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Colloidal construction of porous polysaccharide-supported cadmium sulphide☆

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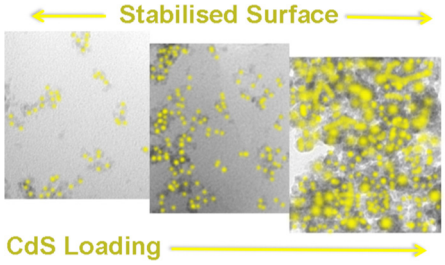
HIGHLIGHTS

- The preparation of high surface area, mesoporous cubic CdS/starch hybrids is presented.
- A colloidal starch gel confines CdS growth to small, cubic nanoparticles (<40 nm).
- The method allows very high CdS loadings (i.e. 1:1 wt/wt).
- The gel and CdS phase interact to maintain surface and porosity of original gel.
- The green route is applicable to a range of quantum dots and polysaccharide gels.

GRAPHICAL ABSTRACT



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ABSTRACT

A method for preparing CdS nanoparticles within the porous confines of a mesoporous starch gel is described. This method utilises the combined colloidal and flexible chemical nature of a porous polysaccharide (i.e. starch) gel to limit CdS growth. The resulting hybrid gels can be dried to produce CdS/starch materials with high surface areas, predominantly mesoporous characteristics and scope for high CdS loading. The synthesis is conducted in aqueous alcoholic solutions without the need for expensive preparation techniques or additional protection/templating strategies. Materials were prepared at increasing CdS loadings on the starch gel, which confined nanoparticle growth and directed size/surface coverage, dispersion and UV–vis absorption profile. The resulting powders presented large mesopore domains with high volumes (pore diameters > 10 nm; V_{meso} > 0.5 $cm^3\ g^{-1}$) and surface areas (S_{BET} > 170 $m^2\ g^{-1}$), interestingly effectively increasing with CdS loading. The synthesised CdS nanoparticles were characterised in the 5–40 nm range of a cubic crystalline structure, increasing in size with loading. A complete surface coverage of the starch gel structure occurs at a CdS/starch ratio = 1 (w/w), allowing the synthesis of a unique mesoporous CdS/polysaccharide hybrid. The presented route is simple, green and in principle extendable to a wide range of QDs and polysaccharide gels, whereby the porous polysaccharide gel acts as the deposition point of Cd^{2+}, directing and stabilising both the growth of the inorganic CdS phase and the expanded high surface area polysaccharide form.

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1. Introduction

Semiconductor quantum dots (QD) are of interest not only as an academic curiosity but also because these nanoparticles show potential as biological labels, photocatalysts, and nano-electronic devices [1–3]. QDs offer a wide range of properties accessible via manipulation of size, chemistry, band gap and photoluminescent properties [4]. In this context, the fabrication of nano inorganic–organic hybrid materials is of particular interest, as the resulting materials may potentially possess the combined characteristics of the two original components [5]. Cadmium-based QDs (e.g. cadmium sulfide (CdS)) are considered attractive for the aforementioned applications due to their bright emission in the visible and near infrared region of the electromagnetic spectrum [6]. However, these semiconductor QDs have a number of application problems associated with the unsuitability of the capping agents employed (e.g. in a biological environment), the retention of particles over a certain size, magnification (e.g. in cells), or degradation/decomposition of these inorganic QD materials. To circumvent these problems a variety of synthetic strategies have been employed to stabilise such QDs [7]. One promising approach is to employ materials (e.g. polymers) that provide coordination sites for Cd^{2+} and in turn stabilise the forming QD phase (e.g. CdS) during synthesis [8]. Therefore, the use of natural polysaccharides seems appropriate as these sugar polymers are relatively inexpensive and can provide functionality, biocompatibility, abundance and non-toxicity [9].

The preparation of QDs enclosed within the porous structure of a biocompatible polymer would offer a route to suitably capped or protected materials for biomedical applications (e.g. imaging) [8]. The advantages of both the QDs and polymeric support could then be combined when the active component (e.g. the QD) is dispersed and stabilised within a biocompatible, inexpensive and potentially highly porous, network [8,10]. In this context aqueous phase or "wet" colloidal chemistry approaches to the synthesis of nano-materials can take inspiration from bio-mineralisation; that is the growth of inorganic crystals within the confines of biological systems – with the use of porous polysaccharide-derived materials seemingly a perfect match for the aforementioned criteria.

