Synthesis of noble metal nanoparticles and their non-ordered superstructures

BY NADJA C. BIGALL1 AND ALEXANDER EYCHMÜLLER2,*

1Fondazione Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
2Physikalische Chemie und Elektrochemie, TU Dresden, Bergstrasse 66b, 01062 Dresden, Germany

This article highlights our recent work concerning the synthesis of metal nanoparticles and their non-ordered superstructures. After a short introduction, the basic synthetic procedures are explained for the nanoparticles used for the assemblies. Furthermore, a fabrication method is itemized for very monodisperse platinum nanoparticles in aqueous solution ranging in diameter from 10 to 100nm showing distinct optical properties. The next section deals with the synthesis of non-ordered hydro- and aerogels from the as-prepared sols. Very light large surface materials from gold, silver, platinum and gold–silver and platinum–silver sols can be fabricated with the given method. Another way to ultralight superstructures of noble metal nanoparticles using fungi as templates is described in the third section. Although fungi grow inside the colloidal solutions they can assemble the nanoparticles onto their surfaces. These hybrid systems are thus extremely interesting supported superstructures for applications in heterogeneous catalysis, since the numbers of nanoparticles on the fungus can easily be tuned, and the fabrication process is cost-effective, environmentally friendly and the organic templates can be easily removed by simple combustion for regaining the noble metal.

Keywords: metal nanoparticles; aerogels; superstructures; non-ordered; biotemplate; platinum

1. Introduction

Scaling down objects to the nanometre size frequently leads to physical properties differing from those of the macroscopic counterparts. This effect is, on the one hand, due to the large specific surface of the nanoparticles, which makes them, for example, more chemically reactive than the bulk materials. On the other hand, even completely new properties appear due to the transition from the macroscopic solid state to the molecule, as can be observed, for example, in the colour change of solutions of semiconductor nanoparticles, as well as in their luminescence properties. Considering metal nanoparticles, plasmon resonances can occur depending on the size and shape of the particles. The excitation of such localized surface plasmons goes along with an enhanced absorption at the respective wavelength of the exciting light, which is finally responsible for the colour of such metallic nanoparticles. As a consequence, metal nanoparticles have

*Author for correspondence (alexander.eychmueller@chemie.tu-dresden.de).

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applications among others in sensorics (Lahav et al. 1999; Willner & Willner 2002; Raschke et al. 2003; Alivisatos 2004; Härtling & Eng 2005), photonics (Liz-Marzan & Mulvaney 2003; Lu et al. 2005a,b, 2006) and in medical diagnostics (O’Neal et al. 2004; Loo et al. 2005); additional toxicity tests are necessary in the last of these (Connor et al. 2005; Nel et al. 2006).

In nanooptics, the optical properties of metal nanoparticles play a key role due to the localized surface plasmons with resonance wavelengths in the visible regime. The scattering cross section and the electric field around the particle can reach very high values in the spectral vicinity of the surface plasmon resonances. Hence, metal nanoparticles find additional applications in the enhancement of field-sensitive optical processes, in, for example, fluorescence enhancement (Käll et al. 2005; Härtling et al. 2007) and surface-enhanced Raman spectroscopy (Otto et al. 1992; Freeman et al. 1995; Grabar et al. 1995; Kneipp et al. 1997; Lu et al. 2005a,b, 2006; Qin et al. 2006; Fan & Brolo 2008; Ko et al. 2008; Lu & Eychmüller 2008), as well as in environmental refractive index sensing (Raschke et al. 2003; Härtling & Eng 2005).

Some metal nanoparticles are also known to have great potential as catalysts. Owing to the ability to lower the activation energy of certain reactions they facilitate the synthesis of important chemicals. Foremost, many transition metals, which already in their bulk state possess catalytic properties as nanoparticles, feature very high catalytic activities owing to their large specific surfaces, opening further important fields of applications (Reetz et al. 1996; Mayer & Mark 1997; Crooks & Zhao 1999a,b; Sulman et al. 1999; Chechik & Crooks 2000; Li et al. 2000; Crooks et al. 2001; Joo et al. 2001; Haruta 2002; Rolison 2003; Narayanan & El-Sayed 2004; Astruc et al. 2005; Bigall et al. 2008a,b; King et al. 2008; Novo et al. 2008).

