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Hybrid Nanorods

Hybrid Co–Au Nanorods: Controlling Au Nucleation and Location[**]

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The synthesis of complex nanoobjects containing different materials in the same nanoparticle may offer many opportunities for applications. A new generation of hybrid nanocrystals accommodating two or more different materials on the same particle has recently appeared in the literature. As well as core–shell nanocrystals, the multifunctional nanostructures so far achieved by wet chemical routes include semiconductor/semiconductor,[1] metal/semiconductor,[2] metal or metal oxide/magnetic oxide,[3] semiconductor/oxide,[4] and metal/metal[3c,5] interfaces. Anisotropically phase-segregated as well as ternary hybrid nanocrystals have also been reported.[6] A recent review on heterostructured nanocrystals summarizes the progress and the perspectives on this emerging field.[7] The preferred positioning of the second material on the tips of semiconductor nanorods has been attributed to several factors: surface defects, difference in the passivation degree between chemically different facets of the same nanocrystal, lattice mismatch, and the minimization of interfacial energies between the different materials.[2,3d] Nanostructures with metal–metal interfaces including a metal nanorod have not yet been reported. However these materials, for example, gold-tipped magnetic nanorods, could be useful for implementation in high-density magnetic recording devices, as such species display a high magnetic anisotropy and are ferromagnetic at room temperature.

The selective growth of Au on the Co nanorods requires the promotion of a) the deposition of Au on Co over galvanic displacement of Co by Au[8] and b) heterogeneous growth over homogeneous nucleation. As homogeneous nucleation is energetically more demanding than growth on preformed nanocrystals, it is in principle possible to find conditions that allow the selective growth of Au on Co nanorods. To influence this selectivity, it is possible to play on the kinetics of the reaction: temperature and nature of the reducing agents, on the choice of the Au precursor,[9] and on the surface chemistry of the cobalt nanorods. Thus the concentration and nature of the surface ligands—specifically their affinity for selected surfaces[10] and their dynamics on these surfaces[11]—may allow the passivation, or lack thereof, of selected faces. Functionalization of metal-tipped Co nanorods could facilitate their attachment and organization on flat substrates or their use in biological and medical applications,[5b,12] whereas selective growth of a noble metal layer on the side of magnetic nanorods could allow the passivation of the particles.

Following our interest for elucidating the role of surface organometallic chemistry in nanoparticle synthesis and reactivity,[13] we show herein that a judicious choice of metal precursor, ligand concentration, and ligand mobility may orientate the growth of gold nanoparticles, either selectively on the tips of Co nanorods or on the whole body of the nanorods.

Co nanorods can be synthesized by decomposition of an organometallic compound under hydrogen in the presence of a long-chain amine and a long-chain acid.[14] In the present work the nanorods were synthesized by decomposition of $[Co\{N(SiMe_3)_2\}_2]$[15a] under H_2 in the presence of lauric acid (LA) and hexadecylamine (HDA) (see the Supporting Information).[16] Two gold precursors were selected: $[AuClPPh_3]$,[15b] and [AuCl(tht)] (tht = tetrahydrothiophene).[15c] [AuCl(tht)] is a reactive precursor that easily loses tht and is spontaneously reduced in toluene,[17] whereas $[AuClPPh_3]$ is stable and does not form any nanoparticles in toluene in the absence of Co nanorods, either alone or in the presence of ligands (HDA, LA, or both), as verified by blank experiments.

The reaction of [AuCl(tht)] with a suspension of Co nanorods (55 % Co content) in toluene at 20 °C leads to dissolution of the rods after 30 minutes (Figure 1). High-resolution electron microscopy (HREM) analysis shows the almost complete destruction of the cobalt structure, in agreement with galvanic displacement of Co by Au. In the presence of HDA, [AuCl(tht)] is transformed into $[AuCl(NH_2R)]$, which is slowly decomposed in solution.[17] However, this reaction is slower than the galvanic displacement and no homogeneous nucleation was observed under the conditions employed. Therefore, [AuCl(tht)] may displace the HDA from the surface of the nanorods, facilitating the access of Au for the galvanic reaction.

