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Functional silsesquioxane-based hierarchical assemblies for antibacterial/antifungal coatings

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The paper reports the first study on functional silsesquioxane-based hierarchical assemblies containing an ordered distribution of silver nanoparticles with a high amount of {111} facets, obtained through sol-gel reaction, intended for antibacterial/antifungal coatings.

Last years, the fabrication of hierarchically structured materials containing both micro- and nanoscale features has received an increased attention. Such structures can enhance the structural functionality of the material and may lead to distinct and improved properties as compared to the individual length scale structures, being used as a tool to understand the phenomena that might have a size effect. The controlled design of hierarchical assemblies leads to applications in advanced catalysts, biosensor arrays, micro/nanofluidics, photonic and electronic devices.[1] Hierarchical architectures were obtained through various approaches such as polymer directed self-assembling, oriented aggregation of nanoscale building units, biomimetic mineralization, as well as hard- and soft-templating synthesis.[2]

Although many studies on the obtaining of hierarchical structures with special morphologies were published last years, only few papers were focused on their properties/usability.[3] The present paper reports the formation of hierarchical structures (nanowires and rod-type nanostructures confined within semi-cylindrical shells of micrometric dimensions) *via* controlled, evaporative self-organization of two silsesquioxane-based hybrid nanocomposites with methacrylate units containing titanium and/or silver nanoparticles. The resulted materials contain silver nanoparticles with a high amount of {111} facets and are aimed for antibacterial/antifungal coatings. The ordered distribution of highly faceted silver nanoparticles on material surface is supposed to be the effect of the well-defined polymer architectures self-assembling in the presence of dodecylamine surfactant, completed by the development of specific interactions between polymer structure and silver nanoparticles in the reaction conditions. The synthesis, characterization and illustration of antibacterial/antifungal activity of the above-mentioned polymers against *Escherichia coli* and *Candida albicans* were previously reported.[4] However, details on the formation of hierarchical assemblies or an analysis of the high antibacterial activity and its relation with the specific structural and topographical features of the material were not published. As known, the antibacterial activity of silver nanoparticles depends not only on their size,[5] but also on their shape[6] and aggregation level,[7] the generation of large, spacious aggregates leading to a loss of the antibacterial activity. To our knowledge, no report on the obtaining of functional hierarchical structures containing an ordered distribution of silver nanoparticles with high-atom-density facets through a cost-effective preparation method, i.e., a sol-gel reaction, has been previously published.

The here reported hierarchical self-assembling process was evidenced by SEM (Fig. 1). In the investigated systems the self-assembling is organized in two levels, i.e., nano and micro. SEM images of the silsesquioxane-based hybrid nanocomposite with silver content (POSS-Ag) (Fig. 1(a) and (b)) show a structure characterized by a short-range order, i.e., nanoparticles oriented perpendicularly to the nanowires with a local orientation ordering, while for the silsesquioxane-based hybrid nanocomposite with titanium and silver units (POSS-AgTi) the rod-type nanostructures (average diameters of 170 – 270 nm/rod) are oriented parallel to shell "ribs" (Fig. 1(c) and (d)).

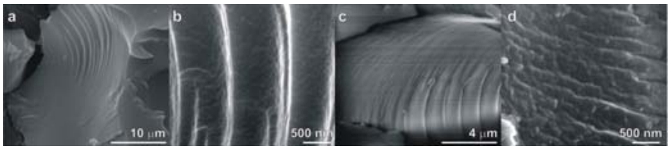

Fig. 1 (a, b) SEM images of POSS-Ag. (c, d) SEM images of POSS-AgTi.

Moreover, in the latter case one may observe the rods polyhedral structure at one extremity. A previous paper reported the formation of similar silsesquioxane networks, i.e., nanofibrils confined within semi-cylindrical shells, therefore one may conclude that the specific morphology of hierarchical assemblies is solely the result of the presence of silsesquioxane units,[3b] without any influence of silver nanoparticles.

