Controlled growth of silver nanoparticle arrays guided by a self-assembled polymer–peptide conjugate†

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Controlled formation of silver nanoparticle arrays with high particle density and short interparticle distances was achieved by using supramolecular nanotapes of PEO–oligopeptide conjugates as templates to direct the nucleation and growth of silver nanoparticles either from silver salt solutions followed by photoreduction, or from preformed fluorescent silver nanoclusters.

Silver nanoparticles have been of interest for many years due to their optical, electronical and pharmacological properties. More recently, control of their size, shape and organization has proven to be mandatory for advanced applications, such as light trapping in solar cells.[1–3] Confinement into self-assembled block copolymer microdomains has been used to control the lateral positions of the particles at the characteristic length scales of tens of nm.[4] To further increase the confinement towards the nm scale, more advanced self-assembling building blocks are required to allow smaller structures.[5] In this respect, biological organization motifs are feasible, *e.g.* protein secondary structures allowed recently well-ordered optoelectronic segments by self-assembly which lead to advanced functions.[6–9] In more general, the biological self-assemblies and motifs represent a valuable platform for nm length scale structuring, useful for nanoelectronics.[3] To incorporate silver nanoparticles, diverse routes exist, but typically, rather harsh reaction conditions are involved, such as chemical reductants,[5] organic solvents[10–12] or high temperatures.[13]

Here we show that controlled nucleation and growth of silver nanoparticles (AgNPs) in ordered one- and two-dimensional arrays can be directed by supramolecular nanotapes which have been assembled from an oligomeric block copolymer consisting of polyethylene oxide (PEO) conjugated with two short peptide chains (Val-Thr-Val-Thr-dimethylGly) (Fig. 1), subsequently denoted as PEO–peptide conjugates. PEO–peptide conjugates with preorganized peptide strands self-assemble into highly stable nanotapes (Fig. 1) with a peptide core forming a β-sheet (cyan), and a PEO shell (grey). The nanostructured tapes stack to double-tapes (ribbons).[14,15] Similar to proteins in biological systems the biomimetic PEO–peptide nanotapes fulfill multiple tasks as they limit the growth, prevent agglomeration and guide the organization of the AgNPs.

The organic–inorganic nanocomposites were prepared by using two different strategies, *i.e.* by *in situ* growth of the AgNPs during irradiation of silver salt solutions on the nanotape template, or by transfer of fluorescent silver nanoclusters consisting of 2–3 Ag atoms (AgFNC) into the nanotapes. In both cases, high particle densities could be achieved in water at room temperature, without significant aggregation and without the use of chemical reducing agents.

Within the first route, an aqueous solution of $AgNO_3$ is simply added into the aqueous medium containing the PEO–peptide tapes, which leads to adsorption of the Ag salts to the tapes, probably due to the high attraction of silver for peptides. Subsequent irradiation with visible light reduces the silver ions to metallic silver. As will be shown in this paper, one- and two-dimensional AgNP arrays are formed by using the nanostructured PEO–peptide ribbons as template.

In TEM images recorded at lower magnification, a highly branched network-like structure composed of bundles of the organic–inorganic nanocomposite can be observed (Fig. 2a). Such behavior is consistent with a recent small-angle neutron scattering study investigating the solution behavior of the PEO–peptide nanostructures.[16] Due to their high persistence length and probably additional attractive secondary interactions, the nanotapes exhibit a high tendency to form nematic bundles.[16] Higher magnification images of thinner sample regions elucidate the inner structure of the organic–inorganic composite bundles. Interestingly, the bundles of PEO–peptide conjugates contain AgNPs of about roughly 7–12 nm in diameter (Fig. 2b) and effectively confine the AgNPs. Thus it is likely that AgNPs nucleate and grow within the organic PEO–peptide nanotapes forming to a certain extent an assembly of discrete nanoparticles along the double-tapes.

The organic template obviously controls the formation of silver aggregates by preventing that neighboring nanoparticles fuse together to form larger nanoparticles or nanowires (Fig. 1c and 2b). Lower initial silver concentration and shorter irradiation time result in smaller AgNPs (<3 nm) organized in parallel rows (Fig. 2c), that resemble the shape of a bundle of linear double-tapes, confirming that AgNPs grow guided by the arrangement of the PEO–peptide conjugate structure. The one-dimensional array of AgNPs, shown in Fig. 2d, is less abundant than AgNPs in parallel rows, but it further proves the organized linear distribution of nanoparticles of uniform size in the peptide core of the double-tapes (Fig. 1b). Although there are several publications describing the synthesis of AgNPs in PEO,[17–19] the higher affinity of peptides for silver[20] suggests that AgNPs are formed in the peptide core instead of in the PEO shell. Furthermore, the presence of a single linear deposition of nanoparticles in isolated double-tapes suggests that nanoparticles might potentially be located in the core of the tape,