The inspiration for this work comes from our and others previous reports on porous polysaccharide-supported metallic nanoparticles, and also from a number of literature reports detailing the synthesis of (non-porous) saccharide-capped CdS nanoparticles [8–12]. Previously, a wide variety of metallic nanoparticles (e.g. Pd, Au, Ag, etc.) have been protected using polysaccharides (e.g. starch, amylose, cellulose), finding application predominantly in absorption and catalysis [11]. Polysaccharides (and saccharides) have previously been employed to stabilise QDs (including CdS) [12], but significantly there have thus far been no reports that describe the use of porous polysaccharides (e.g. mesoporous starch) in the preparation of high surface area, (meso)porous QDs/polysaccharide hybrids. The polysaccharides, and indeed mesoporous forms of these biopolymers, would seem ideal vehicles to contain the growth of QDs to suitable sizes whilst at the same time providing in principle a biologically compatible transport media. Here, the synthesis of high surface area, CdS/mesoporous starch (MS) hybrids are presented, where the unique environment of a starch gel is utilised to confine the growth of the CdS phase. The presented materials have been characterised using X-ray diffraction, N_2 sorption, transmission electron microscopy and diffuse reflectance ultraviolet–visible light spectroscopy. The CdS/MS materials, prepared at increasing CdS/starch (w/w) ratios, are synthesised in a straightforward manner based on green chemistry principles [13], demonstrating the straightforward, utile and transferable nature of the presented approach.

2. Materials and methods

2.1. Materials

Purified high amylose corn starch was purchased from National Starch Food Innovation Plc. (Manchester, UK) and used as received. Ethanol was purchased from Fischer Scientific (UK) and used as received (i.e. 99% purity). Cadmium acetate ($Cd(CH_3CO_2)_2$) and sodium sulphide (Na_2S) were purchased from Sigma–Aldrich and used as received (i.e. >98% purity).

2.2. Preparation of porous starch (MS)-supported CdS

Preparation of said materials was conducted adapting a method proposed by Hullavarad et al. for the preparation of SiO_2 supported CdS materials [14]. MS was prepared in the absence of any reagents as a control sample. 50.0 g of MS gel prepared as reported previously (equivalent to 2.5 g starch) was solvent exchanged to 50% ethanol content. To which the desired amount of cadmium acetate (0.1 M) solution in ethanol was added. Samples were prepared at the following Cd/MS weight ratios: CdS3 (0.01 w/w); CdS2 (0.10 w/w); and (D) CdS1 (1.00 w/w). Bulk CdS prepared in the absence of starch gel in an identical manner. The system was then stirred vigorously for 2 h, before the addition of an appropriate volume of Na_2S (0.1 M) in ethanol. The Cd/S volume ratio employed was 1:5. The formation of the CdS was almost instant upon addition of Na_2S (as indicated by a strong yellow colouration). Samples were left to stir for 2 h to allow for complete reaction. Solvent exchange was continued as prescribed in described previously for the addition of ethanol [15]. Samples were filtered under laboratory vacuum and re-immersed in ethanol. This was repeated in duplicate to remove any unreacted species. Samples were finally dried by rotary vacuum evaporation under mild heating (~40 °C) followed by vacuum oven drying at 50 °C overnight to remove residual ethanol. The final CdS loading was calculated based on the mass recovered relative to the initial starch mass (2.5 g), with marginal variance relative to intended experimental design.

2.3. Characterisation

2.3.1. Diffuse reflectance ultraviolet–visible spectroscopy (DRUVs)

DRUVs spectra of supported nanoparticle materials were recorded on a Jasco V550 UV/VIS spectrophotometer (Jasco UK, Great Dunmow, UK), using a solid-state diffuse reflectance mode analysis cell. Spectra were acquired in the 190–900 nm range, at a scanning speed of 100 nm/min, with a data pitch of 0.5 nm. A Jasco supplied background polystyrene block was used as the spectral reference material (unless otherwise stated in the text).

2.3.2. Nitrogen sorption analysis

Gas sorption analysis was performed using a Micromeritics ASAP 2010 porosimeter, utilising N_2 as the probe molecule. Samples were degassed at 60 °C under vacuum ($p < 10^{-2}$ Pa) on the apparatus for >5 h prior to analysis. Data processing was performed using ASAP 2010 v.5.02 and Origin Lab v.7.5 software. N_2 sorption isotherms were measured at −196 °C. Specific surface areas were determined via the Brunauer, Emmett and Teller (BET) method, based on the cross sectional area of the nitrogen molecule (0.162 nm^2). Surface areas were calculated using a BET plot of at least 5 data points over a relative pressure range of (P/P_0) 0.05–0.30, where a linear relationship was maintained. Pore size distributions and mesopore volumes were calculated using the Barrett, Joyner, and Halenda (BJH) model [*NB*: artefact from nitrogen desorption at 3.7 nm]. Total pore volume was determined at a relative pressure of 0.975. *t*-Plot analysis employed N_2 adsorption data in the P/P_0 range