

Short Communication

Supramacromolecular organization of gold nanocrystals capped with amphiphilic hyperbranched polyethyleneimine

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ARTICLE INFO

Article history:

Received 14 November 2012

Accepted 1 January 2013

Available online 22 January 2013

Keywords:

Supramolecular assembly

Negative thermal expansion

Hyperbranched polymers

ABSTRACT

The supramolecular structural aspects of hetero-assemblies constituted of gold nanoparticles capped with amphiphilic unimolecular micelles were studied using synchrotron-based small angle X-ray scattering (SAXS). Experimental results revealed that straightforward transfer of citrate-capped Au nanoparticles from an aqueous environment to a toluenic solution of amphiphilic hyperbranched polymers results in the spontaneous integration of the nanocrystals into the extended hydrophilic domains of self-assembled supramolecular structures. In this way, we were able to self-organize metal-polymer nanoarchitectures in solution displaying interesting thermoactive functions, i.e.: hybrid assemblies exhibiting negative thermal expansion coefficients. We consider that this strategy has potentiality to realize self-organized supramolecular hetero-assemblies as it provides an alternative methodology to spontaneously integrate nanoscale building blocks into preformed supramolecular objects.

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1. Introduction

The combined use of colloidal nanocrystals and amphiphilic polymers as building blocks for the creation of hybrid nanoassemblies has found incredible resonance within the soft matter research community in recent years. In this context, one of the ongoing challenges for supramolecular materials science is the development of flexible strategies and protocols that can facilitate the assembly of inorganic and polymeric building blocks into organized functional structures [1]. Self-assembly of gold nanoparticles into two-dimensional (2D) or three-dimensional (3D) arrangements has granted access to a myriad of structured nanoscale materials amenable to multiple technological applications [2]. Performance of these assemblies strongly depends on the aggregation state, both in terms of overall size and interparticle distance [3]. As such, devising strategies to control nanoparticle assembly in solution and in the solid state is mandatory to harness the fascinating properties of nanoparticles in practical applications like biosensing or electronic/optoelectronic devices [4,5]. In this way, polymer scaffolds can be exploited not only to stabilize the NP suspension but also to induce ordering or to confer functionality to the metal clusters. Rotello and co-workers pioneered the use of dendrimers as integral components in NP assembly [6]. Electrostatic interac-

tion between Au NPs and PAMAM dendrimers enabled fine control over interparticle distance and provided a route to create thin films of Au NPs spaced by PAMAM dendrimers [7]. Recently, Tang et al. [8] demonstrated that hyperbranched unimicelles, i.e.: dendritic structures with micelle-like properties [9], consisting of palmitic acid-modified hyperbranched polyethylenimine can be successfully employed to transfer citrate-protected Au NPs from water into organic solvents without the aid of other compounds. In contrast to perfectly branched dendrimers, that are monodisperse “nano-objects” prepared through multistep synthesis [10], hyperbranched polymers are prepared in a one-pot synthesis leading to heterogeneous products with a distribution in molar mass and branching [11]. Even so, they also display unique properties as manifested by their globular structure and large number of terminal groups [12]. Up to now there are no studies revealing the presence of supramolecular order and the formation of superstructural assemblies in solutions of Au NPs capped with amphiphilic hyperbranched polymers. Similarly, the integration and processing of such supramolecular systems into thin-film configurations remain unexplored. Under this perspective, we have explored the supramolecular structural aspects of hetero-assemblies constituted of gold nanoparticles capped with amphiphilic unimolecular micelles generated by straightforward phase transfer protocols typically used in nanoparticle synthesis (Fig. 1). Our experimental evidence reveals the spontaneous integration of the gold nanocrystals into self-assembled unimicelle domains, thus leading to the self-organization metal-polymer nanoarchitectures exhibiting thermoactive functions.