A large field within contemporary science focuses on the synthesis and characterization of metal nanoparticles. A variety of different wet chemical so-called bottom-up fabrication methods of nanoparticles are thus already installed in polar as well as in non-polar solvents. As a consequence, today metallic nanoparticles can be synthesized in different sizes, shapes, material compositions and solvents (Schmid 1992; Brust et al. 1994; Ahmadi et al. 1996; Schmid & Chi 1998; Teranishi & Miyake 1998; Murray et al. 2000; Sun & Xian 2002; Jin et al. 2003; Burda et al. 2005; Murphy et al. 2005). However, all these fabrication procedures principally yield only the colloidal solutions of the respective nanoparticles. Colloidal solutions are yet limited in their application spectrum since, for instance, the nanoparticles cannot just simply be separated from their surrounding medium. Additionally, many of the above-mentioned fields of applications are not realizable directly from colloidal solutions but exclusively from the superstructures of the respective nanoparticles. The immobilization of nanoparticles on substrates and the self-assembly of nanoparticles are thus important branches of nanoscience. Besides the associated fundamental research relating to the fabrication of new materials, eventual applications play an important role. Regular arrangements, for instance, are expedient in certain sensors or possibly for the fabrication of novel data storage media (Thurn-Albrecht et al. 2000; Cheng et al. 2001; Gowd et al. 2009; Nandan et al. 2009). Concerning applications in catalysis, the ordering of the particles in superstructures plays an inferior role in providing a large specific surface and the possibility for the gas or liquid to flow through the system.
In the present article our recent work related to the synthesis of noble metal nanoparticles and their superstructures is presented. While the smaller transition metal nanoparticles are fabricated using well-installed methods (Turkevich et al. 1951; Frens 1973; Brown et al. 2000), larger platinum spheres with a narrow size distribution and distinct optical properties can be synthesized by a seed-mediated growth process. In the second part, two different ways for fabricating non-ordered large surface materials from gold, silver, platinum and palladium nanoparticles synthesized in water are described: one approach for non-supported hydro- and aerogels and one templated approach yielding hybrid materials from fungal mycelia and nanoparticles.

(a) Synthesis of transition metal nanoparticles in aqueous solution

For many applications of metal nanoparticles, an exact knowledge and spectral control of the localized surface plasmon resonance is necessary. Therefore, in recent decades, effort has been concentrated intensely on the fabrication of metal nanoparticles of different materials with properties tailored in size and shape. However, in terms of localized surface plasmon resonances, it is still difficult to cover the entire range of wavelengths of interest, e.g. for nanooptics. In particular for the two most commonly used materials, gold and silver, the short-wavelength region is difficult to reach. Here, platinum is an interesting alternative, since the localized surface plasmon resonances of platinum nanoparticles typically range between 450 and 550 nm for larger particles. For platinum nanoparticles, there are many more application fields. Monodisperse large high refractive index particles, for instance, find applications in photonic crystals, complementing the already existing bismuth, lead, silver, palladium spheres and other monodisperse shapes. Platinum nanocrystals also play a key role in heterogeneous catalysis, since they possess both large surface area and large chemical potential.

A variety of methods for the fabrication of aqueous suspensions of gold nanoparticles based on sodium citrate as a reducing agent have been known for several decades (Turkevich et al. 1951; Frens 1973). Following these procedures, the gold salt solution is heated to 100°C followed by the addition of the reducing agent. In order to transfer these kinds of procedures to platinum, palladium and silver nanoparticles (which are needed in the later sections of this article), it must be taken into account that not all of the precursors used react sufficiently quickly in aqueous solution with sodium citrate; so that an extension of the synthetic route introduced by Brown et al. (2000) is chosen. Here, besides the use of sodium citrate, an additional small amount of citric acid and the reducing agent sodium borohydride is used. This fabrication process for aqueous gold nanoparticles is directly projectable onto the systems with silver, platinum and palladium for yielding the respective nanoparticle solutions with only slight variations of the particle sizes.

