Nanotubes self-assembled from calixcrowns are utilized as an organic template for fabricating 1-D nanohybrids with noble metal nanoparticles attached to the nanotubes, which show good catalysis properties.

To precisely construct nanoscale metal-organic hybrids, particularly the low dimensional nanomaterials, has been a subject of intensive research owing to the potential applications in fields ranging from sensors, waveguides, photonics, to piezoelectronics etc. Currently, the template-directed method, as one of the ‘bottom-up’ approaches, has emerged for fabricating nanohybrids through π-stacking, van der Waals or charge-transfer interactions, etc. Thus, one-dimensional nanomaterials, such as tapelike or tubelike nanostructures composed of organic compounds, polymer fibers fabricated by electrospinning and carbon nanotubes modified by polymers or surfactants, have been utilized as the template or frameworks to construct 1-D nanohybrids.

Calixarenes, obtained from phenols and aldehydes, have been a versatile platform of the supramolecular community due to their unique ability for molecular or ion recognition. In most of the calixarene-containing hybrids reported, calixarenes with specific recognition abilities were anchored onto supports, such as electrodes, metal nanoparticles (NPs), polymer membranes, etc., as guest receptors or stabilizers. For instance, Brust et al. reported that monolayer protected metal clusters with thiol functionalized calix[4]arene show specific molecular recognition in water. However, as far as we knew, few examples were reported in which calixarenes or their aggregates were used as nanoreactors or substrates for fabricating hybrid nanomaterials.

In our previous studies, we succeeded in the preparation of nanotubes composed of terminal amino calix[6]crown ethers (TAC) by self-assembly in ethanol/water solutions. It was found that, with increasing solution polarity, e.g. volume ratios of water/ethanol from 1:3 to 1:1, the morphology of TAC aggregates in the solutions evolves from vesicles to nanotubes. This achievement formed the basis of our current research to construct low-dimensional hybrid nanomaterials constituted of calix nanotubes and noble metal NPs. The one-dimensional structure of the nanotubes and the abundant amino groups on their surface inspired us to construct specific functional nanohybrids by combining this kind of nanotube with metal NPs.

The preparation of the nanohybrids typically involves two steps, i.e. the assembly of TAC in the presence of HAuCl4 or AgNO3 solution, and the subsequent reduction by NaBH4. Moreover, we investigated the catalytic ability of this kind of nanohybrid in the hydrogenation of crotonaldehyde.

Typically, with the addition of the HAuCl4 solution (0.5 mg/mL, 1.2 × 10^{-4} mmol/mL) into the TAC ethanol (1 mg/mL, 7.0 × 10^{-4} mmol/mL), the mixture turned to blue opalescence, indicating the formation of aggregates. As observed by TEM (Fig. 1 and S1†), tubular nanoaggregates formed when the volume ratio of ethanol/water reached 1:2. These nanotubes, built from TAC with metal ions, could serve as a novel precursor for fabricating one-dimensional hybrids. The images of the nanotubes in Fig. 1 clearly show the presence of some black spots of size about 30-40 nm although no reduction reagent was added. Energy dispersive X-ray (EDX) measurements of the nanotubes present a peak at 9.6 keV (Fig. S2 and S3†) which can clearly be attributed to gold NPs. Obviously, the NPs were formed by electronic irradiation during the TEM observations. Moreover, as shown in the insert of Fig. 1b, no black spots were observed on the tubular exterior surface and the tubular inner surface is smooth as well, which indicates that all of gold NPs exist within the nanotubes. It implies that the cavity of the TAC nanotube could serve as a nanoreactor for photosensitive or electrosensitive reactions.

In order to reduce AuCl4− in the solution, NaBH4 solution was added. This caused a clear colour change of the solutions, indicating...
the formation of gold NPs. A series of HAuCl₄ solutions with concentrations of 0.05, 0.25, 0.5, and 5 mg/mL were used and the corresponding nanohybrids were denoted as H₁, H₂, H₃ and H₄. With the increase of the concentration of HAuCl₄, the colour of the solution of the TAC nanotubes with gold NPs changes from pale yellow, to wine red, deep red and finally to purple.

