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Enhanced and reproducible photogeneration of blue poly(pentacosadiacetylene) chemisorbed onto silver nanoparticles: An optimized synthetic protocol

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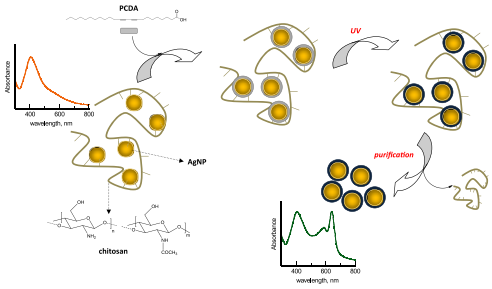
HIGHLIGHTS

- We prepared nanohybrids composed by Ag nanocores coated by a poly-diacetylene shell.
- The nanohybrids show strong and structured absorptions in the visible range.
- An optimized procedure aimed to obtain reproducible results is presented.
- Specific spectroscopic parameters for monitoring the process are individuated.
- Control tests to verify the efficiency of the procedure are reported.

GRAPHICAL ABSTRACT



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ABSTRACT

Polydiacetylenes (PDAs) self-assembled onto silver nanoparticles (AgNPs) show superior performance relative to conventionally-structured PDAs because their unique optical properties are combined with the peculiar features of the nanosized noble metal cores. The present paper presents a study of the experimental factors influencing the photopolymerization of the carboxy-terminated 10,12-pentacosadiynoic acid (PCDA) monomer anchored to silver nanoparticles in an aqueous solution. Specific spectroscopic parameters have been identified that characterize the process both qualitatively and quantitatively, thus allowing the comparison of the polymerization yield carried out under different experimental conditions. On this basis, a well-defined synthetic protocol able to maximize the chromophoric potential of these novel optical transducers, as well as to give reproducible results, is proposed and tested on differently-stabilized and/or aged silver nanoparticles used as substrates for the PCDA chemisorption. The highly-conjugated blue polyPCDA has considerable potential in the optoelectronic, photovoltaic and sensing fields.

1. Introduction

The last decades have witnessed the importance of conjugated polymers as systems that can find promising applications in many fields due to their chromophoric features. Among them,

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polydiacetylenes (PDAs) represent an unique class of polymeric materials because they exhibit an array of peculiar properties related to the extensive electronic delocalization of their highly-aligned backbone [1], including high third-order nonlinear susceptibility [2,3], outstanding photo-conduction characteristics [4] and strong molecular friction anisotropy [5]. Nevertheless, the largest application area of PDAs lies in their dramatic chromogenic and emitting behaviour that can be optically, thermally, chemically or mechanically [6–9] stimulated and observed even at the nanoscale. Most known PDA-based chromophoric sensors work via irreversible routes, although examples of reversible thermal and pH-induced colour transition have been recently reported in the literature [10,11]. Moreover, PDAs show high structural versatility, since they can be prepared in the form of bulk single crystals [12], multilayer [13] and monolayer [14] films, vesicles suspended in liquids [15] and as components integrated into inorganic host matrices [16–19].

More recently, studies on PDAs anchored to SiO_2 or ZnO nanoparticles, which couple the unique spectroscopic properties of the conjugated polymer with the peculiar features of nanostructured inorganic materials, opened novel avenues in materials science and engineering [20,21]. In fact, the core–shell architecture, typical of this new class of PDA-based nano-assemblies, proved to be crucial in allowing a high degree of polymerization of the chemisorbed diacetylenes, so providing significant amplification of the optical signal under external stimuli.

In this context, highly photoresponsive composite materials were obtained in our laboratory by means of a bottom-up approach, consisting in the chemisorption and subsequent photopolymerization of properly-functionalized diacetylenic units onto pre-formed noble metal nanostructures [22–24]. It was shown that on these nanohybrids the PDA photogeneration process in the blue form, which takes place directly in aqueous suspension, is governed by the size, shape and chemical nature of the metal core as well as by the type of the surfactant employed for stabilizing the colloidal solution [25,26]. In these studies, the carboxy-terminated 10,12-pentacosadiynoic acid (PCDA) monomer was used as a model molecule for the self-assembly onto silver nanoparticles (AgNPs) because the high affinity of the carboxylic groups for Ag surfaces [27] favours the compact and ordered organization of the chemisorbed monomers on the metal core. This, in turn, is a prerequisite for the appearance of the polydiacetylene blue form, characterized by an extended conjugation length of the polymeric skeleton. As far as the role of the stabilizer is concerned, chitosan, an amino-substituted polysaccharide able to establish electrostatic interactions with the negatively-charged carboxylic end-groups of the diacetylene monomers, proved to be determinant in conferring stability and homogeneity to the system and, consequently, in increasing the polymerization yield [28].

