Porous Materials

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Selective Fabrication of Ordered Bimetallic Nanostructures with Hierarchical Porosity**

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There has recently been intensive effort to develop porous metallic materials because of their promising applications in catalysis, separation technology, sensors, and fuel cells. The success of these applications strongly relies on the availability of porous metallic materials with specific pore sizes and structures. In the quest to fabricate porous metallic materials with desired pore sizes and structures, attempts have been made to use templates in a replication process.[1–6] For example, anodic alumina[1] and lyotropic liquid crystals[2] were used as templates to fabricate mesoporous (voids <50 nm) metal films with cylindrical and parallel pores. It was also shown that techniques involving colloidal templates could be used to create ordered macroporous (voids >50 nm) metal films.[3–6] The latter method is attractive because of its pore-size tuneability and the ordered structure it produces. A critical issue in using this method is how to controllably fill the interstitial space of the colloidal templates with a desired composition. In previous work,[3–6] the use of this method invariably led to a complete infiltration of the interstitial space with different materials, which, to some extent, limits the application of such a method to produce porous metal materials with novel structures.

Porous hollow metallic spheres often exhibit catalytic activities different from their solid counterparts and have the advantages of low density and the use of less material.[7,8] For example, Hyeon and co-workers[7] showed that hollow Pd spheres possess excellent catalytic activity in Suzuki reactions and can be recycled without loss of the catalytic activity. The extension of such a structure to bimetallic nanomaterials is of great importance since the properties of one metal are usually improved by the addition of another.[9,10] Nevertheless, we are not aware of publications on the generation of such materials with ordered structures that may lead to the formation of hierarchical porosity.

Herein we describe how two different kinds of ordered bimetallic nanostructures with hierarchical porosity, namely a macroporous nanostructure and a nanostructure consisting of hollow spheres, can selectively and conveniently be fabricated by a general template technique on silicon wafers and glass substrates.

The starting material for the template is a colloidal suspension of highly monodisperse silica spheres in ethanol. The silica spheres were prepared by the improved Stöber growing procedure,[11,12] and subsequently modified with 3-aminopropyltrimethoxysilane (APTMS). The closely packed colloidal template was assembled on silicon wafers or glass substrates that were placed vertically in a slowly evaporating dispersion of APTMS-modified silica spheres in ethanol, as described by Jiang et al.[13] The colloidal template was then immersed in an aqueous solution of gold nanoparticles having an average diameter of 3 nm. Since the cross-sectional area of the smallest channel inside the colloidal template is much larger than the gold nanoparticles, the nanoparticles can flow freely throughout the colloidal template. Different kinds of nanostructures can be prepared by varying the immersion times and concentrations of the gold solution (see below and the Experimental Section). Finally, the dried colloidal template with the gold nanoparticles was dipped into a plating solution for coating with platinum. During the plating process, the small gold nanoparticles can serve as seeds to accelerate the reduction of the $PtCl_6^{2-}$ ions by ascorbic acid. Removing the silica template with 4% HF solution gave black self-supporting flakes. Shrinkage of the pores was avoided since the silica template was removed at room temperature.

It is very important to generate high-quality templates for this template-directed method since the quality of any