The colloidal solutions are characterized by absorption spectroscopy. Whereas the gold and silver nanoparticle solutions have absorption maxima at 524 and 402 nm, respectively, the spectra of the platinum and palladium nanoparticles show a strong decrease in absorption with larger wavelengths without any significant plasmon absorption maximum. Transmission electron microscopy yields the average sizes of the nanoparticles to be 24, 8, 5 and 4 nm for the gold, silver, platinum and palladium sol, respectively, and the lattice constants obtained from high-resolution TEM measurements correspond to the fcc values of the respective bulk material.

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In the presence of less citric acid or in the case of lower temperatures of the sodium borohydride solution or very freshly prepared sodium borohydride solutions (which means less of the reducing agent is used), the resulting gold nanoparticles are much smaller (about 3–5 nm in diameter), whereas the mean sizes of the other metal nanoparticles are not affected.

As shown recently by our group (Bigall et al. 2008b), the platinum nanoparticles synthesized can be used as seeds for an easy multi-step seed-mediated growth process. Therefore, additional platinum salt, sodium citrate and ascorbic acid are added to the nanoparticle solution, and the solution is slowly heated to the boiling point, where it is kept until the end of the reaction. Depending on the amount of platinum salt added, this growth step yields platinum nanoparticles with sizes ranging from 10 to 30 nm in diameter, which, again, can be used as seeds to grow nanospheres with mean diameters of up to 107 nm (depending on the number of seeds inserted) and exceptionally small standard deviations of 3 per cent for the large spheres (figure 1). All particles prepared by this method consist of crystallites of 3–8 nm in diameter, which leads to a peak-to-valley surface roughness of 5–10 nm.

In the extinction spectra of the spheres, we observed a shift of the extinction peak to larger wavelengths with increasing sphere diameter from 248 nm (UV) for 29 nm diameter spheres to 494 nm (visible region) for the 107 nm diameter spheres. Plotting the position of the extinction peak maxima versus the particle diameter, we observed a linear correlation, which is in agreement with the previous reports of Langhammer et al. (2006). This property, which is in contrast to that of other materials, such as gold or silver, even holds for smaller particles and makes platinum a very interesting material for nanooptics, since, for example, during the fabrication process, the particle diameter can be monitored easily by measuring the extinction spectra.

When the extinction spectra of the water-dispersed spheres are compared with the corresponding calculated spectra of single particles with the same diameter (using the electrostatic approximation for calculating the spectra of the particles smaller than 30 nm diameter and the multiple multipole method for larger spheres (Hafner 1998, 1999), and using the data of Weaver (1975) for the dielectric function of polycrystalline platinum), a very good agreement in the slope of the curve, but with a constant offset of 25 nm in the position of the maxima, is observed (figure 2). This shift can be explained by taking into account the rough surface of the nanospheres influencing the plasmon resonances. For improving the single particle extinction spectra calculation, a core-shell model was introduced. Therefore, the peak-to-valley surface roughness of 5 nm was taken into account by treating the outermost 5 nm of the spheres as a shell with an effective dielectric function, which was obtained by averaging the dielectric functions of platinum and water in a 1 : 1 ratio. The core of the spheres was treated as pure polycrystalline platinum. With this improved model, excellent agreement of the calculated single particle extinction spectra and the experimentally determined ones from the dispersed ensemble was observed (figure 2).

The synthesized monodisperse platinum nanospheres are highly promising candidates for plasmonic applications, especially in the UV and blue wavelength regime. Owing to their linear dependence of the extinction maximum from the diameter, their sizes can be easily determined. Further particle features specific for platinum, such as the catalytic properties of the material, make the large platinum
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Figure 1. (a) Size distributions of four different batches of nanoparticles. (b) Transmission electron micrographs of Pt nanospheres with mean diameters of 29, 48, 73, and 107 nm, respectively (scale bar, 50 nm).

nanospheres an interesting material for plasmon-assisted UV photochemistry. The very narrow size distribution of the synthesized particles allows them to be applied in single particle as well as in ensemble experiments.