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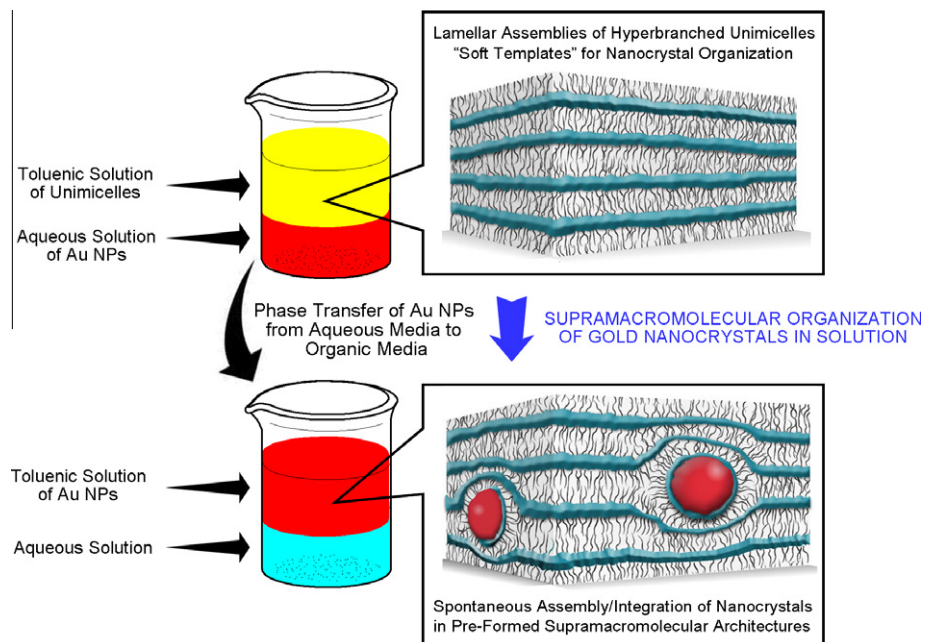


Fig. 1. Simplified scheme illustrating the phase transfer process and the resulting mesostructures derived from the spontaneous integration of gold nanocrystals into the organized assemblies of unimolecular micelles.

2. Results and discussion

In a previous report [13] we demonstrated that unimolecular micelles constituted of hyperbranched polyethyleneimine (hydrophilic core) covalently modified with palmitoyl chains (hydrophobic shell) (HPEI-C16) ($M_n \approx 39.3$ kDa) spontaneously form structured assemblies (mid-long range order) in low polarity solvents like toluene. The structured assemblies are stable below 30 °C being disassembled, in a thermoreversible way, above this temperature. Moreover, the supramolecular structures formed before reaching this self-assembly/disassembly transition display negative thermal expansion (NTE) coefficients [13,14]. This fact reflects the unusual thermal properties of these supramolecular entities and highlights the complex interplay between different interactions stabilizing the structure of these systems. Previous reports [15] also showed that core-shell amphiphilic structures are able to assemble forming lamellar structures when casted over solid substrates. According to Tang et al. non-polar solutions of HPEI-C16 allow transferring gold nanoparticles (Au NPs) from an aqueous environment to an organic media by stabilizing the nanoparticles in the non-polar media. To explore the emergence of supramacromolecular organization in hybrid systems constituted of Au NPs stabilized with HPEI-C16 we proceeded to examine the structural features of these supramolecular systems using synchrotron-based small angle X-ray scattering (SAXS).

To this end we employed aqueous solutions of citrate-capped gold nanocrystals prepared by Turkevich method and toluenic solutions of hyperbranched polyethyleneimine covalently modified with palmitoyl chains, i.e.: HPEI-C16 (Fig. 1). Gold colloids were examined by transmission electron microscopy (TEM) corroborating the crystalline (FCC structure) character of the samples (Fig. 2). The SAXS diagram in Fig. 3 was obtained from toluenic solutions of Au NPs having a diameter (D) ≈ 10.6 nm (Au NP_{10nm}) stabilized by HPEI-C16, at 22 °C. The plot also displays the SAXS data for a solution of HPEI-C16 in absence of Au NPs. Both SAXS patterns are similar, and share the presence of a pronounced Bragg Peak indicating mid-long range order [16]. In the case of HPEI-C16 the Bragg peak at $q = 1.16$ nm⁻¹ corresponds to an interplanar

spacing of 5.4 nm, whereas the HPEIC16 + Au NP_{10nm} system presents a peak at $q = 1.04$ nm⁻¹ indicating a larger interplanar distance of 6.0 nm. We hypothesize that the packing might be very similar in both cases, whereas the variation in interplanar spacing can be ascribed to the intercalation of Au NPs within the supramacromolecular assembly. Similar behaviour was obtained using smaller gold nanoparticles ($D \approx 5.3$ nm, Au NP_{5nm}) (see Supplementary data). The occurrence of structural order in HPEI-C16 in non-polar media can be rationalized by considering the amphiphilic nature of the core-shell structure. Although decorated with palmitoyl chains, the solvent accessibility of the core cannot be fully avoided. Among different interactions between aliphatic chains contributing to the enthalpic component of the free energy, a key component to define the most favourable configuration is the entropic contribution due to solvent ordering around the aliphatic chains. Spontaneous ordering of HPEI-C16 unimicelles can be the consequence of the dramatic increase of entropy due to the release of solvent molecules to the bulk.