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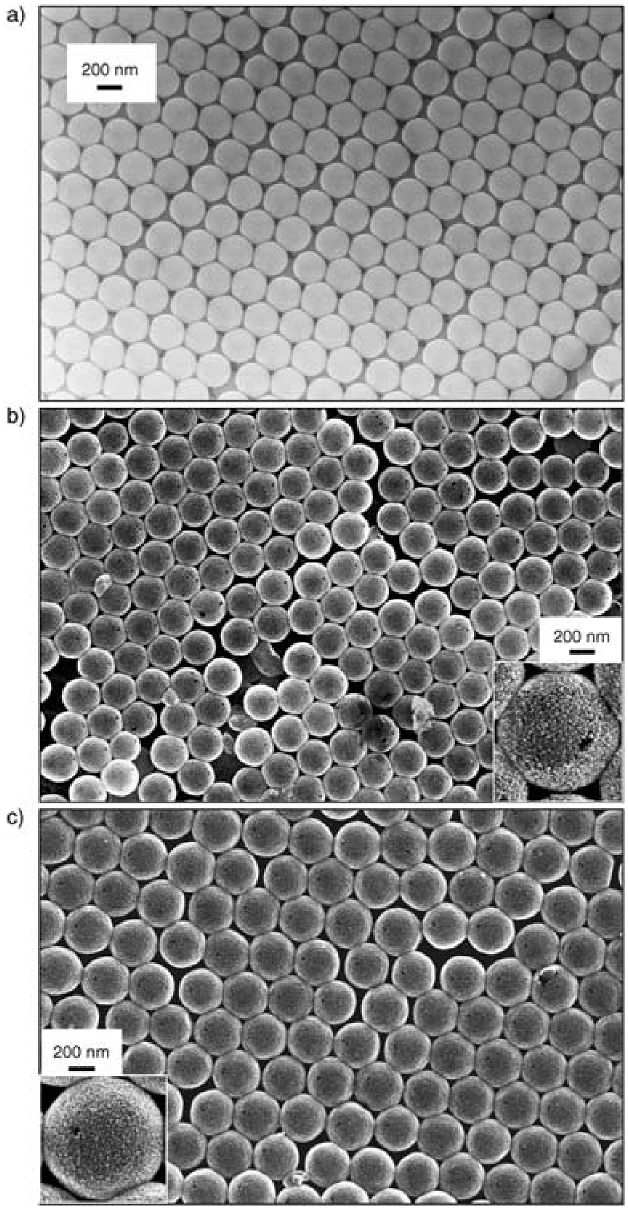

Figure 1. a) SEM image of a template consisting of 267-nm silica particles, and SEM images of typical ordered hollow nanostructures formed using b) 267-nm and c) 300-nm silica colloidal crystals as templates, respectively. The insets show the corresponding high-magnification images.

material formed by this method depends sensitively on the ordering and the properties of the starting template. Figure 1a shows a typical scanning electron microscopy (SEM) image of the top view of one of the silica colloidal templates. The SEM image reveals that the 267-nm silica spheres are organized in a close-packed arrangement with long-range hexagonal order. These high-quality colloidal crystals can be used as templates for the fabrication of ordered structures constructed from hollow metallic spheres. The resulting materials exhibit a tunable hollow volume since the starting template can be formed from silica spheres with different sizes. Figure 1b,c show typical SEM images (top views) of hollow metallic nanostructured materials made by using 267-nm and 300-nm silica colloidal crystals as templates, respectively. It is evident from Figure 1b,c that after removal of the template, the ordering feature—the original porous structure of the starting template—and the spherical shape of the silica spheres have clearly been retained. The hollow structure character of these materials is anticipated by inspection of the broken spheres seen in Figure 1b,c. A closer look at Figure 1b,c reveals another interesting feature, namely the existence of a hole with an average diameter of about 20 nm in almost every hollow sphere. These holes are arranged in order and the distances between neighboring holes are roughly equal to the center-to-center distances of the hollow metallic spheres. The detailed mechanism for the formation for this structural feature will be investigated further since it may open up a new route to the design of novel nanostructured materials. Higher magnification SEM images in Figure 1b,c (insets) show that these hollow spheres consist of small nanoparticles (average diameter below 10 nm), which are interconnected to form relatively uniform porous hollow metallic nanoshells. The average nanoshell thickness of the hollow metal spheres in Figure 1b and c is estimated to be about 20 nm and about 45 nm, respectively. The nanoparticle framework of the as-prepared materials provides yet another level of porosity which gives the structure a very high surface area: the size of the small pores and the overall surface area are determined by the size of the Au/Pt nanoparticles. Nanostructured materials with such controlled hierarchical porosity may be particularly suitable for catalytic applications.