Fig. 2 shows the UV-vis spectra of the nanohybrids obtained with different concentrations of HAuCl₄. The spectrum peaks of the nanohybrids H₁, H₂ and H₃ are located at 508 nm, 515 nm and 519 nm respectively, which shows a red-shift caused by increasing the concentration of HAuCl₄. This red-shift reflects an increase in the NP size.¹² This change in particle size was confirmed by the results of the TEM observations. As shown in Fig. 3a, b and c, the respective average sizes of NPs in H₁, H₂ and H₃ are around 3 nm, 5 nm and 8 nm. It is worth noting that almost all the gold NPs observed by TEM are attached to the nanotubes. This is very different from the gold NPs formed due to electronic irradiation (Fig. 1). This implies that the coordination between AuCl₄⁻ and the nitrogen atoms in the amino groups on the surface of the nanotubes is the key step and prerequisite for fabricating the nanohybrids. Furthermore, the high resolution TEM (HR-TEM) images (Fig. 3d, S4†) of H₃ elucidate the detailed structure of the gold NPs with the TAC nanotubes: all the NPs are perfect spheres and the interfringe distance is measured to be 0.235 nm (Fig. 3d), corresponding to the (111) lattice spacing (0.23 nm) of the face centered cubic (fcc) Au. This is perfectly consistent with the result of XRD measurement, in which the characteristic peaks are at 2θ of 38.55°, 44.79°, 64.99° and 77.89° corresponding to (111), (200), (220) and (311) planes of fcc lattice (Fig. S5†). It is interesting to see that, in all the cases of preparation of the nanohybrids by chemical reduction, the size of the resultant gold NPs (5-8 nm, Fig. 3) is much smaller than that of the gold NPs reduced by the electronic beam or NaBH₄, one-dimensional nanostructures could be also employed as a microreactor to produce silver NPs.

Based on what was mentioned above, a schematic illustration of the formation of the nanohybrids is shown in Scheme 1. When a metal ion solution is injected into TAC ethanol solution, TAC forms nanotubes with the metal ions due to the coordination of metal ions with the amino groups at the tails of TAC. After the subsequent reduction by electronic beam or NaBH₄, one-dimensional nanohybrids, in which gold NPs are tightly attached on the surface of or within the nanotubes, are obtained.

It was reported that supported noble metal NPs show a high selective catalytic ability for hydrogenation of α,β-unsaturated aldehydes due to their high surface-to-volume ratio. The reaction has been studied broadly for use in pharmaceuticals and cosmetics.¹⁴,¹⁵
Obviously, our nanohybrids are novel nanomaterials for catalytic studies because the metal NPs are supported by amphiphilic organic nanotubes. Thus, the catalytic performance of the nanohybrids towards the hydrogenation of crotonaldehyde (CRAL) was preliminarily investigated. Although water is a poor solvent for the catalytic system, it is still used here for the purpose of reducing environmental pollution. The hydrogenation of CRAL leads to the formation of a greater proportion of Au atoms in the (111) plane of Au NPs as shown in the UV-vis spectrum (Fig. S8†) and TEM image (Fig. S9†). Under similar conditions, the silver nanohybrids (H5) show no activity for this reaction. A similar high selectivity (70%) for the hydrogenation of the C==C bond leading to BUAL was also observed when Au/CeO2 was used under similar conditions. As discussed in the literature,17 thermodynamics favors the hydrogenation of the C==C bond, with a standard Gibbs free energy change of −16.9 kcal/mol, vs. only −7.3 kcal/mol for the hydrogenation of the C==O bond. However, the selectivity towards the C==O bond could be elevated in a certain range by increasing the gold NP size as a result of a greater proportion of Au atoms in the (111) plane of Au NPs with larger sizes.18 Thus, nanohybrids prepared by using HAuCl4 of 2.5 mg/mL rather than 0.5 mg/mL for H3 were used. Consequently, a definitely higher selectivity (28.9%) for the hydrogenation of the C==O bond (Table S2†) was observed with an increase of the gold NP size as shown in the UV-vis spectrum (Fig. S8†) and TEM image (Fig. S9†). This confirmed that the hydrogenation of the C==O bond of CRAL is favored on the (111) plane of gold NPs with the increase of gold NPs. Evidence for hydrogenation of C==O activated on the (111) plane of gold NPs has also been observed in the hydrogenation of acrolein.18 In the following 20 h, the conversion reached nearly 100% and, due to secondary hydrogenation, the selectivity for CROLE decreased to 17.8% and butanal became the main product. Although the hybrids based on TAC nanotubes underwent rigorous reaction conditions (373 K, in water), the recovered hybrids after the reaction did not show any shifting in the UV-vis spectrum, which indicated that no agglomeration of the gold NPs took place. Actually, TEM observation (Fig. S10†) proved that the nanostructure of the nanohybrids still remained after the hydrogenation. So we may conclude that TAC nanohybrids containing variable metal NPs may provide a promising platform to investigate their potential applications in catalysis, such as hydrogenation of α,β-unsaturated aldehydes, oxidation of carbon monoxide and so on.19

In summary, we have demonstrated a convenient and efficient synthesis of a novel kind of nanohybrid under mild conditions, in which noble metal NPs adhere firmly to TAC nanotubes. This strategy is based on the coordination of metal ions with nitrogen atoms in TAC and the subsequent in situ reduction of the metal ions. To the best of our knowledge, our finding is the first example of using calixarene aggregates as a nanoreactor to fabricate organic-metal hybrids. This kind of nanohybrid, in which metal NPs are uniformly distributed on or within the TAC nanotubes, is probably a promising candidate for nanocatalysis. Moreover, the one-dimensional structure of the nanohybrids makes them attractive for the study of transport of electrical charges in nanomaterials.

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Notes and references


