



Cadmium sulfide nanoparticles with controllable morphology, photoluminescence and photocatalytic activity templated by worm-like dendronized poly(amido amine)s



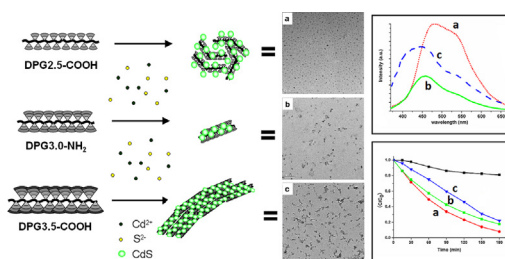
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HIGHLIGHTS

- Dendronized poly(amido amine)s are synthesized to prepare hybrid cadmium sulfide nanoparticles.
- The nanoparticles have controllable spherical or nanowire morphologies.
- The photoluminescence and photocatalytic activity of the nanoparticles are characterized.
- The photoluminescence and photocatalytic activity are dominated by the morphologies of the nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study reports that dendronized poly(amido amine)s (DPs) can be used as templates for the preparation of organic–inorganic hybrid cadmium sulfide nanoparticles (CdS NPs) with controllable morphology and performance. The DPs are synthesized via the combination of macromonomer strategy and “graft-from” strategy. It is found that the concentration and molecular structures (generation and peripheral groups) of DPs dominate the morphology of CdS NPs, forming CdS quantum dots aggregates exhibiting spherical or nanowire morphologies, as characterized by UV–vis spectroscopy and transmission electron microscopy. The obtained PG/CdS NPs have both photoluminescence and photocatalytic activity, as evaluated by fluorescence spectroscopy and UV-degradation of methyl orange, respectively. The quantum yields and photocatalytic reaction rates are dominated by their morphologies and peripheral groups. The results show that the structures of dendronized polymer templates have significant impact on the morphology of CdS NPs, and further dominate their photoluminescence and photocatalytic activity.

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1. Introduction

Nanoparticles (NPs) such as quantum dots (QDs) and nanowires (NWs) are a class of fascinating materials which have received wide attention during the last decade [1–5]. Considerable efforts

have been made in fabricating NPs owing to their broad applications in electronic devices, photovoltaic devices, catalysts, sensors, bio-imaging and plasmon [6,7]. Among the various preparation methods, template method has attracted relatively more attention due to its high efficiency and precise control of NPs morphology [8–22]. For example, biological materials such as DNAs [8,9], proteins and peptides [10–12], viruses and phages [13,14], and organic materials such as surfactants and micelles [15–17], elastin-like polymers [18], block, alternating or brush co-polymers

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[19–22] could all be used as templates for the fabrication of organic–inorganic hybrid nanomaterials including QDs, NWs and the like.

Apart from the above substances, dendrimers have also become an important class of remarkable templates for inorganic nanomaterials [23–41]. Poly(amido amine)s (PAMAMs) and poly(propylene imine)s (PPIs) are the most commonly used dendrimer templates since their unique inner space can act as ideal nanocontainers for inorganic materials to form the so called dendrimer-encapsulated NPs (DENs) [23]. And they bear inert (hydroxyl) or charged (amino, carboxyl) peripheral groups as well as inner tertiary amines or amides groups, making them efficient nanoreactors which can well stabilize the incorporated inorganic nanomaterials. Due to all these unique characteristics, PAMAM or PPI dendrimers have been widely used as templates for fabricating inorganic NPs including metal oxide [26,27], CdS [28,29], CdSe [30], CdTe [31], gold [32–34], silver [35], palladium [36,37], platinum [37,38], or bi-component NPs [39–41], which have been used mainly in the fields of catalyst, sensing, imaging and biomedicine.

According to the above examples, the functions of dendrimers involved in fabricating organic–inorganic hybrid nanomaterials can be generally summarized as encapsulation agent and stabilization agent, i.e., dendrimers encapsulate inorganic components in the inner space or surround the inorganic nanoparticles. However, the functioning fashion of organic templates may go beyond. It is traditionally considered that excess organic stabilizers may inhibit the transformation of inorganic nanocrystals into NWs via dipole–dipole interactions [42,43], but people gradually realize that the organic components may also play a role in the morphological evolution of inorganic NPs [44]. For example, organic components could direct gold nanorods to self-assemble into NWs [45]. And similar morphological control may also be conducted by dendrimers: PPI dendrimers can be used to fabricate organic–inorganic hybrid nanofibers by forming unidirectional linking of CdSe QDs [46]. Besides encapsulation or stabilization, PPI dendrimers here act as linkers that lead to the formation of one-dimensional (1D) nanofibers. The nanofibers obtained may further initiate the mineralization of gold NPs, forming bi-component inorganic 1D nanostructures.

