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Alumina Membranes — Templates for Novel Nanocomposites

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Three different examples have shown that nanoporous alumina membranes serve as ideal templates for the formation of nanostructured materials and also as a support of those materials in composites. The unique properties of such membranes (transparency, chemical resistivity, thermal stability, adjustable pore sizes etc.) and the very simple mode of generating these composites are the benefits of using this inorganic template material.

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INTRODUCTION

Since nanosized materials show significant changes in their physical and chemical properties compared with the bulk material, they become more and more interesting for many reasons. For example, they exhibit electronic properties due to quantum size effects as well as a change in chemical reactivity. The broad synthetic approach to nanostructured materials ranges from the reduction of bulk structures to the generation of nanoparticles by chemical synthesis from atomic or molecular building units.

By using this 'bottom-up' approach it is important to stop the formation process at distinct sizes to prevent the formation of larger particles. This could be achieved either by classical chemical approaches or by the template-assisted formation of nanoparticles. In the latter case the particle size is determined by the space in the cavity where the chemical reaction proceeds. So, by varying the size of the template, the size of the nanomaterial can be changed very easily. In this field the use of nanoporous alumina has proved to be very useful.[1–4] By anodic oxidation of high-purity aluminum in polyprotic acids, transparent alumina membranes are synthesized with pore diameters between <10 nm and 250 nm and thicknesses ranging from a few nanometers up to hundreds of micrometers. Most important here is that the pore size can be adjusted by the applied anodic potential (1.0–1.2 nm V^{-1}). Figure 1(a) shows the surface of an alumina membrane formed at 25 V and imaged by scanning electron microscopy (SEM). Figure 1(b) presents a cross-sectioned membrane formed at 60 V, imaged by transmission electron microscopy (TEM).

Figures 1(a) and 1(b) prove the narrow size distribution of the pores as well as the high porosity of such membranes. Chemical processes in the almost parallel nanopores are automatically quantum-confined and limited by the pore size. In this paper we present the formation of three types of nanocomposites by very different synthetic approaches to prove the potential of nanoporous alumina in the field of nanomaterials. We start out with electrochemically or chemically generated metallic nanowires which have possible applications in the field of novel electronic and optical or magnetic materials. In the second example the formation of luminescent siloxenes by a chemical vapor deposition (CVD) like process inside the pores is shown which may be a useful approach to new electroluminescent devices. In the last example the formation of pore walls decorated by metal clusters is shown with possible applications in heterogeneous catalysis as well as in new sensor materials.

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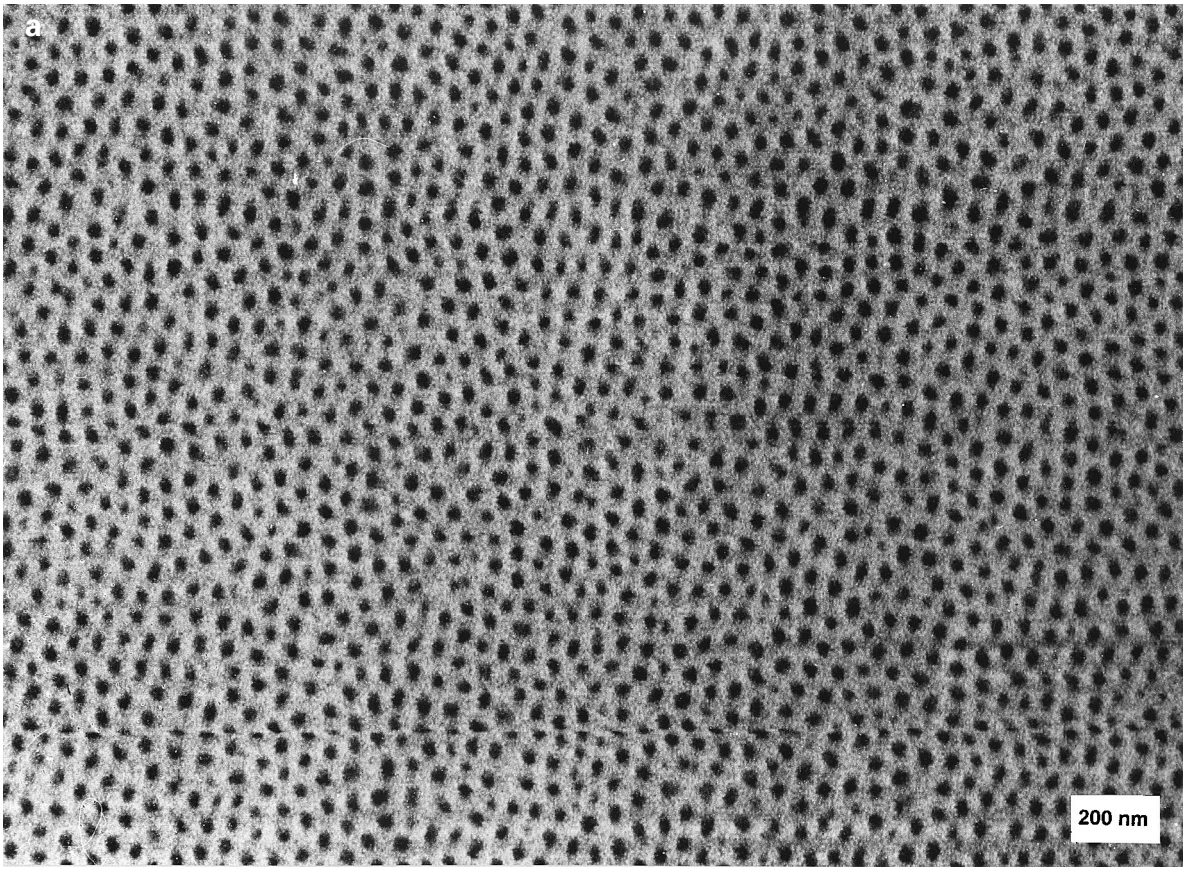


