Nanostructures

Aligning Au Nanorods by Using Carbon Nanotubes as Templates**

*Miguel A. Correa-Duarte, Jorge Pérez-Juste, Ana Sánchez-Iglesias, Michael Giersig, and Luis M. Liz-Marzán**

One of the most exciting challenges in modern chemistry and materials science is the manipulation and assembly at the nanoscale.[1] This is particularly interesting since the properties of the nanomaterials are dependent on their aggregation state, and thus collective properties are in general different from the properties of single nanoparticles.[2] A clear example of such sensitivity to aggregation and interparticle distance is found in metal nanoparticles, which display peculiar optical properties as a result of surface plasmon resonance phenomena.[3] The resonance conditions depend on a number of parameters, such as particle size and shape, surface charge, and the nature of the dielectric environment, but also on interparticle coupling when the separation is small.[4] Furthermore, the formation of anisotropic nanoparticles and assemblies provides a new way to control the optical response through the selective excitation of longitudinal or transverse plasmon modes by polarized light.[5]

The formation of strings of metal nanoparticles in general,[6–8] and metal nanorods in particular,[9,10] has recently attracted a great deal of attention, since such assemblies have

[*] Dr. M. A. Correa-Duarte, Dr. J. Pérez-Juste, A. Sánchez-Iglesias, Prof. L. M. Liz-Marzán
Departamento de Química Física
Universidade de Vigo
36310 Vigo (Spain)
Fax: (+34) 986-812-556
E-mail: lmarzan@uvigo.es
Prof. M. Giersig
Center of Advanced European Studies and Research (CAESAR)
Ludwig-Erhard-Allee 2, 53175 Bonn (Germany)

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potential uses as waveguides that would allow the miniaturization of devices below the diffraction limit[11] and as catalytic motors.[12]

Herein we present the formation of strings of Au nanorods by using multiwall carbon nanotubes (MWNTs) as templates. The use of MWNTs to template the assembly of aligned nanoparticles is not new,[8] but this is the first example in which the nanorods are assembled with a preferential stringlike alignment. The resulting nanocomposites show broadened absorption bands, as a result of end-to-end plasmon coupling between neighboring nanorods. Additionally, the nanorods can serve as a label to monitor the alignment of carbon nanotubes within polymer films, as demonstrated through optical absorption measurements on stretched poly(vinyl alcohol) (PVA) films loaded with the nanocomposite arrays.

The formation of the aligned composites is based in the polyelectrolyte layer-by-layer (LBL) approach,[13,14] which has been recently applied to assemble silica-coated gold nanoparticles on MWNTs.[8] Gold nanorods were synthesized by the seed-mediated procedure recently published by Nikoobakht and El-Sayed,[15] and the surfactant (cetyl trimethylammonium bromide, CTAB) was exchanged with poly(vinylpyrrolidone) (PVP) to clean the colloid (remove excess surfactant) and reverse the surface charge.[16] Prior to the assembly of nanorods, the MWNTs were wrapped with a negatively charged polyelectrolyte (polystyrene sulfonate, PSS), followed by electrostatic assembly of a positively charged polyelectrolyte (poly(diallyldimethyl) ammonium chloride, PDDA). PSS has been shown to adsorb on MWNTs as a result of suppression of the hydrophobic surface.[17] Once this first (charged) monolayer had been deposited, the standard LBL procedure could be applied.

Figure 1 shows TEM images of Au nanorods assembled on MWNTs at various magnifications. The low-magnification image (Figure 1 a) shows that the assembly is extremely uniform over long distances in the whole sample, while the higher magnification images (Figure 1 b,c) show the high degree of alignment of the nanorods, which in general form stripes, though defects (rods with different orientation) are also observed. It is interesting to note that there is a clear tendency for the particles to align in stripes on opposite sides of the MWNTs, rather than uniformly covering the surface (even though a large excess of nanorods was used) and aiming to achieve maximum coverage. Similar images were obtained for the assembly of nanorods with different aspect ratios of the same carbon nanotubes. The reason for not achieving a full coverage of the MWNTs is related to the anisotropic surface potential of the nanorods. It has been recently shown[18] that the potential decays more rapidly in areas with larger curvature (near the tips) so that the approach of a like-charged object (in this case another nanorod) is more favorable towards the tip than the side, thus favoring a stringlike conformation. It could be argued that such a chainlike structure is derived from the drying process on the TEM grid, which would imply some sort of rearrangement of the nanorods on the MWNTs. This is, however, rather unlikely since the electrostatic interactions involved are relatively strong and thus diffusion of the rods on the MWNT surface is restricted. Additionally, the optical properties in solution (see below) point toward uniaxial plasmon coupling, which would not be expected for a random distribution of nanorods on the nanotubes.