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Figure 2. (a) Experimentally determined extinction spectra of the platinum particles in aqueous solution. (b) Extinction peaks calculated for a core-shell platinum sphere (a and b: solid line, 29 nm; dotted line, 48 nm; dashed line, 73 nm; dash-dotted line, 107 nm). (c) Extinction peak positions of the experimental data (squares) and calculated values for massive platinum spheres (dots) as well as for core-shell particles (triangles). All lines depict linear fits to the respective data points.
2. Hydrogels and aerogels from noble metal nanoparticles

One possibility for generating porous large-surface superstructures of metal nanoparticles is given by hydro- and aerogels of the sols. Generally, aerogels from inorganic materials are highly porous macroscopic materials from self-assembled nanoscopic building blocks whose properties can be conserved yielding monoliths with exceptional catalytic, piezoelectric, thermoresistant or antiseptic properties (Kistler 1931; Gesser & Goswami 1989; Hüsing & Schubert 1998). Since a technique was introduced very recently to make aerogels from metal chalcogenide nanoparticles (Eychmüller 2005; Mohanan et al. 2005; Arachchige & Brock 2006, 2007a,b; Brock et al. 2006; Bag et al. 2007, 2008; Bag & Kanatzidis 2008; Gaponik et al. 2008), a lot of effort has been made to create monoliths from nanoparticles. A variation of this technique was recently applied to sols of metal nanoparticles by Bigall et al. (2009). While previous approaches for metal aerogels were based on the modification of oxide-based aerogels with metal nanoparticles for obtaining highly catalytically active materials (Pajonk 1997; Hüsing & Schubert 1998; Campbell 2004; Jiang & Gao 2006; Vallribera & Molins 2008), with this approach the resulting highly porous macroscopic monoliths are completely non-supportedly built only from metal nanoparticles. Owing to their large surface and the lack of supporting material, these monoliths have an enormous advantage in comparison with previously reported superstructural materials from metal nanoparticles such as mesoporous platinum–carbon composites (Warren et al. 2008), gold nanoparticles interlinked with dithiols (Joseph et al. 2009), nanochains of hybrid palladium–lipid nanospheres as reported by Zhou et al. (2009), electrocatalytically active nanoporous platinum aggregates as reported by Viswanath et al. (2009), foams (Banhart 2001; Schroers et al. 2003) and highly ordered two-dimensional and three-dimensional supercrystals (Kiely et al. 1998; Rabani et al. 2003; Fan et al. 2004; Kalsin et al. 2006; Shevchenko et al. 2006), artificial opals (Lu et al. 2005a,b), fungal templated (Bigall et al. 2008a) or even non-supported assemblies of dithiol-cross-linked supraspheres (Klajn et al. 2007, 2008).

The averaged densities of the novel metal nanoparticle hydro- and aerogels were determined to be 0.016 g cm\(^{-3}\) corresponding to approximately 1/1000th of the averaged bulk density of gold and silver, which is two orders of magnitude lower than that of the reported foams. Also, the primary structural units matched the size range of single nanoparticles (5–20 nm), which was an order of magnitude smaller than that of the supraspheres assembled by means of chemical cross-linkers (Klajn et al. 2008). The formation of the recently reported monometallic and bimetallic noble metal nanoparticle-based mesoporous aerogels is substantial progress towards self-supported monoliths with an extremely high catalytically active surface.