TEM images of droplets of POSS-Ag subjected to slow evaporation on Cu grids after the reduction process show the presence of rhombohedral (hexagonal) silsesquioxane clusters (4-20 nm, Fig. 2(a) and (b)) which self-assemble into two types of co-existing structures, i.e., comb-like nanowires (with diameters of ~ 25 nm, Fig. 2c) and large worm- or strut-like segregated nanophase regions (hexagonal structures of around 100 nm in diameter size, Fig. 2d) stabilized by the surfactant. Both silsesquioxane-based hybrid nanocomposites act as templates for the most likely octahedral silver nanoparticles with dimensions of 4-7 nm (Fig. 2(a) and (d)) evidence for silver nanoparticles a large contrast between the centres and the edges, thus suggesting that these ones are rather octahedrons than flat rhombus). The existence of both attraction and repulsive interactions between several functional groups belonging to polymer network may be considered responsible for the formation of the molecular clusters similar to block copolymers, thus inducing the phase separation of the components.[8] For POSS-AgTi, star- or mats-like (highly ordered nanorods of around 4 nm in diameter and 200 nm length) and ordered cubic structures with nanometer-sized domains can be observed in TEM images (Fig. 2(e) and (f)). Moreover, one hexagonal silver nanoprism that directs toward the surface of a larger silsesquioxane particle (Fig. 2g), as well as the appearance of twin triangular silver nanoparticles (overlapped on one corner) with sharp vertices that practically cover the core of POSS-AgTi surface (Fig. 2h) may be observed. The hexagon diameter is identical to the size of the triangular structures, i.e., around 30 nm, thus suggesting that all triangular silver nanoparticles are in fact hexagonal nanoprisms. The formation of the strut hexagonal structure (POSS-Ag) can be related to the retarded velocity of mesophase formation *vs.* polycondensation in solvent-deficient conditions, while the cubic one (POSS-AgTi) is favoured by the presence of a higher amount of solvent (higher affinity of titanium precursor for the hydroxyl groups from isopropyl alcohol).

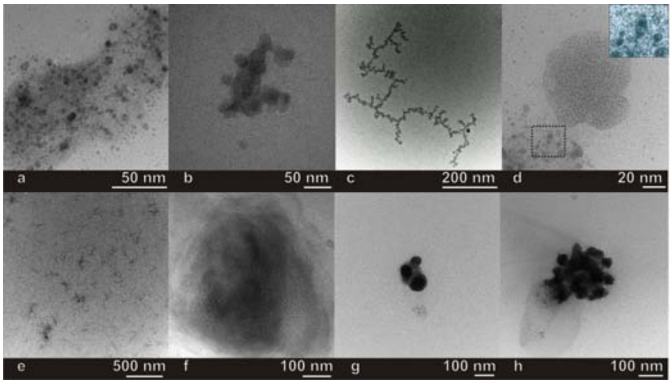

Fig. 2 TEM images of POSS-Ag. (a, b) hexagonal silsesquioxane clusters. (c) comb-like nanowires. (d) worm-like nanophase region. TEM images of POSS-AgTi. (e) star-like nanorods. (f) cubic structure. (g) orientation of one hexagonal silver nanoprism toward the surface of a silsesquioxane particle. (h) formation of twin triangular silver nanoparticles (overlapped on one corner) with sharp vertices onto the surface of a larger silsesquioxane particle.

For both synthesized compounds, AFM evidences the presence of triangular-shaped silver nanoparticles (Fig. 3). For POSS-Ag, one can observe at 500 nm scale the co-existance of both lamellar-like silsesquioxane nanorods formed by the mutual affinity of silsesquioxane nanowires (long range order) and a pyramidal structure of silver nanoparticles which starts to grow on a silsesquioxane structure (Fig. 3a). At a larger scale (1 µm), the coverage of all silsesquioxane-based nanorods with truncated triangular shape silver nanoparticles can be seen (Fig. 3b). As for POSS-AgTi, one may observe the appearance of twin triangular shape silver nanoparticles with sharp vertices organized on the top of silsesquioxane nanorods only at the 5 µm scale (Fig. 3f).

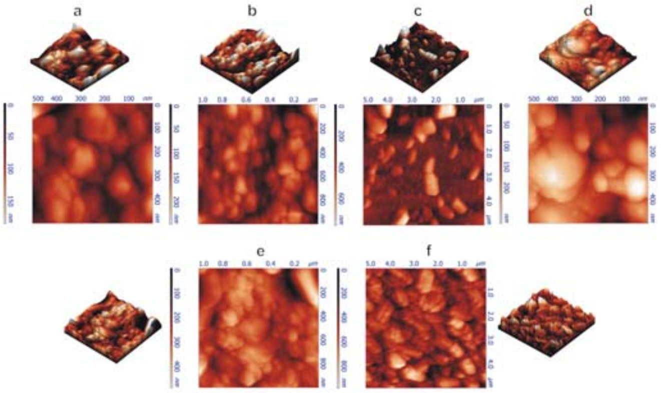

Fig. 3 AFM images of POSS-Ag at different scales. (a) 500 nm. (b) 1 µm. (c) 5 µm. AFM images of POSS-AgTi at different scales. (d) 500 nm. (e) 1 µm. (f) 5 µm.

