ITO thin film. Finally, the bacterial synthesis of CdS NPs entails lower Cd concentrations and has the promise to produce less toxic waste than comparable CBD methods. Taken together, our results show the great promise bacteria have for the fabrication of tunable, transition metal NPs with useful electronic properties. Our approach is likely more general and we currently extend it for the precipitation of other transition metal NPs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

(a) TEM micrograph showing larger CdS NPs in stained *E. coli* (Mag = 53kx). (b) TEM micrograph of a single CdS NP in the periplasmic space of the *E. coli* membrane (Mag = 200kx). (c) High-resolution micrograph of embedded crystallites (Mag = 700kx).

Fig. 2.

Surface composition and crystalline structure of bacterially precipitated CdS NPs extracted from lysed bacteria. (a) High-resolution XPS spectra of the Cd 3d doublet with deconvolution. (b) XRD of bacterially precipitated CdS NPs, blue lines indicate reference XRD patterns for cubic (fcc) CdS (PDF no. 01-089-0440).

Fig. 3.

TEM images of CdS Clusters. Row 1: Increasing CdCl₂ concentrations of 0.01, 0.04, 0.1, 0.2, 0.3, and 0.4 mM with 0.1 mM IPTG and 1 mM cysteine in each. Row 2: Increasing cysteine concentrations of 0.1, 0.4, 1, 2, 3, and 4 mM with 0.1 mM CdCl₂ and 0.1 mM IPTG in each. Row 3: Increasing IPTG concentrations of 0.01, 0.04, 0.1, 0.2, 0.3, and 0.4 mM and 0.1 mM CdCl₂ and 1 mM cysteine in each (Mag = 25kx).

Fig. 4.

Histograms showing the diameter distribution of isolated, bacterially precipitated CdS crystallites with mean diameter size for each sample. Left column: increasing CdCl₂ concentrations at constant 0.1 mM IPTG and 1 mM cysteine. Middle column: increasing cysteine concentrations with constant 0.1 mM CdCl₂ and 0.1 mM IPTG. Right column: increasing IPTG concentrations with constant 0.1 mM CdCl₂ and 1 mM cysteine.

Fig. 5. Calculated bandgap energies and NP diameters plotted as a function of (a) CdCl_2 concentration, (b) cysteine concentration, and (c) IPTG concentration. (d) High-resolution TEM micrographs of representative isolated NP samples taken from experiments at three different $[\text{CdCl}_2]$ indicated in (a) (Mag = 700kx).

Fig. 6. Effect of timing of CdCl_2 addition on CdS NP precipitation. Growth curves and representative TEM images of the cultures taken 2, 6, and 24 hours after CdCl_2 addition (Mag = 25kx). Yellow-filled circles indicate the time point of CdCl_2 addition. (a) Addition of CdCl_2 after 24 hours of growth (*i.e.*, bacteria fully grown) (b) Addition of CdCl_2 after 10 hours of growth (*i.e.*, towards the end of growth phase), and (c) CdCl_2 already present upon seeding of the bacterial culture.

Fig. 7. Transient photocurrent testing of bacterially synthesized CdS NPs. The red curve shows the current density as a function of time obtained across a thin film of bacterially precipitated CdS NPs deposited onto ITO glass, when irradiated (on) and blocked (off) from visible light. The blue and black curves represent the current density across a CBD CdS thin film on ITO, and through the bare ITO control sample, respectively.