Figure 1 (a) SEM image of the surface of a 25 V alumina membrane. (b) TEM image of a sectioned 60 V alumina membrane. The voids, visible in the pore areas, are caused by the anodizing procedure and are located in the solid Al_2O_3 material between the pores.

FORMATION OF METALLIC NANORODS

Since nanoporous aluminum oxide membranes provide pores of adjustable diameter and length, it is possible to produce metal columns of varying sizes within the pores. Two methods of depositing metals are possible: an ac deposition procedure for various metals and an electroless plating procedure for gold.

For the ac (50 Hz) deposition procedure for various metals at room temperature, used in this work, graphite serves as counter electrode, the aluminum as cathode, and the barrier layer between the porous membrane and the metal is left intact. Due to the fact that aluminum oxide conducts mainly in the cathodic direction the metal can be deposited within the pores during the cathodic half-cycles but cannot be re-oxidized during the anodic half-cycles. Table 1 shows the conditions applied to deposit silver, gold, copper and iron. Figure 2 shows a TEM image of a membrane produced at 20 V in sulfuric acid and filled with silver afterwards. After depositing the metal the aluminum can be removed by $HgCl_2$.

For further applications the membranes are ion-milled to remove the barrier layer (ac deposition) and to obtain a very smooth surface. The metal columns produced by either of these methods can, for example, be combined with ligand-stabilized metal clusters, such as $Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6$, by a bifunctional spacer molecule. The combination of nanorods with nanometals (clusters) is expected to lead to the application of metal clusters as