Besides the characteristic peaks of crystalline and amorphous units due to the polymeric moiety,[4] the XRD patterns of POSS-Ag and POSS-AgTi (Fig. S1†) revealed the presence of two peaks at $2\theta = 38.2°$ and 44.1°, respectively, corresponding to {111} and {200} crystalline planes of face-centered cubic (fcc) silver. Moreover, the intensity ratio of {200} to {111} diffraction peaks is 0.47, a lower value than the bulk intensity ratio, i.e., 0.52, thus suggesting that the (111) plane is the main predominant orientation at the hybrid materials surface.

XPS results revealed no interaction between silver and amine groups from dodecylamine (Fig. S2†, Tab. S1†), probably due to the protonation of the latter ones, yielding a reduced number of available binding sites. Moreover, the shift of the binding energy of C=O groups from both silsesquioxane-based polymers as compared to the standard O1s binding energy of C=O units was attributed to the electrostatic interaction between the oxygen and the surface of silver nanoparticles.

The combination of the sol-gel reaction with the molecular self-assembling process induced by solvent evaporation, as well as the nucleation of silver nanoparticles yielded the formation of new types of silsesquioxane methacrylate-based hybrid nanocomposites containing titanium and/or silver nanoparticles. The two levels of hierarchical morphology (nanowires and rod-type nanostructures confined within the polymeric semi-cylindrical shells of micrometric dimensions) have been ascribed to a combination between self-assembly of the mesophases, controlled phase separation, sol-gel transitions and stabilization of silver nanoparticles through electrostatic interaction. In the present study, the initial homogeneous solutions containing titanium and/or silica precursors, dodecylammonium nitrate in an amount below cmc and isopropyl alcohol – water mixture undergo a preferential evaporation. During isopropyl alcohol evaporation, mesophases self-assembling and controlled phase separation take place simultaneously. Due to solvent evaporation, a progressive increase of surfactant concentration above cmc and the manifestation of both attraction and repulsive interactions occur simultaneously. The ordered assembled structures are the result of the hydrogen bonds acting between hydroxyl and carbonyl groups, close-packing of the resulted structures *via* Van der Waals interactions and self-assembling of the ordered bulky pendant silsesquioxane units. In time, the cooperative self-assembling of the involved species, i.e., the silica-surfactant molecular clusters, dodecylammonium nitrate and silicate polyanions can be taken into account, directing the reactions toward the formation of silica-surfactant structures with hexagonal (POSS-Ag) or cubic (POSS-AgTi) order, as well as comb- or star-like structures. The association of these structures (building blocks) decreases the degree of structures conformational freedom and directs the reaction pathway to predictable hierarchical structures where the morphology of the final hybrid nanocomposites resembles the characteristic shape of the building blocks. As follows, the POSS-Ag comb-like structures start to associate into small bundles of nanofibrils that are repeating at equal distances from one another, "stacking" between these ones several associated hexagonal polymer structures. In a similar manner, the final organization of POSS-AgTi into rod-type nanostructures can be related to the attachment of star-like assemblies in cubic polymer matrix, followed by the preferential attachment of twin silver nanoparticles on top of the polymeric structure.

The kinetics of the growth of metal nanoparticles in solution is influenced by the concentration of the metal precursor, the rate of its reduction, the presence of capping agents or soft templates, as well as the adsorption of the capping agents to specific crystallographic planes.[9] In the initial stage, colloidal silica prepared through acid-catalyzed sol–gel reaction promotes the reduction of Ag+ ions into Ag atoms that are further agglomerated into small clusters. Through addition or random combination of these clusters, Ag nanoparticles are growing from the initial seeds. Most likely, the specific interactions between the carbonyl groups, the hydrophobic silsesquioxane nanophases and Ag^0 atoms represent the driving force of this step. Taking into account the octahedral shape of silver nanoparticles in POSS-Ag, i.e., the octahedrons fully covered with {111} facets with diameters of 4 – 7 nm (Fig. 2c), one may assume that these ones evolve from a cubooctahedral shape seed, the optimal shape of a free fcc metal crystal.[10] The truncated pyramidal shape of silver nanoparticles, characterized by an increase of the lateral diameters of the exposed four facets (around 90 nm, Fig. 3a), can be correlated with the selective adsorption of silsesquioxane-based polymer at the {100} facets of silver plane,[11] the bottom of the initial bi-pyramidal structure being incorporated into the polymeric template. Further nucleation of silver nanoparticles yields the formation of short silver nanowires (Fig. 3b) due to a preferential deposition of reduced silver atoms onto the {111} silver planes[12] and to the enlargement of the total area of {100} silver facets stabilized by the adsorption of the silsesquioxane-based polymer (Fig. 4a).

