Nanoreactors

DOI: 10.1002/anie.201402212

Tea-Bag-Like Polymer Nanoreactors Filled with Gold Nanoparticles**

*Fabian Mitschang, Holger Schmalz, Seema Agarwal, and Andreas Greiner**

***Abstract:** Gold-containing polymer nanotubes, which showed both catalytic activity and resistance to leaching, were prepared by the "tubes by fiber templates" (TUFT) process. For this purpose, electrospun polymer nonwovens with incorporated poly(L-lactide)-stabilized gold nanoparticles were coated with poly(p-xylylene) by the chemical vapor deposition process, and then the inner fiber templates were removed. The resulting polymer tubes carried encapsulated gold nanoparticles which were shown to be immobilized and featured pronounced catalytic activity towards the hydrolytic oxidation of dimethylphenylsilane and the alcoholysis of dimethylphenylsilane with n-butanol. The macroscopic nonwovens could be used as tea-bag-like catalyst systems and showed excellent reusability.*

Gold nanoparticles and -wires are of great interest in the nanosciences due to their potential in microsensorics, microelectronics, catalysis, and biomedical applications.[1,2] However, since nanomaterials tend to agglomerate in order to minimize their surface energy,[3] a variety of methods for stabilization have been established, such as steric and electrostatic stabilization.[4] Polymer-stabilized gold nanoparticles allow for their incorporation in polymer matrices as well as the preparation of homogeneous dispersions.[5] In many cases, the nanomaterials must be immobilized onto carriers. There is a demand for tea-bag-like catalyst systems for multiple batch production cycles as well as for reactive filter systems for continuous production.[6,7] Suitable catalyst supports could be either porous materials like membranes and zeolites or fabrics with thin fiber diameters and hence a high surface area.[8] Further, fully encapsulated catalysts can display selectivity and prevent potential incompatibilities.[9]

A promising hybrid system that also sets a great challenge for synthesis consists of continuous polymer nanotubes with encapsulated nanoparticles. Most of the research on the interactions between nanoparticles and nanotubes, as well as on the incorporation of nanoparticles into nanotubes, is based on single- and multiwalled carbon nanotubes.[10] In addition, there are corresponding studies on inorganic nanotubes, such as titanium dioxide tubes,[11] and on polymer nanotubes, where the length of the tubes is highly restricted.[12] Noble-metal nanoparticles have been encapsulated by the use of electrospun polymer fibers doped with precursor salts following the concept of the "tubes by fiber templates" (TUFT) process.[13]

Herein, we report the preparation of highly efficient heterogeneous tea-bag-like gold-nanoparticle-based catalysts by the TUFT process. We studied in detail the preparation of well-dispersed gold nanoparticles, their immobilization in poly(L-lactide) (PLLA) composite fibers, their coating with poly(*p*-xylylene) (PPX) by chemical vapor deposition (CVD), and the subsequent quantitative removal of PLLA by pyrolysis. The leaching of gold nanoparticles from the resulting PPX tubes was studied as well as their catalytic activity.

Figure 1 illustrates the underlying concept based on the TUFT process.[14] First, a dispersion of poly(L-lactide)-stabilized gold nanoparticles (PLLA@Au) and the template matrix polymer PLLA were electrospun using a high voltage potential difference.[15] It is important to emphasize that electrospinning polymers like PLLA generally results in macroscopic nonwovens which makes them particularly useful in handling as tea-bag-like catalysts. After the resulting composite nanofibers had been coated with PPX by CVD,[16] the inner PLLA template material was removed quantitatively by thermal degradation,[17] resulting in PPX tubes with encapsulated gold nanoparticles.