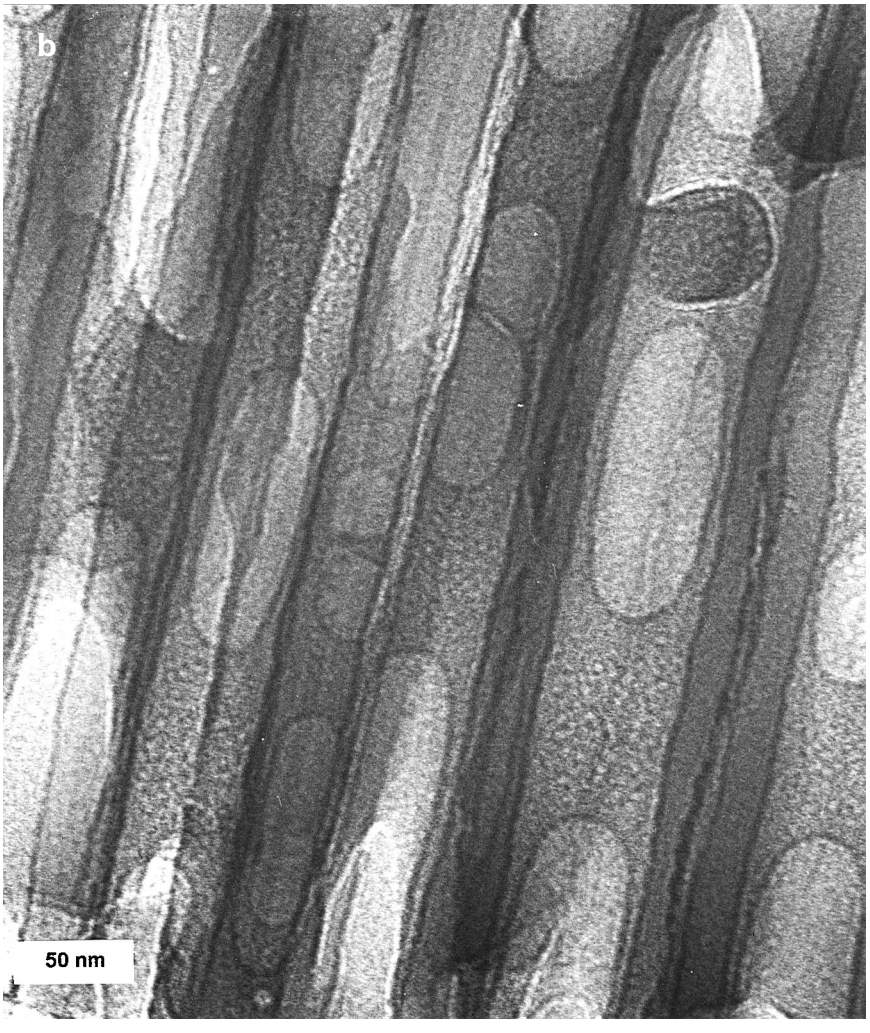


Figure 1 *continued.*

quantum dots in single-electron tunneling (SET) devices. The magnetic properties of iron-filled membranes will also be investigated.

LUMINESCENT SILOXENES

The thermal decomposition of metastable silanes has been shown to open a route to generate quantum-confined silicon films on various substrates.[5–9] It is a challenge to generate luminescent silicon structures for new optoelectronic applications in the field of semiconductor devices. Thus it is of great importance to control the size and the surface chemistry of such films. In the case of alumina membranes, the vacuum filling and decomposition of silanes in the pores leads to the formation of siloxene-like structures with a very simple control of size and surface chemistry by spontaneous changing of the pore size and the decomposition procedures.[10] In a first step the thermal decomposition of pentamethylcyclopentadienylsilane[11] in an atmosphere of nitrogen at 800 °C gives highly reactive silicon atoms which react immediately with the Al–OH moieties of the alumina pore wall to give stable Si–O–Al bondings (Eqn [1]).

Table 1 Depositing conditions for silver, gold, iron and copper in alumina

Metal	Electrolyte	pH	Voltage (V)	Current density (mA cm^{-2})
Silver	1 g/l^{-1} $AgNO_3$ + 41 g/l^{-1} $MgSO_4 \cdot 7\ H_2O$	2.0	9	1.9
Gold	1 g/l^{-1} $HAuCl_4$ + 20 g/l^{-1} $MgSO_4 \cdot 7\ H_2O$	1.7	9	2.2
Iron	120 g/l^{-1} $FeSO_4 \cdot 7\ H_2O$ + 45 g/l^{-1} H_3BO_3 + 1 g/l^{-1} ascorbic acid	2.9	16	4.4
Copper	35 g/l^{-1} $CuSO_4$ + 41 g/l^{-1} $MgSO_4 \cdot 7\ H_2O$	2.1	6	1.5

$$Cp^*SiH_3 \xrightarrow{800\,^\circ C} Cp^*H + H_2 + Si \qquad [1]$$

A network of Si atoms then forms a layer of a siloxene-like composition characterized by hydrogen and hydroxyl substituents on its surface. Figure 3 illustrates the situation in a simplified manner. The Si–H and the SiO–H moieties are indicated by their stretching modes in the IR spectra in Fig. 4.[5] The CO_2 vibration is caused by a small amount of oxygen present during the decomposition process.