The gels were fabricated by systematically applying various methods of slow de-stabilization developed for quantum dot-based gels previously reported by Arachchige & Brock (2007a,b) and Gaponik et al. (2008) to the aqueous colloidal solutions of small citrate-stabilized platinum, silver and gold nanoparticles. For gelation of the present nanoparticles, however, the solutions had to be concentrated before the addition of the de-stabilizer, owing to the high stability of the as-prepared low-concentrated metal sols. Then, by the addition of, for
Figure 3. Scanning electron microscope (a,b) and transmission electron microscope images (c and d) of aerogels from platinum nanoparticles de-stabilized from solution by the addition of ethanol. The fractal morphology of the gel is homogeneously dispersed over large areas of the sample. The gel consists of nanoparticles with approximately the same size as in the original sol. Scale bars (a) 2.5 μm; (b) 250 nm; (c) 100 nm and (d) 50 nm.

example, ethanol or hydrogen peroxide to the concentrated colloids gel formation was achieved. When the hydrogel had formed, supercritical drying (Kistler 1931; Tewari et al. 1985) with liquid CO₂ yielded aerogels of the respective material. Gold, silver, platinum monometallic and gold–silver and platinum–silver bimetallic aerogels could be fabricated. While the monometallic gold and silver gels were found to be composed of pre-agglomerates (so-called secondary or tertiary particles) with large grain diameters of around 50 nm in the case of silver and hundreds of nanometres in the case of gold, the platinum gel consisted of ultrathin structures with typical dimensions on the same size scale as the diameter of the original nanoparticles (4–5 nm; figure 3). Presumably the platinum gel formed directly from the original colloidal platinum particles without pre-agglomeration of the nanoparticles.

While these successful fabrications of monometallic aerogels had reaction times of several weeks to months and varied in reproducibility, the bimetallic gold–silver and platinum–silver nanoparticles are obtained with strongly increased reproducibility in decreased process duration. The bimetallic hydro- and aerogels were even more voluminous and no morphologies with grains of higher order were observed. Here, by mixing concentrated gold and silver or platinum and silver nanoparticle solutions and adding a small amount of 30 per cent hydrogen
peroxide or pure ethanol, gel formation was achieved after about 10 days, and, even if no de-stabilizer was added, gels were obtained approximately 15 days after mixing the two colloidal solutions. Supercritical drying of the hydrogels yielded the final bimetallic aerogels, while the macroscopic sizes of the gels were retained.

All obtained bimetallic hydro- and aerogels did not possess a characteristic colour but were black, as can be seen from the colour photograph in figure 4a. A slightly coloured supernatant, which was observed at the beginning of the gel formation, cleared up within a few days, indicating that all nanoparticles were associated with the gel. The gold–silver aerogel shown in figure 4b had a diameter of 3–4 mm. The average density of the material was determined to be 0.016 g cm$^{-3}$, which corresponds to approximately 1/1000th of the averaged bulk density of gold and silver, which shows the unique physical properties of this new material.

The gold–silver gels had a highly branched wire-like polycrystalline morphology with typical thicknesses of 3–10 nm. In contrast to previously reported gels from different nanoscopic materials (Arachchige & Brock 2006), the nanoparticles were not well separated from each other but fused into a wire-like network, which might be the reason for the appearance of the black colour. In the case of platinum–silver the gels showed a morphology suggesting that the gels were composed of as-synthesized metal nanoparticles being attached to each other without further alloying or growth of secondary particles (figure 5). In this case, owing to the lattice distance differences of platinum and silver, within the same high-resolution transmission electron microscope image some nanoparticles could be identified to be silver and some to be platinum (figure 5c). We presume the direct contact between nanoparticles forming the percolating aerogel structure to be responsible
Figure 5. Scanning electron micrographs of platinum–silver aerogels at different magnifications (a,b), as well as TEM micrographs of (c) platinum–silver hydrogel and (d) aerogel. (e) HR-TEM image of the Pt–Ag nanochains showing individual silver and platinum nanodots (diameters approx. 3–6 nm). The lattice distances for the particles indicated were $d(111)_{\text{Ag}} = 2.36 \text{Å}$ and $d(111)_{\text{Pt}} = 2.22 \text{Å}$. Scale bars (a) 800 nm; (b) 100 nm; (c,d) 20 nm and (e) 2 nm.

for the observed conductivity of bulk aerogel species, which was determined to be in the range of tens of kOhm$^{-1}$ for a piece of Au–Ag aerogel of 2–3 mm in diameter.