This aligned structure is reminescent of that recently reported by Kamat and co-workers[10] in which mercaptopropionic acid was used as a linker molecule. The optical effect derived from such an alignment is described[10] as uniaxial plasmon coupling, and is reflected in the disappearance of the longitudinal plasmon band and the appearance of a new, broader band centered at longer wavelengths. The same effect is observed during the formation of the anisotropic nanocomposite colloids reported here, as shown in Figure 2, where UV/Vis spectra of the precursor nanorods and the final nanorod–MWNT assemblies are displayed for nanorods with various aspect ratios. The variation in the aspect ratio allows precise tuning of the position of the longitudinal plasmon band of the nanorods, and in all three cases the spectra measured after assembly show broader and red-shifted bands, which reflect the uniaxial plasmon coupling between neighboring nanorods.

Since the longitudinal and transverse surface plasmon modes can be selectively excited by using light polarized with the electric field parallel or perpendicular, respectively, to the long axis of the rods, the oriented assembly of nanorods on the surface of the carbon nanotubes can in principle be used as a sensor of the alignment of the nanotubes themselves; this property is of high relevance for reinforcement applications.[19] We have tested this possibility through the preparation of thin films of the gold nanorod–MWNT composites dispersed in poly(vinyl alcohol) (PVA) thin films. The process

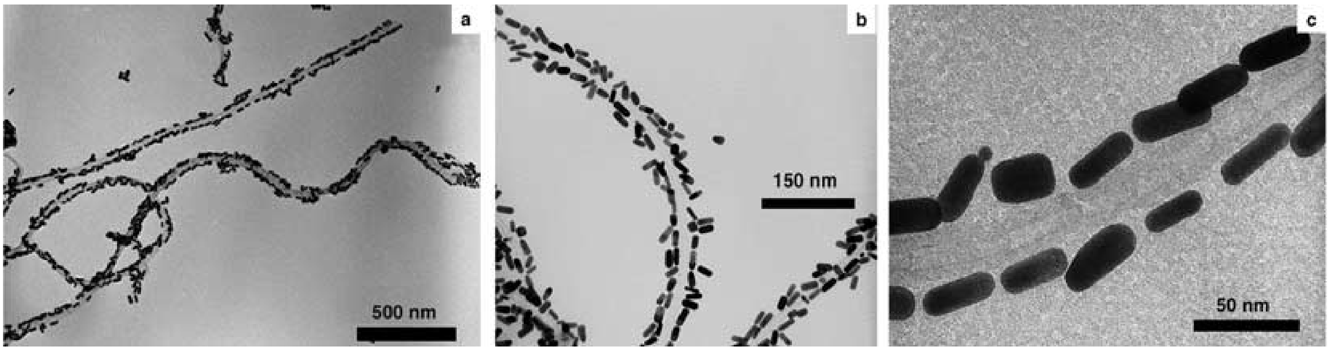

Figure 1. TEM images of Au nanorods (average aspect ratio 2.94), assembled on MWNTs (average diameter 30 nm) at various magnifications.