Energy-dispersive X-ray analysis (EDX) is a technique that enables the elemental composition of a small selected area of the sample to be identified with a sensitivity of about 1% for elements heavier than beryllium. Figure 2a shows an EDX analysis of the hollow nanostructures shown in Figure 1b before (left) and after removal (right) of the SiO_2 template as an example. The EDX analysis shows strong Au and Pt peaks from the hollow nanostructures. The reasonably strong O peak present before removal stems from the SiO_2 template. The Si peak in both Figures originates most probably from the silicon wafer. The appearance of the remaining very weak O peak after the removal of the template can be attributed to the reduction reagents (citrate ions or ascorbic acid); this proposal is further supported by the presence of the C peaks (not shown). On the basis of the above EDX analysis it is reasonable to conclude that the silica template is completely removed and, thus, ordered hollow Au/Pt nanostructures are formed. Figure 2b presents an X-ray diffraction (XRD) pattern of the sample shown in Figure 1b. Broad diffraction peaks corresponding to metallic Au and Pt are observed which are indicative of the presence of nanosized Au/Pt particles (see the bulk reflexes, bottom of Figure 2b).

Ordered macroporous metallic nanostructures are another kind of important porous material. We found that the current method is also applicable to the formation of such structures if the experimental conditions are suitably controlled (see Experimental Section, Method B). Figure 3 shows a typical SEM image (top view) of the macroporous structure

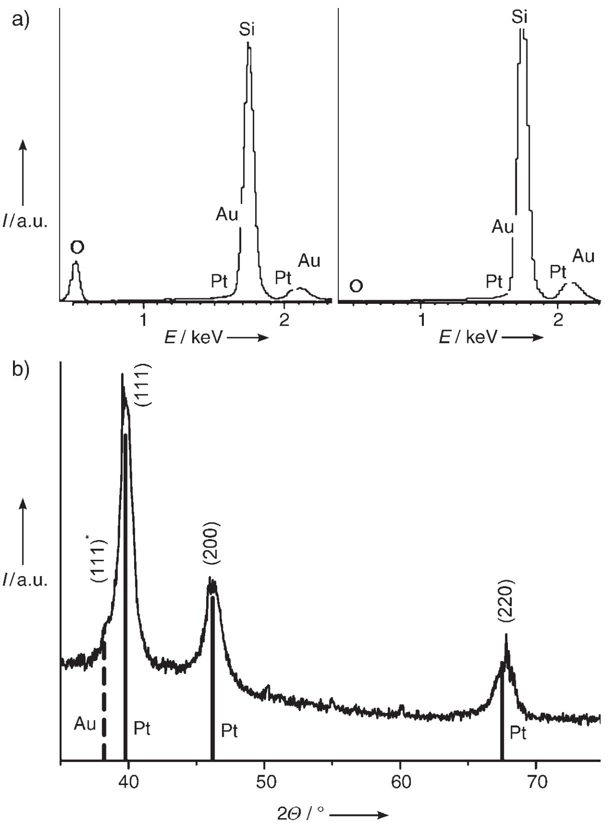

Figure 2. a) EDX analysis of the ordered Au/Pt nanostructures shown in Figure 1 b before (left) and after (right) HF treatment, and b) XRD pattern of the hollow nanostructure from Figure 1 b.

formed by this method. It is evident that the resulting material exhibits relatively uniform porosity with hexagonal close packing, while the pores match the size of the starting silica, thus indicating that negligible shrinkage of the metallic structure occurs.[3a] The ordered regions can extend to several hundreds of micrometers. The small nanoparticles around the large pores in the original interstitial space can be clearly observed in the corresponding higher magnification images (Figure 3, inset). EDX and XRD analysis show that the as-prepared materials consist of nanosized metallic Pt and Au.

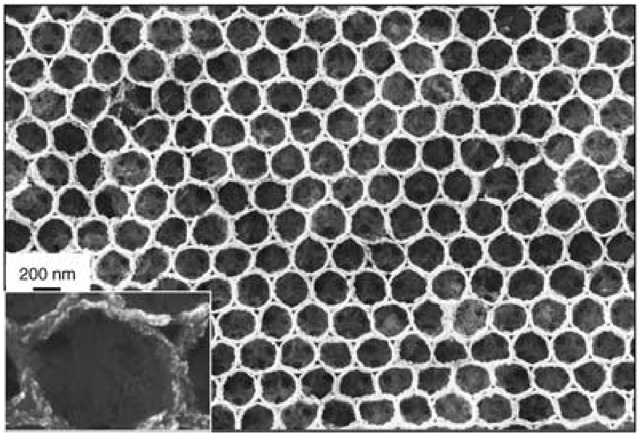

Figure 3. Typical SEM image of an ordered macroporous Au/Pt nanostructure. The inset shows a corresponding high-magnification image.