For POSS-AgTi, the formation of silver nanostructures in the form of twin hexagonal nanoprisms (overlapped on one corner) with sharp vertices, surrounding POSS-AgTi aggregates surface was evidenced (Fig. 2f). The hexagonal shape can be correlated with the fast and uniform growth of all lateral directions along the twinning defects during nanoclusters aggregation.[13] The initial silver nanoprisms are formed in the star-like structures made by the superposition of silsesquioxane nanorods (Fig. 2e). Furthermore, silsesquioxane nanophases are hindering further silver aggregation and crystal growth, thus inducing a control of the assembling. More specifically, the silsesquioxane-based hybrid nanocomposite selectively adsorbs on the specific {100} facets of silver planes, this process being followed by the reduction of Ag+ at specific crystallographic planes of Ag nuclei, without or with less adsorbed silsesquioxane-based hybrid nanocomposite, the final anisotropic growth of silver nuclei toward hexagonal nanoprisms being evidenced (Fig. 4b). The lack of influence of POSS-AgTi on the growth of initial silver hexagonal nanoprisms (as compared to the influence of POSS-Ag on the growth of silver octahedrons) of these types of structures may be related to the catalytic effect of titanium toward the reduction of silver precursor.

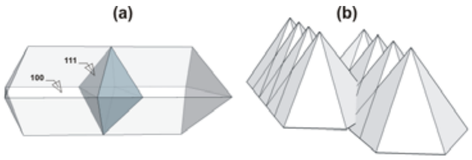

Fig. 4 Nucleation of silver nanoparticles. (a) octahedron silver nanowires in POSS-Ag. (b) twin hexagonal nanoprisms in POSS-AgTi.

The hexagonal silver nanoprisms are mainly composed of flat (111) crystals facets, while the edges contain either (100), (110) or (112) facets.[14] Considering the presence of specific crystallographic planes determined through XRD analysis, the carbonyl group affinity toward the (100) silver plane and the overlapping of the silver nanoprisms on one corner, one may assume that only one edge of these structures is mainly composed of a (100) facet to which silsesquioxane-based hybrid nanocomposite is selectively adsorbed. Therefore, although POSS-AgTi has a smaller influence on the growing of silver nanoprisms, it plays an important role in establishing the final morphology. The appearance of silver nanoprisms can be evidenced on the top of the silsequioxane rods only at a higher scale (Fig. 3f), this suggesting that the self-assembling of POSS nanorods based star-like structures incorporating silver nanoprisms and the formation of silsesquioxane rods based on the cubic polymer matrix are occuring in parallel. This process ends with the preferential attachment of the new polymer structures covered by silver nanoprisms to the silsesquioxane rods. One can conclude that both silsesquioxane-based hybrid nanocomposites act, on one hand, as "soft templates" to direct the anisotropic growth of silver nanoparticles, and on the other hand, as shape-directing agents. Previous reports on the role of polyvinylpirrolidone, a polymer bearing carbonyl groups, evidenced that this one does not play a shape-directing role in the synthesis of silver nanoprisms, rather slowing the nanoprism development and preventing their aggregation.[15] Due to the binding affinities of both compounds toward the {100} silver planes (shape control by making some facets of silver nanoparticles thermodynamically more favorable), one may consider that both silsesquioxane-based hybrid nanocomposites (together with process conditions) influence the shape and the final size of silver nanoparticles, preventing their aggregation, as well.