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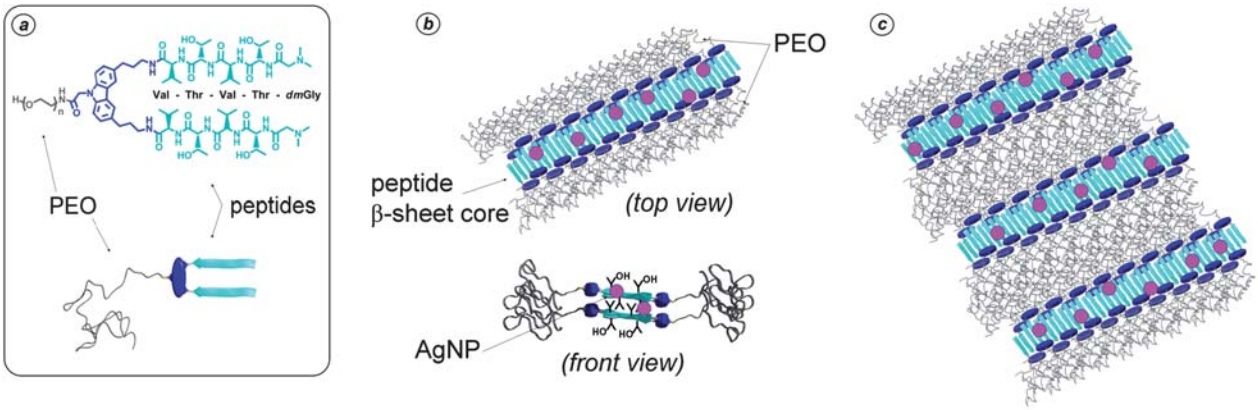

Fig. 1 Schematic representation of (a) PEO–peptide conjugate. (b) PEO–peptide double-tape constructs with a β-sheet peptide core (cyan) and a PEO shell (grey) and AgNPs (pink). (c) Stacks of (b).

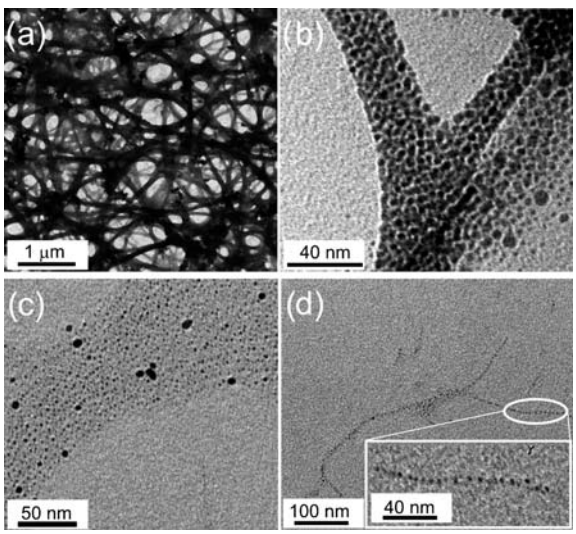

Fig. 2 Arrays of AgNPs prepared from PEO–peptide nanotapes and silver salt solutions followed by photoreduction. The samples in (a) and (b) were synthesised using $[AgNO_3] = 0.47$ M and 2 hours of irradiation. (a) Net of planar bundles of PEO–peptides double-tapes containing AgNPs. (b) Higher magnification showing AgNPs assembled in arrays. The samples in (c) and (d) were synthesised using $[AgNO_3] = 0.28$ M and 1 hour of irradiation. (c) AgNPs assembled in arrays. (d) One-dimensional arrangement of AgNPs in a single PEO–peptide double-tape.

otherwise two lines of nanoparticles should be seen, corresponding to the two PEO sides of individual double-tapes (Fig. 2d, inset).

The second route incorporates transfer of silver nanoclusters on the template. Fluorescent silver nanoclusters (AgFNCs) are species of only 2 or 3 atoms in size, and they exhibit strong absorbance and luminescence due to quantized electronic transitions.[21] Planar arrays of silver nanoparticles can be also formed using fluorescent silver nanoclusters as precursor.