The success of the current method for selective fabrication of two different kinds of ordered bimetallic nanostructures with hierarchical porosity is rationalized as follows. According to previous reports,[3] in which the colloidal template was immersed in an aqueous solution of gold nanoparticles, small gold nanoparticles were deposited in the interstices of the colloidal template by an infiltration process to form a mesoporous structure around the silica spheres. Since the porosity allowed the solvent to flow freely through the structure, the pores can be completely filled with gold nanoparticles. However, the situation is different in the present study. Modification of the silica spheres with APTMS results in the APTMS molecules bonding to the surface of the silica spheres with their NH_2 groups directed outwards. Immersion of this modified colloidal template leads to an intense coverage of gold nanoparticles on the surface of the silica spheres through the interaction between the negatively charged gold nanoparticles and the positively charged NH_2 groups (see also ref. [14]). If the concentration of the gold nanoparticles is relatively low ([Au] = 0.06 mM) and the immersion time in the gold solution is comparatively short (8 h), the assembly of the gold nanoparticles on the surface of the silica spheres predominates. A small quantity of residual gold nanoparticles in the interstices of the colloidal template can be removed by rinsing with deionized water (and/or by deposition on the surface of the silica spheres during the drying process). This is followed by a 16-minute electroless deposition of Pt only on the surface of the silica spheres (Method A). As a result, the removal of the template leads to the formation of ordered porous Au/Pt nanostructures constructed from hollow spheres. In contrast, if the concentration of the gold nanoparticles is higher ([Au] = 0.3 mM) and the immersion time in the gold solution is long (16 h), besides the assembly of gold nanoparticles on the surface of the silica spheres, the relatively large amount of small gold nanoparticles in the interstices of the colloidal template in combination with those on the surface of the silica spheres associate into a larger, mesoporous structure. The following 16-minute Pt deposition leads to almost complete infiltration of the pores of the colloidal template, and macroporous Au/Pt nanostructures are obtained after removal of the template (Method B).

In a second set of experiments, monodisperse but non-ordered APTMS-modified silica spheres were used as templates and the same experimental procedures were performed. We found that only hollow porous Au/Pt nanostructures were obtained by both Methods A and B (Figure 4 a). As evidenced in higher magnification images, the shell of the hollow spheres is built-up by stringlike, structured aggregates consisting of small Au/Pt nanoparticles which results in many pores with an average diameter of 32 nm. Such nanostructured materials can be particularly desirable for application in catalytic nanoreactors. This result further strengthens our above explanation: Since the templates are non-ordered and the silica spheres within the template are loosely arranged, the assembly of the gold nanoparticles and the following Pt deposition only occurred on the surface of the silica spheres. As a result, only hollow nanostructures can be formed under Methods A or B. Interestingly, porous