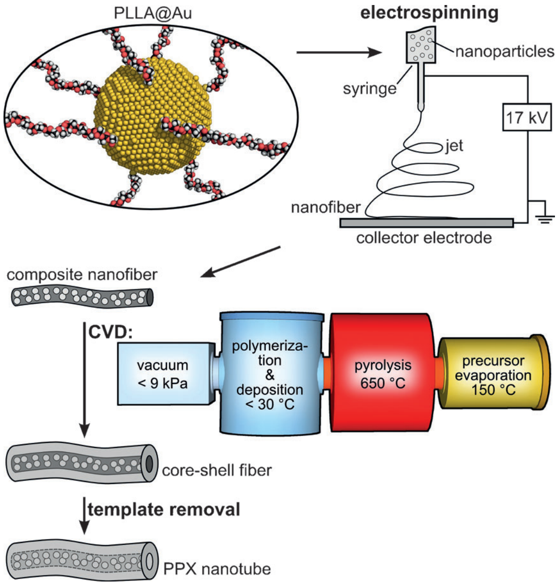


Figure 1. Electrospun composite nanofibers with incorporated PLLA-stabilized gold nanoparticles were coated with poly(*p*-xylylene) using the chemical vapor deposition process. Subsequently, the inner PLLA template material was removed by thermal degradation resulting in gold-containing PPX tubes.

---

[*] F. Mitschang, Dr. H. Schmalz, Prof. Dr. S. Agarwal,
Prof. Dr. A. Greiner
Macromolecular Chemistry II
and Bayreuth Center for Colloids and Interfaces
Univerität Bayreuth
Universitätsstrasse 30, 95440 Bayreuth (Germany)
E-mail: greiner@uni-bayreuth.de
Homepage: http://www.mcii.uni-bayreuth.de/en/ag-greiner/index.html

[**] We are indebted to Deutsche Forschungsgemeinschaft (DFG) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402212.

The availability of well-dispersed gold nanoparticles is crucial for the preparation of composite nanofibers by electrospinning. Therefore, PLLA-stabilized gold nanoparticles (PLLA@Au) were prepared based on PLLA featuring a thiol end-group (PLLA-SH) (Figure 2a). The corresponding PLLA-SH precursor was synthesized in analogy to poly(DL-lactide) with a thiol end-group[18] but under modified conditions. The bulk polymerization was carried out for 5 days at 130 °C using an aluminum catalyst and a protected thiol as the initiator. As determined by NMR spectroscopy, the molecular weight of the prepared PLLA-SH was about 2400 $\mathrm{g\,mol^{-1}}$. Gel permeation chromatography (GPC, poly(methyl methacrylate) calibration) showed a dispersity $Đ_M$ of 1.25. Subsequent reduction of chloroauric acid using lithium triethylborohydride[19] in the presence of PLLA-SH yielded in PLLA@Au. The nanoparticles were isolated as a deep purple solid and showed an excellent redispersibility as well as a pronounced stability in organic solvents such as dichloromethane, trichloromethane, and tetrahydrofuran. Thermogravimetric analysis (TGA) indicated a gold content about 20 wt %, whereas elemental analysis by atomic absorption spectroscopy indicated 18 wt % gold. The corresponding transmission electron microscopy (TEM) images as well as the results of the characterization by GPC coupled with a diode array detector[20] are shown in Figure 2.