Siloxenes have been shown to be direct band gap materials.[12,13] Therefore luminescence should be possible by exciting the siloxene layers on the pore walls. Indeed, there is an intense luminescence at 540 and 506 nm for an alumina membrane with pores of 40 nm diameter, as shown in Fig. 5. By varying the pore diameter, the intensity of the luminescence may be shifted from 506 nm to 540 nm due to the formation of different types of siloxenes or even silicon nanoparticles which

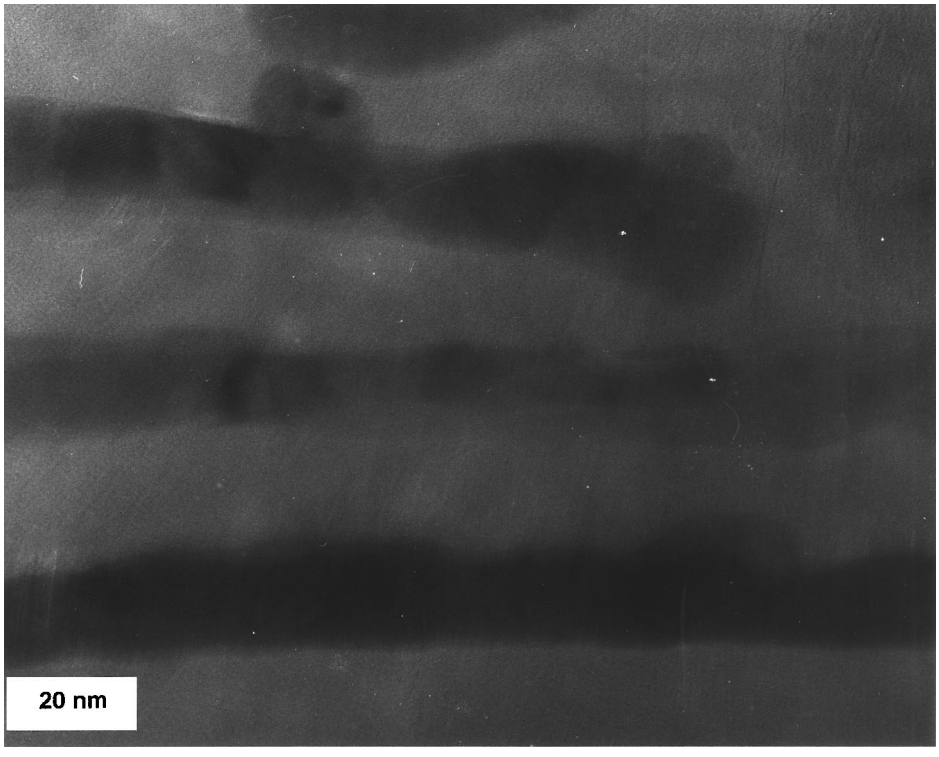


Figure 2 Silver-filled pores in nanoporous alumina.

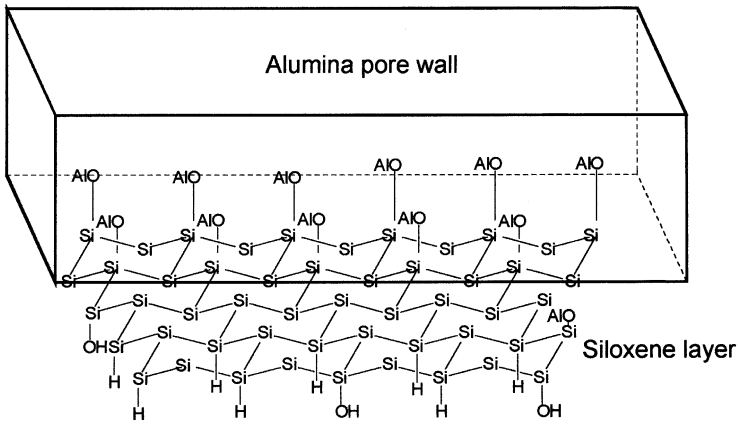


Figure 3 Sketch of a siloxene layer on the pore wall of nanoporous alumina.

cannot be observed by TEM in the alumina pores. Further studies will include solid-state ^{29}Si NMR to explain the observed shift in luminescence. Thus, by simple thermal decomposition of organometallic precursors in alumina nanopores, quantum-confined materials can be formed and supported in one step.

COLLOIDAL ARRAYS IN NANOPORES

Three-dimensional assemblies of metal clusters are important candidates for fabrication of nanomaterials aimed at applications for optics, sensors and catalysts.[14–19] Uniform and parallel pores of anodized alumina membranes are highly appropriate for assembling clusters, because particles immobilized on a well-defined structure give qualified nanoarray structures. In order to realize this goal, we chose the strategy of self-assembly of clusters by using organic molecules anchored on the wall (Scheme 1).[20–24]

To attach the anchor molecules, mono-, di- and tri-alkoxysilanes with functional groups, such as Y