Our working hypothesis relies on the fact that the thermodynamic driving force favours the formation of structures governed by interacting alkyl chains. In this scenario, at least two possibilities arise: either the alkyl chains interpenetrate stabilizing a close packed structure or the unimicelles reorganize and the aliphatic chains fold-up to optimize the hydrophilic core-core interaction and minimize the exposure of the polar core to the toluenic environment [17]. However, the interaction between the polar surface of the citrate-capped gold nanocrystals and the HPEI-C16 can be only rationalized assuming that the unimicelle interacts with the NPs by exposing their cores to the citrate shell. Following this line of reasoning and considering previous reports by other groups [7,15], it would be plausible to suggest that the HPEIC16 + Au NP_{10nm} assembly exhibits a lamellar-like architecture with gold nanoparticles embedded in the hydrophilic domains (Fig. 1).

To date, the formation of structured nanoparticle assemblies has been almost exclusively based on the manipulation of the surface modification of the nanocrystals and the interparticle forces in solution [18,19]. However, the present system poses a completely new scenario in supramolecular organization of nanoparticles. In

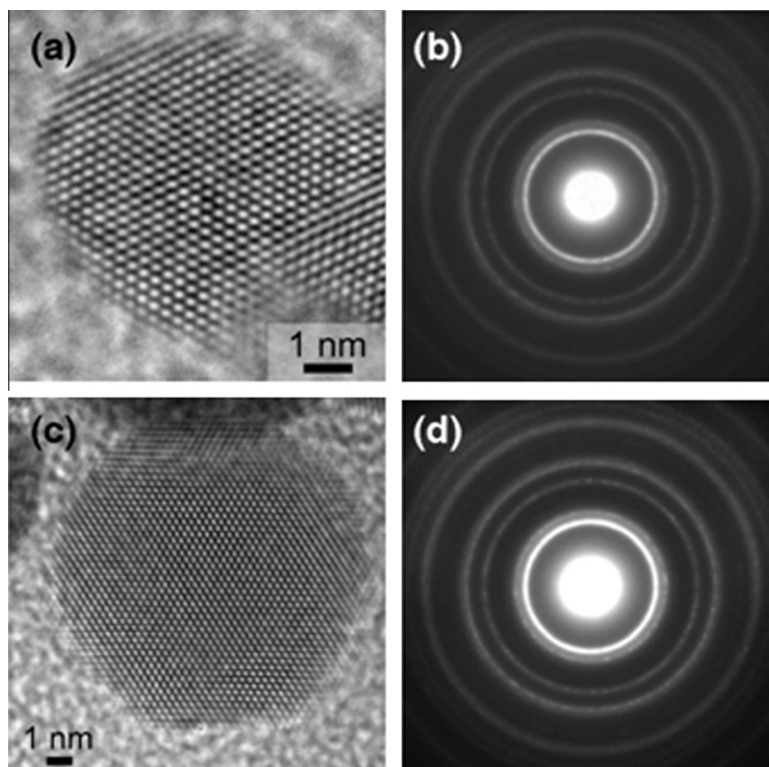


Fig. 2. HR-TEM images and the corresponding diffraction patterns for gold FCC nanocrystals of different dimensions: (a and b) Au NP_{5nm} and (c and d) Au NP_{10nm}.

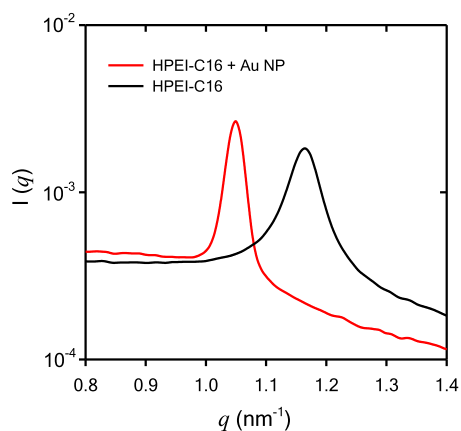


Fig. 3. SAXS data obtained from toluenic solution of HPEI-C16 (black) and HPEI-C16 + Au NP_{10nm} (red).

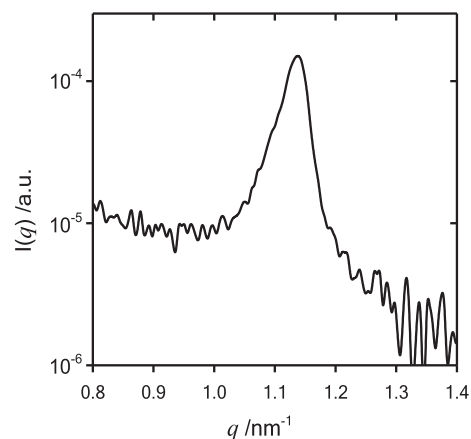


Fig. 4. Raw SAXS data for HPEI-C16 + Au NP_{5nm} deposited on Mylar films.

our case the mechanism is completely different, HPEI-C16 unimicelles arrange themselves to form a supramacromolecular assembly in solution that act as a “soft” nanotemplate for the site-selective incorporation of citrate-capped Au nanocrystals within the self-organized hydrophilic domains. To the best of our knowledge, this is the first example of the use of hyperbranched unimicelles as templates for directing the organization of gold nanocrystals in solution.