Both silsesquioxane-based hybrid nanocomposites proved to be active against a Gram-positive bacterium (*Staphylococcus aureus*), a Gram-negative bacterium (*Escherichia coli*) and a fungus (*Candida albicans*) (Fig. S3†, Tab. S2†). The results indicate that the POSS-AgTi coatings were more likely to display a higher antibacterial/antifungal activity (larger inhibition zone for *Candida albicans* and *Escherichia coli*, respectively, and an inhibition zone similar to the one exerted by POSS-Ag for *Staphylococcus aureus*). Therefore, besides a higher activity of POSS-AgTi, one may take into account a specific action as a function of bacteria/fungus type. Since all antibacterial/antifungal experiments were performed without UV activation and POSS-AgTi presented no visible-light photocatalytic activity (UV photocatalytic activity, Fig. S4†, Scheme S1†), a synergetic effect of several factors can be considered for both compounds. Among the factors that may influence the improvement of POSS-AgTi antibacterial/antifungal ability one can mention the presence of a higher amount of metallic silver at the surface, the enhancement of TiO_2 photocatalytic activity with silver loading, the shape of Ag nanoparticles and the topographical features of the coating. XPS measurements evidenced a higher amount of metallic silver at POSS-Ag surface (Ag^0 – peak area: 96.82 % and 85.70 % for POSS-Ag and POSS-AgTi, respectively), therefore the solely action of metallic nanosilver cannot be taken into account for the higher antibacterial/antifungal activity of POSS-AgTi. Moreover, due to the detrimental effect of silver on anatase photoactivity, the active sites of TiO_2 are blocked and therefore a lack of anatase influence on POSS-AgTi antibacterial ability is to be expected. As for the interaction of silver nanoparticles of different shapes with bacteria, the combination of both nanoscale dimensions and the presence of {111} high-atom-density lattice plans leads to a higher antibacterial activity.[13] In this study, both types of silver nanoparticles present a high percentage of {111} facets. In a similar manner, one cannot attribute the higher antibacterial/antifungal activity of POSS-AgTi only to the presence of the {111} lattice plans belonging to the specific shape of silver nanoparticles. Within this context, one may speculate that the sharp twin vertices can easily penetrate the bacteria cell membrane and can provide a larger contact area, thus contributing to the higher antibacterial/antifungal activity of POSS-AgTi. Moreover, considering the relative diameters of the nanowires (27 - 55 nm) associated into small fibre bundles (130 - 200 nm) and rod-type nanostructures (170 - 270 nm/rod), one expects a higher adhesion and interaction between POSS-AgTi nanostructures and bacteria, since several measurements of the adhesive forces between different nanofibers and probes evidenced the growth of the adhesion forces with increasing nanofiber diameter.[3b] The decreased bacterial area extension for POSS-AgTi may be induced by the reduced number of contact points (disconnected focal adhesion) due to the topography of the rods (covered with twin hexagonal silver nanoprisms). For POSS-Ag, the silver nanoparticles are closely interconnected, this leading to an increased number of contact points that might yield a higher bacterial adhesion. One may further consider the influence of the air trapped between the two length scale features that contributes to the limitation of the contact area between bacteria and surface coatings.[3b]

The analysis of average pore size evidenced that both silsesquioxane-based hybrid nanocomposites are microporous (1.43 nm – POSS-Ag; 1.52 nm – POSS-AgTi). The pores are too small to allow the adhesion of *Escherichia coli* (~ 0.5 – 3 μm), *Staphylococcus aureus* (~ 0.6 - 1 μm) and *Candida albicans* (~ 2 - 8.5 μm).[3b] Moreover, the microporous coatings allow the material to "breath" – moisture traces can circulate freely while impeding the atmospheric water to penetrate through the coating. Both silsesquioxane-based coatings contain microporous and hydrophobic networks (Fig. S5†), and therefore the adherence of bacteria is significantly hindered.

Conclusions

The formation of hierarchical assemblies has been ascribed to a combination of self-assembling of mesophases, phase separation, sol-gel transitions, and stabilization of silver nanoparticles through electrostatic interaction. Due to the presence of carbonyl groups, silsesquioxane-based hybrid nanocomposites influence the shape and the final size of silver nanoparticles by acting both as "soft templates" and shape-directing agents. This leads to an ordered distribution of highly {111} faceted silver nanoparticles of pyramidal structures with triangular appearance. Their antibacterial/antifungal properties toward *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* were studied in aqueous solution and were found to be mainly influenced by the topographical features, the specific shape of silver nanoparticles and the microporous nature of the coating. Despite the absence of photocatalytic activity in the visible domain, the silsesquioxane-based hybrid nanocomposite with titanium and silver content exhibits a similar or even higher antibacterial/antifungal activity as compared to the one containing only silver.