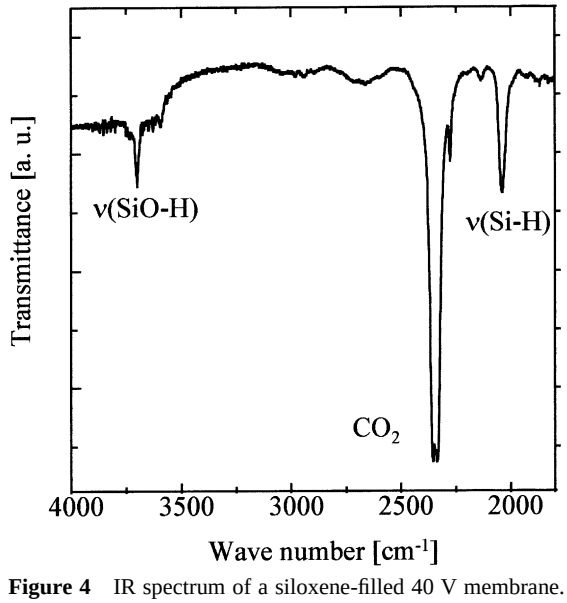


Figure 4 IR spectrum of a siloxene-filled 40 V membrane.

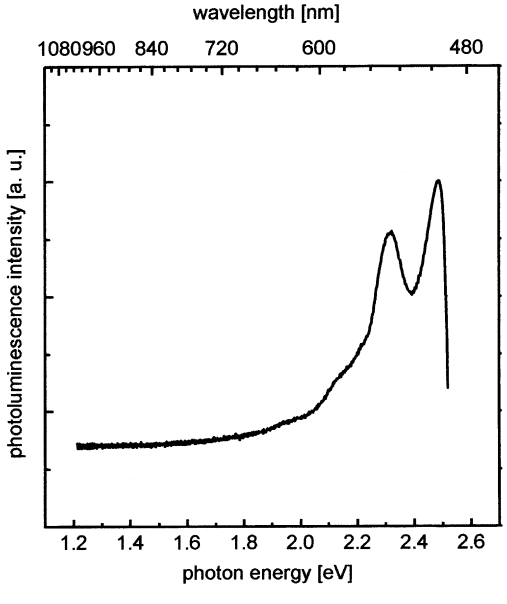
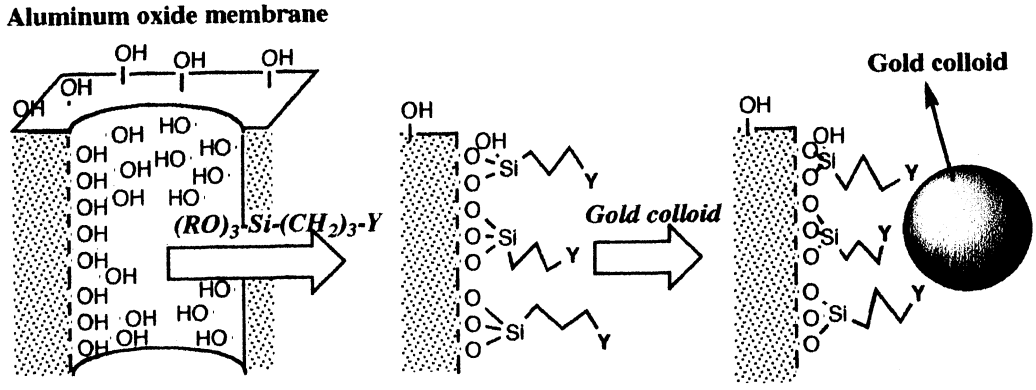


Figure 5 Photoluminescence spectrum of a siloxene-filled 40 V alumina membrane recorded after excitation with an Ar ion laser at 488 nm.



Scheme 1

$(CH_2)_xSi(OR)_3$, are reacted with alumina membranes by heating in dry toluene. A commercially available anodized alumina membrane, Anopore™ (d = 220 nm), was also used for these experiments. As functional groups Y NH_2 and SH were selected, with consideration of their affinity towards metal clusters. This reaction forms Al–O–Si bonds by condensation and fixes huge numbers of functional groups to the pore walls. The fixation of anchor molecules was confirmed by IR spectra of the reacted membrane. After the remaining organics had been completely rinsed out, a solution of gold clusters (particle diameter *ca* 13 nm) was introduced to immobilize itself on the pore by the vacuum-filling method. This procedure immediately gave immobilized gold particles.