Energy-dispersive X-ray spectroscopy (EDX) mapping revealed equal distributions of gold and silver or platinum and silver for the gold–silver or platinum–silver bimetallic aerogels respectively (figure 4c).
By performing nitrogen adsorption measurements (Brunauer–Emmett–Teller) on the Ag–Au and Pt–Ag aerogels after activation at 50°C, the specific surface was determined to be 48 m² g⁻¹ and 46 m² g⁻¹, respectively. This very large value is consistent with the estimated specific surface of 38 m² g⁻¹ obtained by assuming a long network of wires being 7 nm in diameter and averaging the density of silver and gold. The specific surface of the Ag–Au aerogel, for example, corresponds to a molar surface of $7.2 \times 10^3$ m² mol⁻¹, compared with typical molar surfaces of $30 \times 10^3$ and maximum values of approximately $10 \times 10^4$ m² mol⁻¹ for silica aerogels. All of the determined surface of the metal aerogels could be acting as the active area in heterogeneous catalysis, since these presented structures are non-supported and consist nearly entirely of the catalytically active metals.

3. Fungal templates for noble metal nanoparticles and their application in catalysis

Another possibility for fabricating large-surface nanostructures for catalysis or sensorics is given by the presumably nutrition-driven assembly of nanoparticles onto fungal surfaces during the growth of living entities. The use of small biological forms as templates for nanotechnological applications has recently become the focus of interest, since microbiological entities are easily removable low-cost templates with a broad variation in microscopic shapes. Recent reports have been on the incorporation of magnetic or semiconducting nanoparticles into bacterial superstructures (Davis et al. 1998), assembling of functionalized, DNA-modified gold nanoparticles or even cetyltrimethylammonium bromide-terminated gold nanoparticles of different shapes onto the surface of bacteria (Berry et al. 2004, 2005), diatoms and fungi (Li et al. 2003a,b; Rosi et al. 2004a,b).

In a different approach reported by Sugunan et al. (2007), fungal growth was achieved in gold nanoparticle solutions fabricated by means of sodium glutamate as a reducing agent. During the growth of the fungus, gold was accumulated macroscopically onto the fungal mycelia, yielding a gold–fungus hybrid structure that exhibited the optical properties of gold and an electric resistivity close to that of bulk gold.

We have recently demonstrated the possibility of fungal growth directly in the as-prepared citrate-stabilized nanoparticle solutions, presuming the residual citrate molecules from the synthesis of the metal nanoparticles (according to Turkevich et al. (1951); Frens (1973); Brown et al. (2000), as described in the previous section) to be the nutrient of the fungus. On the fungal surface, decoration with non-agglomerated nanoparticles was observed without any further functionalization. The outer dimensions of the resulting hybrid systems were about 0.1 cm³, and their optical properties were similar to those of the respective nanoparticle solutions (figure 6).

In the first experiment, Bjerkandera adusta, Nematoloma frowardii, Neurospora crassa, Trichoderma viride, Phoma herbarum Westendorp, Phanaerochaete chrysosporium, Chloridium virescens var. chlamydosporum, Fusarium, Trametes versicolor, Penicillium citreonigrum and seven other fungi differing in morphology were grown for one month under sterile conditions at room temperature in a liquid medium consisting of sodium citrate and citric acid in water, and transferred, again under sterile conditions, to an as-prepared gold nanoparticle
Figure 6. (a) Scanning electron micrograph taken in the backscattering mode of a critical point dried gold–Penicillium citreonigrum hybrid structure after several months of growth; gold appears as bright areas (scale bar, 20 μm). (b) Enlargement of the area indicated, showing the hollow character of the hybrid structure (scale bar, 2 μm).