Derived from dendrimers, dendronized polymers have hyper-branched architectures with 1D worm-like molecular morphologies resembling that of rod-like viruses [47–49], and are the largest but still precise synthetic structures comparable to biological molecules [47]. They consist of polymeric mainchains and numerous dendrons decorated around the mainchains. The confined inner space, peripheral reactive groups and intrinsic worm-like morphologies make them possible candidates for templates of inorganic NPs. However, few investigations [50] have reported the use of dendronized polymers as templates for inorganic nanostructures, and the formation mechanism of organic–inorganic hybrid NPs directed by dendronized PAMAMs is not fully studied.

In this work, the effects of dendronized PAMAMs (DPs) on templating the formation of organic–inorganic hybrid CdS NPs are investigated, by characterizing their morphology and evaluating their photoluminescence and photocatalytic activity. For this purpose, we synthesized dendronized PAMAMs of different generations (DPG_n, where “G_n” represents “n generation”) bearing peripheral amino groups (DPG3.0-NH₂) or carboxyl groups (DPG2.5-COOH and DPG3.5-COOH), as shown in Scheme 1. Their capabilities in templating CdS NPs with different morphologies, photoluminescence and photocatalytic properties are investigated. It is found that the concentration and structural characteristics (generation and peripheral groups) of the DPs play a predominant role in controlling the NPs morphology. These DPs act not only as encapsulator or stabilizer of CdS QDs, but also as linkers that direct single CdS QDs to form spherical or 1D aggregates. The

variations of NPs morphology further determine the differences of their photoluminescence properties and photocatalytic activities in UV-degradation of methyl orange (MO). The findings in the present work may give new insights into the structure–property relationship of organic–inorganic hybrid nanoparticles, for the purpose of fabricating new functional materials.

2. Experimental

2.1. Materials

Methacryloyl chloride (MAC) was purchased from Adamas-Beta. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from J&K Scientific. Methyl acrylate (MA), ethanol amine (EA), ethylene diamine (EDA) and triethylamine (TEA) were all purchased from Tianjin Bodi Chemical Holding Co., Ltd. Cadmium chloride (CdCl₂), sodium sulfide (Na₂S·9H₂O) and methyl orange (MO) were all purchased from Chengdu Kelong Chemical Co., Ltd. Ultra-pure water was used throughout, all chemicals were of AR grade and were used as received. All glassware used was soaked in H₂O/HNO₃ (65%)/H₂O₂ (1:1:1 v/v/v) solution, rinsed with ultrapure water, and finally dried with acetone.

2.2. Synthesis of dendronized PAMAMs (DPs)

2.2.1. PAMAM G2.5 macromonomer (PG2.5)

First, 2.5 generation PAMAM dendron with an ethanol amine core was synthesized as previously reported via conventional divergent method [51,52]. Starting from EA, the dendron architecture was constructed by successive utilization of an excess of MA and EDA in methanol solution under room temperature. The PG2.5 macromonomer was prepared as follows: PAMAM G2.5 dendron (11.5 g, 8.0 mmol), dry TEA (5.5 mL, 40.0 mmol, 5 eq.) and DMAP (195 mg, 1.6 mmol, 0.2 eq.) were dissolved in 50 mL dry DCM in a 250 mL three-necked flask, followed by drop-wise addition of MAC (3.9 mL, 40.0 mmol, 5 eq., in 30 mL DCM solution) under ice-bath and N₂ protection within 1 h. The reaction mixture was then allowed to warm to room temperature and stirred for additional 18 h. After the crystalline precipitate was filtered off, DCM was vacuum-evaporated at 30 °C, followed by the addition of 70 mL saturated NaHCO₃ aqueous solution to re-dissolve the product. The solution was then extracted by DCM (3 × 100 mL). And to get the crude product, the combined organic phase was evaporated at 30 °C after being backwashed by saturated NaHCO₃. Purification by silica chromatography using CHCl₃/MeOH (8:1) as the eluent gave the macromonomer with a yield of 93% and purity above 99%. ¹H NMR data is given (CDCl₃, 400 MHz, δ, ppm): 1.93 (s, 3H, C=C-CH₃); 2.25–2.45 (m, 28H, -CH₂-CONH- and -CH₂-COO-); 2.50–2.95 (m, 42H, >N-CH₂-); 3.25–3.35 (m, 12H, -CONH-CH₂-); 3.65–3.70 (s, 24H, -COO-CH₃); 4.15–4.25 (t, 2H, CO-O-CH₂-); 5.52 (s, 1H, H-CH=C-); 6.08 (s, 1H, H-CH=C-).

2.2.2. Dendronized PAMAM G2.5 (DPG2.5)

DPG2.5 was obtained by radical polymerization of the above macromonomer in the bulk. The macromonomer (10.0 g) and AIBN (50 mg, 0.5 wt%) were dissolved in DCM, and then were vacuum-evaporated under low temperature until complete removal of the solvent. The reaction mixture was heated to 90 °C with magnetic stirring, the stirring become difficult after 20 min due to increasing viscosity, but the reaction was allowed to keep for a total of 2 h. After cooled to room temperature, the mixture was gradually dissolved in methanol and precipitated twice in cold diethyl ether. The precipitant was vacuum dried and gave DPG2.5 as yellowish foam. Yield: 69%.

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