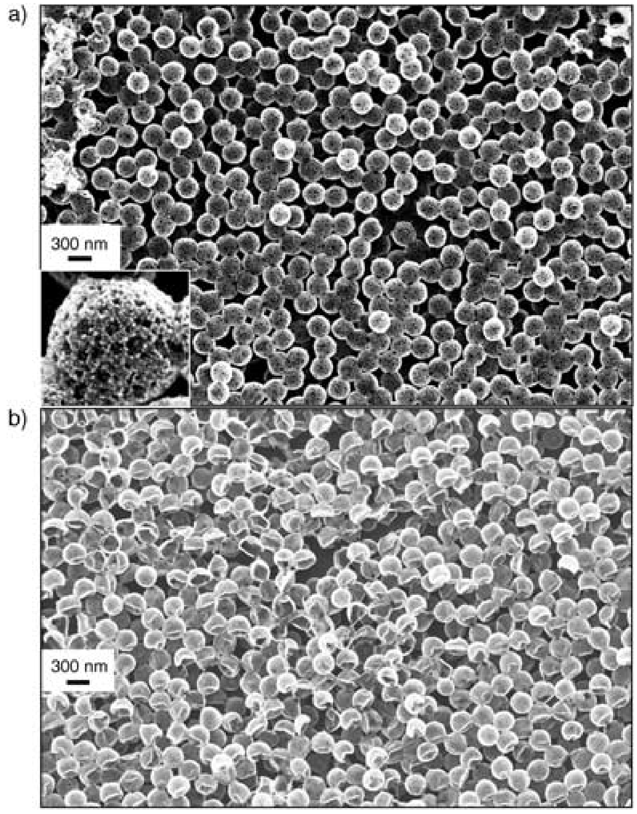

Figure 4. SEM images of a) hollow spheres prepared by Method B, and b) hollow hemispheres prepared by Method A with a concentration of gold of 0.06 mM, an immersion time in the gold solution of 10 h, and a Pt plating time of 12 min. Non-ordered APTMS-modified silica spheres on silicon wafers were used as templates.

hollow Au/Pt hemispheres can also be fabricated under appropriate experimental conditions (such as, for example, an increase in the Au concentration compared to Method A; Figure 4b), which may provide an alternative method for the synthesis of such materials.

In summary, ordered Au/Pt nanostructures with hierarchical porosity, such as macroporous nanostructures and nanostructures constructed from hollow spheres, can be selectively and conveniently prepared by a general template technique on silicon wafers and glass substrates. A possible explanation for the selective fabrication of the above-mentioned nanostructures is given. Furthermore, since protocols exist for the deposition of many other metals, such as Cu,[15] Pd,[16] and Ag,[17] this method could be successfully extended to other bimetallic systems including Au/Cu, Au/Pd, and Au/Ag (see Supporting Information). These ordered metallic nanostructures with hierarchical porosity could be useful in industrial applications including catalytic nanoreactors (see Supporting Information), sensors, porous electrodes, and fuel cells.

Experimental Section

3-nm gold nanoparticles:[18] A 1% solution of $HAuCl_4$ (1 mL) was added to water (90 mL) at room temperature. After stirring the mixture for 1 min, 1% sodium citrate solution (2 mL) was added. Freshly prepared 0.075% $NaBH_4$ (in 1% sodium citrate solution; 1 mL) was added 1 min later. The resulting solution was stirred for an additional 5 min and kept at about 4°C until use.

Synthesis and modification of the silica spheres: Equal volumes of a solution containing absolute ethanol (50 mL) and 0.2 M tetraethyl orthosilicate (TEOS), and another containing absolute ethanol (50 mL), water (28 mL), and ammonia (28–30%; 4 mL) to give a total volume of about 100 mL were mixed rapidly. The reaction was allowed to continue for 6 h at room temperature. APTMS (100 μL) was then added and the mixed solution was stirred for an additional 12 h. The resultant APTMS-modified silica spheres were cleaned by consecutive centrifuging, decanting, and redispersing in ethanol by sonication (five times). Removal of aggregates and smaller spheres was performed by fractionation by removing the upper and the lower fractions (three times).

Assembly of the silica template and introduction of gold nanoparticles and deposition of platinum: The APTMS-modified silica spheres were assembled onto a silicon wafer that was placed vertically in a slowly evaporating dispersion of silica spheres in ethanol for 2 days. The dried colloidal template was then immersed in solutions of the gold nanoparticles at different concentrations for different times. The dried colloidal templates with the gold nanoparticles were dipped into a plating solution (50 mL) that contained 10% H_2PtCl_6 (1 mL) and 0.1 M ascorbic acid (3 mL) for different times (Method A: [Au] = 0.06 mM, immersion time in the gold solution = 8 h, Pt plating time = 16 min; Method B: [Au] = 0.3 mM, immersion time in gold solution = 16 h, Pt plating time = 16 min). All samples were placed into deionized water and were dried in air.

Removal of the colloidal template: All samples were dipped into 4% HF solution for 5 min. The metallic film could then be peeled off the silica wafer. This procedure was repeated to completely remove the silica spheres.

Characterization: SEM images were obtained with a Leo 1550 supra instrument equipped with an EDX Si-detector (Oxford Instruments). All structures were characterized by XRD (Philips; X'pert MPD).