Control of the structural and optical properties of these nanohybrids is critical in determining the intrinsic technological advantages offered by the resulting composite materials. To this end, the availability of a defined synthetic protocol that enables reproducible results to be attained would clearly facilitate the refinement of preparation procedures. Such conditions have not yet been achieved, since the self-assembly of PCDA onto pre-formed silver cores has been found to be a complex process, which needs to be investigated as a function of the many factors that influence the process.

In this paper, a synthetic procedure aimed at standardizing the formation of polyPCDA onto AgNPs is reported. Our efforts were mainly devoted to identify the experimental conditions favouring the photogeneration of a “pure” blue phase, that could be exploited for sensing, optoelectronic and photovoltaic purposes. The achievement of this objective is, in our opinion, the first step in developing strategies for the fabrication of PDA-based colorimetric devices.

This paper is organized as follows. Firstly, the synthesis of the chitosan-protected metal cores used as substrates for the monomer chemisorption together with the wet preparation of PCDA-decorated AgNPs is reported. Secondly, photogeneration of the “blue” polymer on the nano-assemblies, monitored step by step by UV–Vis spectroscopy, is described. The monomer-to-polymer conversion efficiency, evaluated through specific polymerization indicators [29], is investigated as a function of strategic experimental parameters involved in the self-assembly process, such as the reaction timescale, the aging of the pre-existing colloids and the molecular properties of the chitosan stabilizer. Finally, in order to check the reliability of the proposed procedure, experiments carried out on different Chit-AgNPs batches, prepared under different conditions, as well as on another type of organically-passivated nanoclusters, *i.e.* tyrosine-decorated silver nanoparticles (Tyr/AgNPs), are presented and discussed. The choice of the amino-acid tyrosine as comparative stabilizer was dictated by its capability of reducing silver ions under alkaline conditions to yield clean, highly stable, water dispersed silver nanoparticles through a one-step process [30].

2. Materials and methods

2.1. Chemicals

All reagents and solvents employed were commercial-grade products used as received. Chitosan (22.8% acetylation degree, $M_w \sim 1.34 \times 10^6$ in terms of repeating units) was purchased from Fluka. The diacetylene monomer 10,12-pentacosadiynoic acid (PCDA), purchased from Lancaster, was purified to remove traces of spontaneously-formed polymer through dissolution in ethanol followed by filtration with a 0.20-μm PTFE syringe filter. All aqueous solutions were made with ultra-high-purity water, twice distilled prior to use.

2.2. Degradation of high molecular mass chitosan

The commercial chitosan (H-Chit) was degraded to lower molecular mass products by partial acid hydrolysis of the β-glycosidic bonds, carried out at different temperatures for the same time interval (2 h). In a typical procedure, an appropriate amount (~2 g) of the pristine polysaccharide was dissolved in 200 mL of 0.6 mol L^{-1} HCl, and the solution heated to the desired temperature for the established time under magnetic stirring. At the end of the reaction, the solution was cooled to room temperature and added of 300 mL of a EtOH:NH_4OH (28–30% aqueous solution):H_2O mixture (7:2:1 are the corresponding volume ratios) to induce the polymer precipitation. Once obtained, the product was washed to neutrality with EtOH and dried in an oven at 40 °C for 48 h. In our experiments, two procedures of hydrolysis were carried out: the first one at 60 °C in order to obtain medium molecular mass chitosan (M-Chit), and the second one at 90 °C in order to obtain low molecular mass chitosan (L-Chit).

The molecular mass of the commercial product as well as that of the degraded polymers was assessed by viscosimetry in acetic medium (0.1 mol L^{-1} aqueous acetic acid solution containing 0.2 mol L^{-1} NaCl), employing a Ubbelohde viscosimeter.

2.3. Synthesis of chitosan-protected silver nanoparticles

Silver nanoparticles stabilized with high, medium and low molecular mass chitosan (H-Chit/AgNPs, M-Chit/AgNPs and L-Chit/AgNPs, respectively) were obtained through a wet chemical