In order to evaluate the possibility of transferring the self-organized structures onto flat substrates we assembled HPEI-C16 + Au NP_{5nm} on Mylar films using the drop-casting method. Fig. 4 displays the corresponding SAXS plot obtained in transmission mode. The characteristic Bragg peak indicates that the deposition process do not modify the supramolecular organization existing in solution.

We have recently reported that HPEI-C16 assemblies exhibit negative thermal expansion (NTE) properties, a very rare and unusual behaviour from supramolecular systems [20]. Along these lines, we explored the thermoresponsive properties of HPEI-C16 + Au NP_{5nm} assemblies in order investigate any disruptive effect of the metal nanocrystals on the intrinsic NTE characteristics of the supramolecular template (Fig. 5a). Experimental observation reveals that the position of the Bragg peak is highly dependent on the thermal conditions as well as the interplanar spacing of the composite supramolecular material gradually decreases upon increasing the temperature (Fig. 4b). This implies that the hybrid composite with embedded nanocrystals exhibits NTE properties. The thermally induced structural transformation undergone by the composite is less pronounced than that observed in the NP-free lamellar template provided that coefficients of thermal expansion

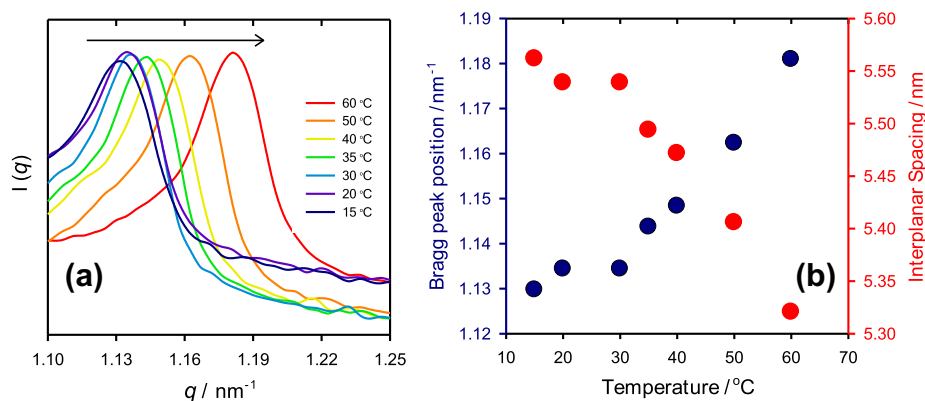


Fig. 5. (a) SAXS plots for HPEI-C16 + Au NP_{5nm} at different temperatures. (b) Bragg peak position and interplanar spacing as a function of temperature.

are $-0.95 \times 10^{-3} \text{ K}^{-1}$ and $-6.5 \times 10^{-3} \text{ K}^{-1}$, respectively. However, this value is comparable to that recently reported by Müllen and co-workers for supramolecular assemblies of nanographenes [21].

3. Conclusions

We have addressed a new strategy in “integrative chemistry” [22] using supramacromolecular assemblies of hyperbranched unimicelles as soft nanotemplates in solution. Straightforward transfer of citrate-capped Au nanoparticles from an aqueous environment to a toluenic solution of amphiphilic hyperbranched polymers results in the spontaneous integration of the nanocrystals into the extended hydrophilic domains of self-assembled supramolecular structures. In this way, we were able to self-organize metal–polymer nanoarchitectures in solution displaying interesting thermoactive functions, i.e.: NTE. This feature is of particular relevance for further application in plasmonics. We envisage that this strategy to generate supramolecular hetero-assemblies will yield new opportunities in materials science provided that it offers an alternative methodology to arrange nanoscale building blocks in predetermined configurations that could lead to supramolecular objects with certain structural complexity.

Acknowledgments

A.S.P. is recipient of a CONICET doctoral fellowship. E.Z., O.A. and M.C. are staff members of CONICET (Argentina). O.A. gratefully acknowledges financial support from the Max Planck Society (Germany), ANPCyT (Argentina, Projects: PICT/PRH 163/08 and PICT-2010-2554). O.A. and M.C. acknowledges Laboratório Nacional de Luz Síncrotron (Campinas – Brazil) (LNLS; Projects: D11A-SAXS1-8575/9108/9868). A.S.P., O.A. and M.C. acknowledge Dr. Carolina Vericat (INIFTA) for kindly providing colloidal gold nanoparticles.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2013.01.004>.

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