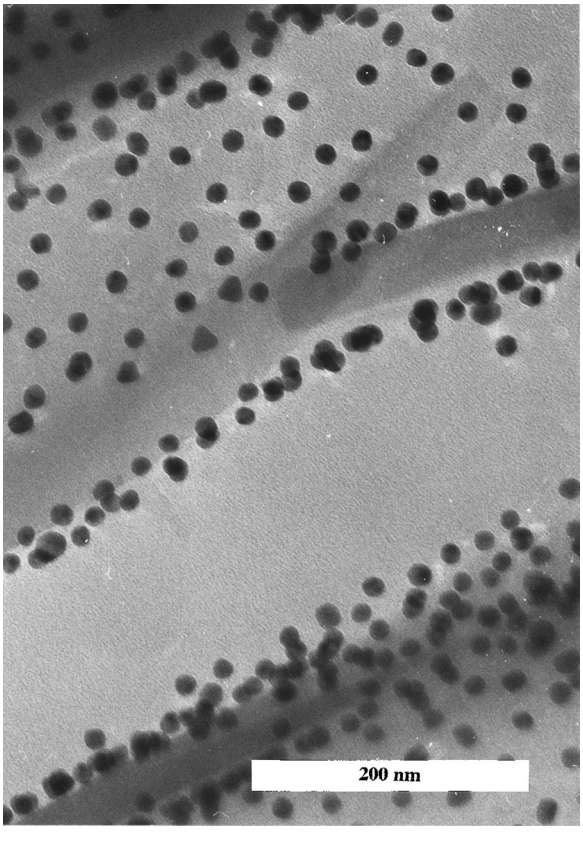


Figure 6 TEM image of a sectioned alumina membrane indicating two different insights. Bottom: the back and front sides of the pore are removed, so that only the colloids on the walls perpendicular to the plane of projection are observed. Top: only the front of the pore is opened, and the colloids on the back of the pore are visible.

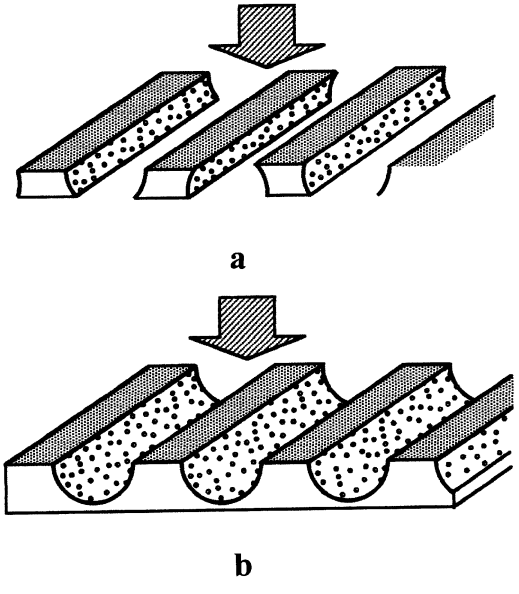


Figure 7 Schematic illustration of the situation shown in Fig. 6: (a) corresponds to the bottom part and (b) to the upper part of the TEM image.

The cluster-containing membranes were characterized by spectroscopic methods and TEM. When a combination of 3-aminopropylmethyldiethoxysilane (APDMS) and a gold cluster is used to prepare the structure, UV–VIS spectra show only one peak (λ_{max} = 525 nm), which is attributable to plasmon resonance.[25] This means that the gold particles are well dispersed in a matrix without forming larger particles. TEM analyses strongly support this result. Uniformly and randomly dispersed gold particles are observed on the pore walls as a sub-monolayer without any aggregation (Fig. 6). 'No aggregation' means that the colloids are tightly fixed to the walls, i.e. difficult to move and aggregate. The diameters of the fixed particles are obviously not affected by the immobilization process. The surface coverage with colloids is lower than a monolayer and was calculated to range around 25%. This value is attributable to an electrostatic repulsion between colloids.[26] Repeated sectioning of cluster-containing membranes offers another view of dispersed clusters on the wall. Figures 7a and 7b illustrate the structure described above. On the other hand, because underivatized membranes show very different images, namely partially aggregated small numbers of particles on the walls, a strong affinity between clusters and functional groups is considered to play an important role for assembling the clusters.

This preparation method was proved to be advantageous for the development of nanomaterials via clusters that are tunable in pore size, and may be extended to other colloidal metals.

CONCLUSION

Three different examples have shown that nanoporous alumina membranes serve as ideal templates for the formation of nanostructured materials and also as a support of those materials in composites. The unique properties of such membranes (transparency, chemical resistivity, thermal stability, adjustable pore sizes etc.) and the very simple mode of generating these composites are the benefits of using this inorganic template material.

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