The same reaction using $[AuCl(PPh_3)]$ as a precursor results in the slow and specific growth of Au nanoparticles on the Co nanorods (Figure 2). The Au particles are identified by their increased contrast. Furthermore, a selected-area elec-

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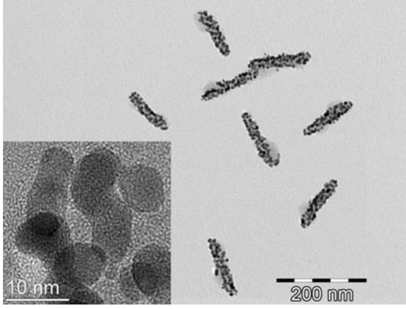

Figure 1. Gold formation around Co nanorods. Galvanic displacement almost completely destroys the Co structure. [Co] = 1.3×10^{-3} M, [Au] = 1.3×10^{-4} M, reaction time 30 min. Inset: HREM micrograph, in which only gold can be seen.

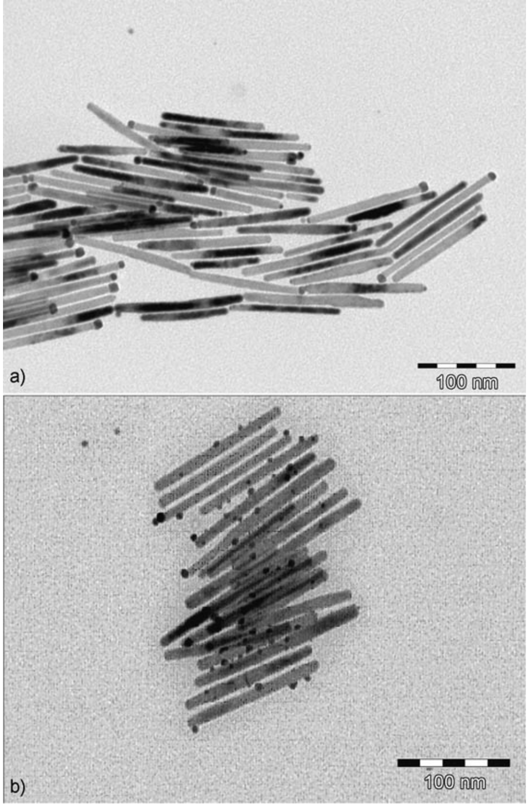

Figure 2. TEM images of a) gold-tipped Co nanorods prepared at 40 °C and b) gold-decorated Co nanorods prepared at 20 °C. For both, [Co] = 1.3×10^{-3} M, [Au] = 1.34×10^{-4} M, reaction time 48 h.

tron diffraction pattern (SAEDP) shows that well crystallized gold is present on the nanoparticles (see the Supporting Information). The reaction is temperature-dependent, as Au nanoparticles are deposited selectively on the tips of the nanorods after 2 days at 40 °C (Figure 2a), whereas at 20 °C nonselective deposition of Au particles over the whole nanorod surface is observed (Figure 2b). The location of the nanoparticles is also dependent upon the ligand concentration. Thus, in another set of experiments but using a higher Co/Au ratio, the same reaction was carried out at 20 °C with nanorods of 65% Co content. In the absence of additional ligand, we observed a nonselective deposition of gold as described above, whereas in the presence of extra ligands (1 equiv of amine, acid, or both with respect to Co) the growth of Au happened exclusively on the rod tips, thus indicating that full coverage of the nanorods sides prevents gold nucleation (see the Supporting Information). No trace of gold was found on the main body of Au-tipped nanorods, as indicated by several energy-dispersive X-ray (EDX) spectra collected with the electron microscope operating in scanning (STEM) mode (see the Supporting Information). Finally, we checked that once deposited the nanoparticles did not move either from tips to body or from body to tips.

The dimensions of the Co nanorods before and after Au growth are not modified, indicating a pure heterogeneous growth mechanism in which Co is not oxidized but serves strictly as a seed for the Au growth. In our study, no extra reducing agent was added; the organic stabilizers present on the nanorods surface serve as mild reductants.[2b,18] This experiment also reveals the role of PPh_3 to stabilize the gold complex and avoid galvanic reactions. Figure 2a shows a TEM micrograph of gold-tipped nanorods grown at 40 °C.