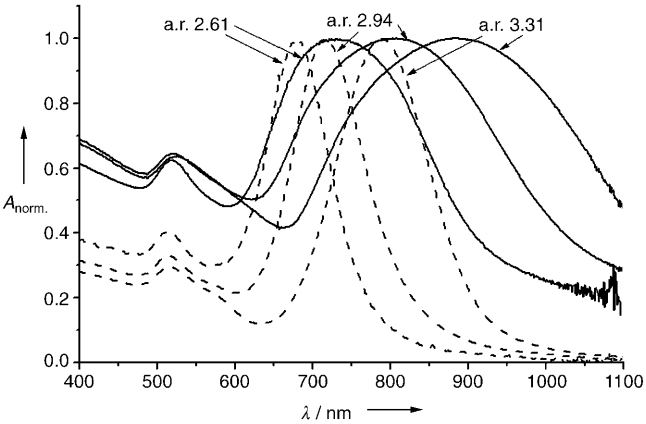

Figure 2. UV/Vis spectra of aqueous dispersions of individual Au nanorods (dashed lines) and nanorods attached on MWNTs (solid lines). The average aspect ratios (a.r.) of the nanorods are indicated.

consisted simply of drying a colloid in the presence of dissolved PVA; this approach has been successfully used by other research groups with silver spheres[20] as well as gold and silver nanorods.[5,21,22] Once the film has been completely dried, alignment is obtained through gently heating and stretching the nanocomposite polymer film. In the case of Au and Ag nanorods, the elongation of the polymer molecules[23] drives the alignment of the small particles toward a preferential direction. We wondered whether the much longer and flexible carbon nanotubes would also get aligned as a result of the stretching of the polymer; this is a very interesting feature for applications in plastic reinforcement. This question was answered by examination of the UV/Vis spectra (Figure 3). The solid black line corresponds to the freshly dried polymer film. Since the nanotubes are randomly oriented, the shape of the spectrum basically coincides with that of the aqueous dispersion, with both plasmon bands clearly visible. Both bands are still visible after stretching the sample (----) since unpolarized light can excite both resonances, irrespective of

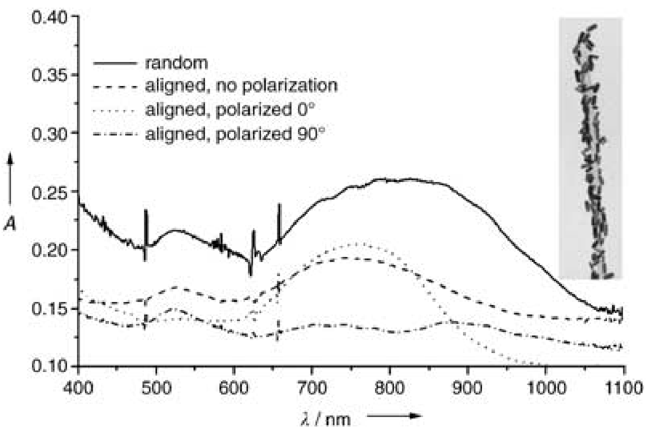

Figure 3. UV/Vis spectra of Au nanorod/MWNT nanocomposites dispersed in a PVA film before (-----) and after (——) stretching. Spectra of the stretched film using polarized light (•••••: 0°; –•–•: 90°) are also shown. The aspect ratio of the rods is 2.94. The inset shows a TEM image of a stretched Au/CNT composite in PVA.

the nanoparticle orientation. The only difference here is that the longitudinal band is narrower, thus indicating a lower degree of interaction when the nanorod–nanotube composites are pulled and separated from each other. However, the most interesting aspect and definitive indication that a high degree of orientation has been achieved within the film is provided by the spectra of the stretched film obtained using polarized light. The transverse resonance band is fully suppressed and only the longitudinal one is observed when the polarization is parallel to the long axis (•••••, 0°). Conversely, the longitudinal band is suppressed and only the transverse mode is excited when the film is illuminated with light polarized perpendicular to the long axis (–•–•, 90°). Such a result can only be obtained if the nanorods (and in turn the nanotubes) display a well-defined preferential orientation within the film. TEM experiments on this sort of system involve ultramicrotoming of the film and are thus extremely laborious and time consuming, especially when the loading of the CNTs is low, since various experiments are required to actually find the particles. It is however possible (see inset of Figure 3), and this confirms the spectroscopic indication that the nanorods are preferentially oriented within the film.

In summary, we have demonstrated the uniform electrostatic assembly of gold nanorods on multiwall carbon nanotubes in such a way that the rods form strings with end-to-end contacts. Such a morphology results in uniaxial plasmon coupling, but can be used to monitor the degree of alignment of carbon nanotubes within polymer films or other nanostructured systems.

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