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[1] H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466–1468.
[2] G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, *Science* **1997**, *278*, 838–848.
[3] a) O. D. Velev, P. M. Tessier, A. M. Lenhoff, E. W. Kaler, *Nature* **1999**, *401*, 548; b) P. M. Tessier, O. D. Velev, A. T. Kalambur, J. F. Rabolt, A. M. Lenhoff, E. W. Kaler, *J. Am. Chem. Soc.* **2000**, *122*, 9554–9555; c) P. M. Tessier, O. D. Velev, A. T. Kalambur, A. M. Lenhoff, J. F. Rabolt, E. W. Kaler, *Adv. Mater.* **2001**, *13*, 396–400.
[4] a) P. Jiang, J. F. Bertone, V. L. Colvin, *Science* **2001**, *291*, 453–457; b) P. Jiang, J. Cizeron, J. F. Bertone, V. L. Colvin, *J. Am. Chem. Soc.* **1999**, *121*, 7957–7958; c) K. M. Kulinowski, P. Jiang, H. Harsha, V. L. Colvin, *Adv. Mater.* **2000**, *12*, 833–838.
[5] a) H. W. Yan, C. F. Blanford, B. T. Holland, M. Parent, W. H. Smyrl, A. Stein, *Adv. Mater.* **1999**, *11*, 1003–1006; b) H. W. Yan, C. F. Blanford, J. C. Lytle, C. B. Carter, W. H. Smyrl, A. Stein, *Chem. Mater.* **2001**, *13*, 4314–4321; c) H. W. Yan, C. F. Blanford, W. H. Smyrl, A. Stein, *Chem. Commun.* **2000**, 1477–1478.
[6] a) J. E. G. J. Wijinhoven, S. J. M. Zevenhuizen, M. A. Hendriks, D. Vanmaekelbergh, J. J. Kelly, W. L. Vos, *Adv. Mater.* **2000**, *12*, 888–890; b) Q. Luo, Z. Liu, L. Li, S. H. Xie, J. L. Kong, D. Y. Zhao, *Adv. Mater.* **2001**, *13*, 286–289; c) Z. Liang, A. S. Susha, F. Caruso, *Adv. Mater.* **2002**, *14*, 1160–1164; d) Z. Liang, A. S. Susha, F. Caruso, *Chem. Mater.* **2003**, *15*, 3176–3183.

[7] S. W. Kim, M. Kim, W. Y. Lee, T. Hyeon, *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643.
[8] H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan, C. L. Bai, *Angew. Chem.* **2004**, *116*, 1566–1569; *Angew. Chem. Int. Ed.* **2004**, *43*, 1540–1543.
[9] S. U. Son, Y. Jiang, J. Park, H. B. Na, H. M. Park, H. J. Yun, J. Lee, T. Hyeon, *J. Am. Chem. Soc.* **2004**, *126*, 5026–5027.
[10] R. W. Scott, A. K. Datye, R. M. Crooks, *J. Am. Chem. Soc.* **2003**, *125*, 3708–3709.
[11] W. Wang, B. H. Gu, L. Y. Liang, W. Hamilton, *J. Phys. Chem. B* **2003**, *107*, 3400–3404.
[12] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
[13] P. Jiang, J. F. Bertone, K. S. Kwang, V. L. Colvin, *Chem. Mater.* **1999**, *11*, 2132–2140.
[14] S. L. Westcott, S. J. Oldenburg, T. R. Lee, N. J. Halas, *Langmuir* **1998**, *14*, 5396–5401.
[15] E. Kim, Y. N. Xia, G. M. Whitesides, *J. Am. Chem. Soc.* **1996**, *118*, 5722–5731.
[16] L. H. Lu, H. S. Wang, S. Q. Xi, H. J. Zhang, *J. Mater. Chem.* **2002**, *12*, 156–158.
[17] Z. Chen, P. Zhan, Z. L. Wang, J. H. Zhang, W. Y. Zhang, N. B. Ming, C. T. Chan, P. Shen, *Adv. Mater.* **2004**, *16*, 417–422.
[18] K. R. Brown, D. G. Walter, M. J. Natan, *Chem. Mater.* **2000**, *12*, 306–313.