Notes and references

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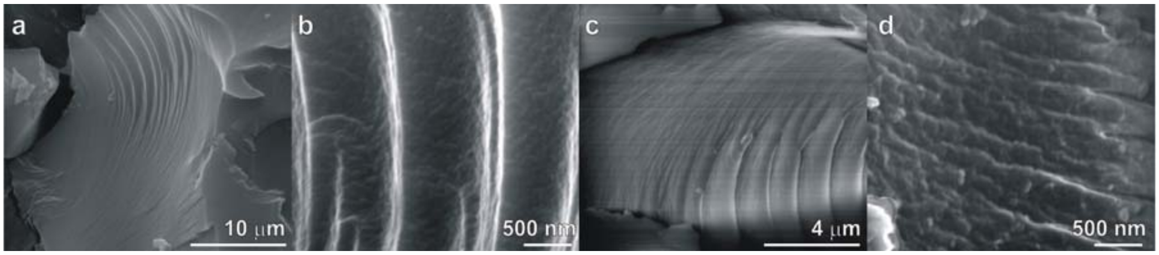
1 (a) A. Boker, Y. Lin, K. Chiapperini, R. Horowitz, M. Thompson, V. Carreon, T. Xu, C. Abetz, H. Skaff, A. D. Dinsmore, T. Emrick and T. P. Russell, *Nat. Mater*., 2004, **3**, 302; (b) C. Wang and Y. Zhang, *Adv. Mater.*, 2005, **17**, 150.
2 (a) H. T. Shi, L. M. Qi, J. M. Ma and H. M. Cheng, *J. Am. Chem. Soc*., 2003, **125**, 3450; (b) Z. P. Zhang, H. P. Sun, X. Q. Shao, D. F. Li, H. D. Yu and M. Y. Han, *Adv. Mater.,* 2005, **17**, 42; (c) H. Cöfen and S. Mann, *Angew. Chem. Int. Ed*., 2003, **42**, 2350.
3 (a) X. Zhu, L. Wang and J. Lin, *Macromolecules*, 2011, **44**, 8314; (b) B. Simionescu, I. E. Bordianu, M. Aflori, F. Doroftei, M. Mareş, X. Patras, A. Nicolescu and M. Olaru, *Mat. Chem. Phys*., 2012, **134**, 190; (c) X.-S. Zhang, F.-Y. Zhu, M.-D. Han, X.-M. Sun, X.-H. Peng, H.-X. Zhang, *Langmuir*, 2013, **29**, 10769.
4 M. Aflori, B. Simionescu, I.-E. Bordianu, L. Sacarescu,C.-D. Varganici, F. Doroftei, A. Nicolescu and M. Olaru, *Mat. Sci. Engineer. B*, 2013, **178**, 1339.
5 C. Carlson, S. M. Hussain, A. M. Schrand, L. K. Braydich-Stolle, K. L. Hess, R. L. Jones and J. J. Schlager, *J. Phys. Chem. B*, 2008, **112**, 13608.
6 S. Pal, Y. K. Tak and J. M. Song, *Appl. Environ. Microbiol.*, 2007, **73**, 1712.
7 C.-N. Lok, C.-M. Ho, R. Chen, Q.-Y. He, W.-Y. Yu, H. Sun, P. K.-H. Tam, J.-F. Chiu and C.-M. Che, *J. Biol. Inorg. Chem.*, 2007, **12**, 527.
8 U. Scubert and N. Hüsing, in Synthesis of Inorganic Materials, John Wiley & Sons, 2005.
9 (a) R. C. Jin, Y. W. CaO, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901; (b) S. Chen and D. L. Carroll, *Nano Lett.*, 2002, **2**, 1003.
10 A. Tao, P. Sinsermsuksakul and P. Yang, *Angew. Chem. Int. Ed.*, 2006, **45**, 4597; (b) Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176.
11 A. Tao, P. Sinsermsuksakul and P. Yang, *Angew. Chem. Int. Ed.*, 2006, **45**, 4597.
12 N. R. Jana, L. Gearheart and C. J. Murphy, *Chem. Commun.*, 2001, **7**, 617.
13 G. P. Lee, A. I. Minett, P. C. Innis, G. G. Wallace, *J. Mater. Chem.*, 2009, **19**, 8294.
14 J. E. Millstone, Synthesis, Properties, and Applications of Colloidal Gold Nanoprisms, Dissertation thesis, Illinois, USA, 2008, p. 29.
15 (a) C. M. Cobley, M. Rycenga, F. Zhou, Z.-Y. Li and Y. Xia, *Angew. Chem., Int. Ed.*, 2009, **48**, 4824; G. S. Metraux and C. A. Mirkin, *Adv. Mater.* 2005, **17**, 412.



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