HREM experiments show that, in the case of gold tipped nanorods, the (111) gold lattice planes ($d(hkl) = 2.35$ Å) grow parallel to the direction of the (002) planes ($d(hkl) = 2.02$ Å) of the cobalt structure. Only the two expected angles (0° and 70.5°) can be measured between the two planes (Figure 3a).

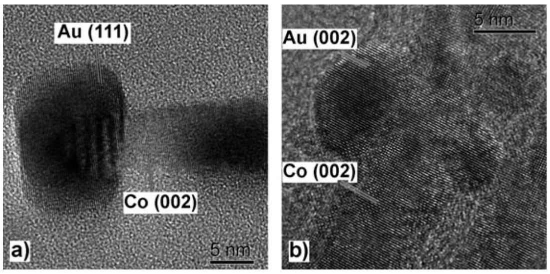

Figure 3. HREM images of: a) gold-tipped nanorods, with the (111) gold lattice planes parallel to the (002) of the cobalt nanorod (relaxed growth) and b) gold-decorated nanorod, in which the Au particles grow epitaxially on the nanorod sides, and the (002) gold lattice planes are aligned with the (002) of the cobalt.

The large mismatch of the lattice parameters prevents simple epitaxial growth. Fourier analysis of the HRTEM images indicates that the lattice parameters progressively relax to the Au bulk lattice parameters after a few lattice planes from the Co nanorod. Interestingly, HREM analysis of the gold-decorated nanorods showed that the Au nanoparticles have grown epitaxially on the lateral sides of the Co nanorods. The gold (002) planes ($d(hkl) = 2.04$ Å) grew on those (002) ($d = 2.02$ Å) of the cobalt nanorods (Figure 3b).

In a hypothetical situation in which nanorods are completely free of stabilizers, we would expect that epitaxial growth would be thermodynamically favored over constrained growth. In that case, increasing the temperature would tend to favor the "thermodynamic product", that is, the preferential deposition of Au on the lateral sides, for which the lattice mismatch is minimum.[19] In the other extreme case, namely in the presence of a large excess of ligands (Co content 10%), we checked that the growth of Au particles is almost completely suppressed. For intermediate situations but at high ligand concentration, we only observe the growth of gold on the cobalt tips, in agreement with the hypothesis that the stabilizing ligands are coordinated preferentially on the sides of the nanorods. The temperature effects observed at low ligand concentration (Figure 2) are, however, more difficult to understand, since by increasing the temperature the tip position (constrained growth) is favored. At low temperature, the results can be explained if we consider that the attack of [AuClPPh$_3$] happens on ligand deficient sites on the nanorods surface. In such samples, ligand-depleted sites are found both on tips and on the lateral sides. At higher temperature and for the lateral sides of the nanorods, fast exchange of ligands[11] would not permit enough resting time for the nucleation of Au to take place. This fast exchange of the ligands on the nanorods sides has no influence on the nucleation of Au on the tips since these areas are expected to accommodate a lower concentration of ligands. Another indication of the importance of the timescale for the formation of the primary nuclei is that practically no growth of Au takes place if the reaction mixture is stirred. In an analogous way to crystal formation, stirring suppresses the formation of the primary nuclei for further crystal growth.

In conclusion, we report the synthesis of hybrid gold–cobalt nanorods. The present results support the hypothesis that the stabilizing ligands are coordinated preferentially on the sides of the nanorods and that a fast exchange occurs on the surface of the rods which involves the stabilizing ligands and also probably PPh$_3$. Moreover, we show that chemical control of both the gold precursors and the ligands allow 1) control of the gold growth process (heterogeneous nucleation versus galvanic displacement) and 2) control of the location of the gold nanoparticle growth (tip or whole body) through kinetic control of the reaction. This result makes possible the selective production of gold-tipped ferromagnetic cobalt nanorods. We are currently studying the physical properties of these new nanoobjects: preliminary optical measurements show in both cases (gold nanoparticles random or gold nanoparticles on the tips) the presence of absorptions near 550 nm attributed to a plasmon absorption as well as a very weak one near 720 nm,[20] whereas magnetic properties of the new Au–Co nanorods are currently under examination to investigate the effect of Au presence and location on the magnetic anisotropy of these objects.

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