This synthesis required two steps, first the generation of AgFNC in poly(methacrylic acid) (PMAA) (described elsewhere[21]) and secondly the insertion of nanoclusters into double-tapes. When a solution of PEO–peptide nanotapes and a solution of AgFNC are mixed, the nanoclusters spontaneously incorporate into the double-tapes (Fig. 3a and b). TEM images were recorded right after mixing, without irradiation, suggesting that the silver nanoparticles in the arrays are the result of a controlled aggregation of the few-atom silver nanoclusters in double-tapes. Larger silver nanoparticles can be found along the borders of the bundles and in the junctions between bundles. Free silver ions contained in the nanocluster solution do not play a role in the formation of the nanoparticles due to the absence of irradiation or chemical reductant. A control experiment by mixing PEO–peptide nanotapes and silver ions demonstrates that no AgNPs form in the nanotapes without irradiation.

The formation of arrays does not occur by clusters settling down onto the nanotapes during preparation (drying) of the TEM grid but it may rather occur in solution due to the higher affinity of silver for peptides[20] compared to poly(methacrylic acid). The attraction of

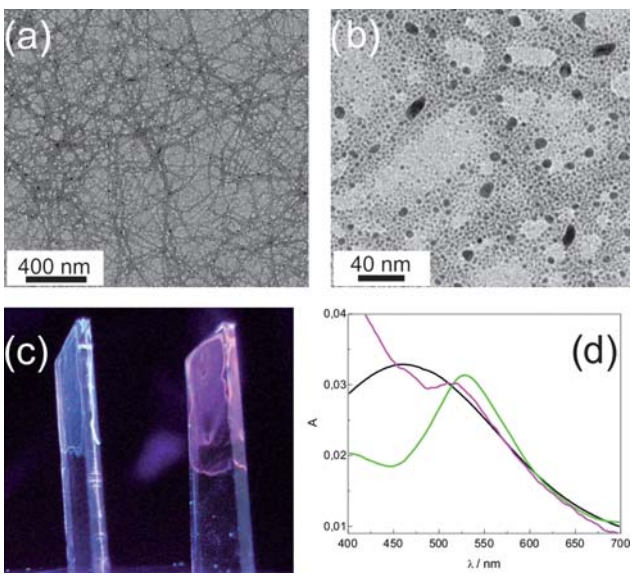

Fig. 3 Arrays of AgNPs prepared from PEO-peptide nanotapes and preformed fluorescent silver nanoclusters. (a) Net of bundles of PEO–peptide double-tapes containing AgNPs. (b) Higher magnification showing AgNP arrays. (c) PEO–peptide film before (left) and after (right) dipping in a AgFNC solution. (d) Absorption spectra of a solution prepared by irradiation of silver salt in the presence of PEO–peptide, for $[AgNO_3] = 0.28$ M and 1 hour of irradiation (black, first approach); a solution of AgFNC formed in PMAA (green, reactant in second approach); and a solution prepared by mixing PEO–peptide with AgFNC (pink, second approach).

silver nanoclusters for peptides was demonstrated by dipping a cast film of PEO–peptide nanotapes into a AgFNC solution for 24 hours followed by thorough rinsing in water. The image of the rinsed film under UV illumination clearly shows that the film contains fluorescent pink AgFNC (Fig. 3c).

Films of PEO–peptide/silver were differently prepared when compared to the silver NP arrays in solution. The film was prepared by using a more concentrated starting solution. Furthermore, in solution the spontaneous assembly occurs rapidly after mixing whereas in the film, due to the lack of mobility of the components, the assembly occurs slowly. Even though the film and solution are different systems, it is reasonable to assume that if the PEO–peptide/silver film shows such strong luminescence due to bound AgFNC, the PEO–peptide/silver solution must contain both AgNPs (as shown in Fig. 3a and b) and AgFNCs.

The absorption spectrum of PEO–peptide/AgNPs solution prepared in the first approach shows a broad peak centered at ~465 nm assigned to AgNPs (Fig. 3d). The spectrum of AgFNC formed in PMAA (the precursor in the second approach) presents a narrow peak located at ~528 nm. Curiously, the spectrum of the solution prepared by mixing PEO–peptide with AgFNC (second approach) presents two features, one small peak centered at ~463 nm that corresponds to AgNPs, and another peak at ~517 nm that could correspond to AgFNC bound to PEO–peptide nanotapes. The blue shift in the absorption maxima of AgFNC in PEO–peptide compared to the starting AgFNC solution could be due to the migration of silver nanoclusters from a PMAA template to a peptide template, taking into account that the optical properties of AgFNC are quite sensitive to environmental changes.[21,22]

In summary, we demonstrated a simple method for the formation of well ordered arrays of silver nanoparticles with high particle density using a PEO–peptide conjugate as self-assembled nanoscale template for the nucleation and growth of the nanoparticles. We foresee that this approach is expandable to other types of templates with two or more blocks interacting dissimilarly with metal ions.

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