Figure 7. Colour photographs of (a) gold–Penicillium citreonigrum hybrid structure in a gold nanoparticle solution and (b) after critical point drying (scale bar, 0.1 cm).

solution. The samples were stored for two months at room temperature in the dark. After completely exchanging the medium with de-ionized water, the fungi were transferred into dry acetone, and further dried in supercritical carbon dioxide so that the three-dimensional macroscopic shape was conserved (figure 7).

All investigated fungi exhibited the ability to accumulate nanoparticles on their surfaces, whereby the metal content determined by EDX strongly varied with different fungal species (figure 8).

Different fungi show differences in their affinity to the metal nanoparticles, which was shown in a second experiment. Under the same conditions, as-prepared solutions of gold, platinum, palladium and silver nanoparticles were used as media for the growth of P. citreonigrum, C. virescens var. chlamydosporum, T. viride, P. herbarum Westendorp, N. crassa, B. adusta and another fungus. The resulting hybrids were again supercritically dried.

Best growth of the fungi was observed in gold nanoparticle solution, followed by platinum and palladium. Growth in silver nanoparticle solution was observed only for B. adusta.
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In all cases, assembly of metal particles on the living entities took place. The hybrid structures showed the typical colours of the respective metal nanoparticle solutions, indicating that the nanoparticles were separately present on the fungal mycelia, which could be proven in the case of the larger gold nanoparticles by backscattering scanning electron micrographs (figure 9).

The metal contents determined by EDX (figure 10) were largest in the case of gold, followed by palladium, platinum and silver.

Within one system, morphological differences (e.g. spores) in the fungal mycelia were found together with differences in the metal affinities, which were observed by scanning electron micrographs in the ‘metal-sensitive’ backscattering mode (figure 11).

Considering the system to be a tube, an estimate revealed a specific surface of a hybrid from gold nanoparticles and *P. herbarum* Westendorp to be 0.4 m$^2$ g$^{-1}$.

In order to investigate whether all of the catalytically active sites on these hybrid structures were covered, a potassium hexacyanoferrate(III) reduction reaction via sodium thiosulphate was conducted in the presence of a hybrid from platinum nanoparticles and *P. herbarum* Westendorp. The results clearly indicated that the nanocrystals retain catalytic activity even when assembled onto the fungi.

These hybrid systems are thus extremely interesting supported superstructures for an application in heterogeneous catalysis, since the amount of nanoparticles on the fungus can easily be tuned, and the fabrication process is cost-effective, environmentally friendly and the organic templates will be easily removable by simple combustion for regaining the noble metal.

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Figure 9. (a) Single gold nanoparticles assembled on the hyphae of *Neurospora crassa* shown by scanning electron microscopy in the backscattering mode (scale bar, 250 nm). *Trichoderma viride* after two months of growth in a (b) gold nanoparticle solution (scale bar, 25 μm) and (c) gold-free sodium citrate medium.

Figure 10. Different metal affinities (obtained from EDX analysis) of seven different fungi grown for two months in identically prepared colloidal solutions.
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Figure 11. Scanning electron micrographs of similar regions within a hybrid structure \((a,c):\) secondary electron mode, \((b,d):\) backscattering mode. The spores (i.e. the spherical entities) of the fungus E07AS \((a,b)\) show significant assembly of gold nanoparticles, whereas the spores of the fungus O07AS \((c,d)\) do not. Scale bars \((a)\) 5 μm and \((c)\) 20 μm.

The effect of nanoparticle assembling on fungal mycelia could also be a useful tool for biochemical investigations, such as changing the impact of catalytically active nanoparticles on the metabolism of the microbiological systems, or concerning the fungal heavy-metal-accumulation effect. Other applications for silver- or gold-containing hybrids could be their use as templates for surface-enhanced Raman spectroscopy (SERS), or even the identification of fungi using SERS (Rösch et al. 2005; Szeghalmi et al. 2007; Hering et al. 2008). Other sensoric applications can be thought of by considering the plasmonic properties of the assembled nanoparticles or the conductivity of these systems, which still has to be determined. Silver fungus hybrids could serve as disinfecting objects owing to their high porosity and the disinfection capability of silver.

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