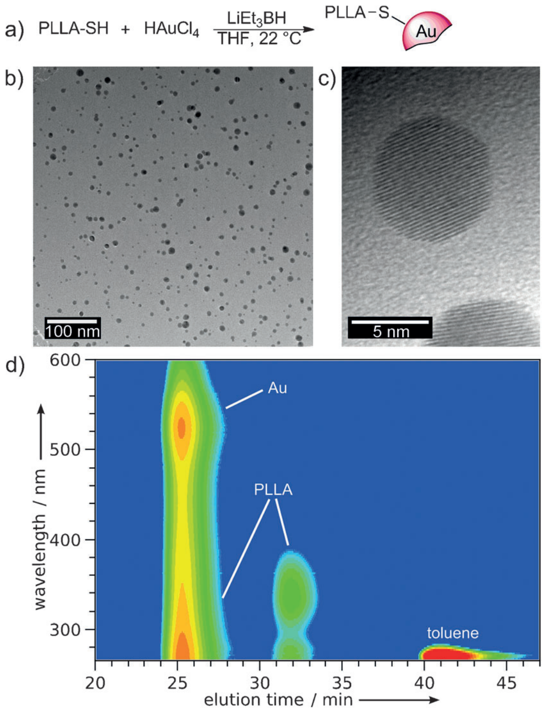


Figure 2. Synthesis and characterization of PLLA@Au. a) In situ preparation of the nanoparticles based on PLLA-SH. b) TEM image showing homogeneously dispersed particles. c) High-resolution TEM image revealing the characteristic lattice planes of gold particles. d) Measurement conducted with a GPC coupled with a diode array detector proving the connection between PLLA and the gold particles.

The spherical gold nanoparticles had an average diameter of (9.5 ± 2.8) nm as determined by TEM image analysis. The corresponding spacing of the lattice planes was 0.24 nm, which matched the (111) planes of face-centered cubic gold.[2,21] Using GPC coupled with a diode array detector, it was found that poly(L-lactide) was indeed attached to the gold nanoparticles, due to the combined characteristic absorption of nanoparticulate gold (see below) and PLLA (325 nm) at 25.3 min. Moreover, free PLLA-SH, which was eluted at 32 min, presumably arose either because of exchange reactions (the sample was measured in dimethylformamide in the presence of lithium bromide) or due to incomplete grafting of the polymer onto the gold surface. Further, both the X-ray powder diffraction pattern and the UV/Vis spectrum of PLLA@Au confirmed the presence of nanometer-scale particles (Supporting Information, Figures S1 and S2). Aside from the characteristic pattern of the semicrystalline PLLA,[22] the corresponding reflections of the gold particles showed distinct line broadening.[23] In addition, the UV/Vis spectrum showed the characteristic plasmon resonance absorption of nanoparticulate gold at 522 nm.[24]

Composite nanofibers were electrospun from a dispersion of 10 wt % PLLA@Au, 0.5 wt % PLLA, and 0.25 wt % of the salt tetraoctylammonium bromide (TOAB), which is soluble in organic solvent. The free polymer was necessary to improve the mechanical properties of the fibers, whereas the salt suppressed the formation of beads.[25] Scanning electron microscopy (SEM) revealed an average fiber diameter of (322 ± 72) nm (Figure 3a). Further, the composite fibers were free of beads and consisted of 19 wt % gold, as determined by TGA. According to the TEM picture in Figure 3b, the gold nanoparticles were homogeneously distributed throughout the PLLA matrix.

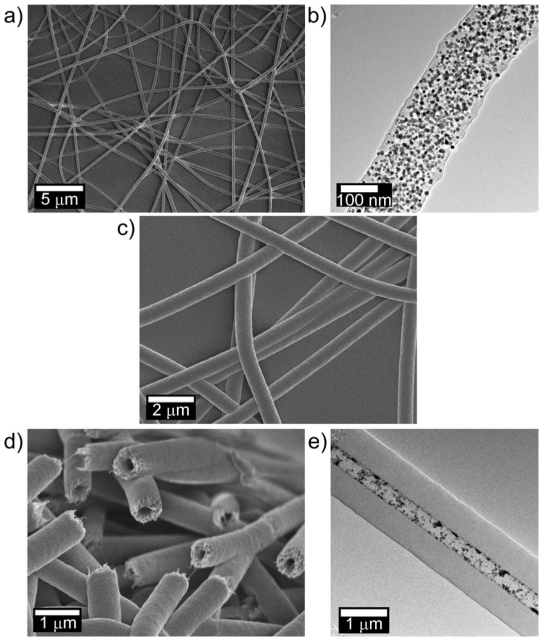
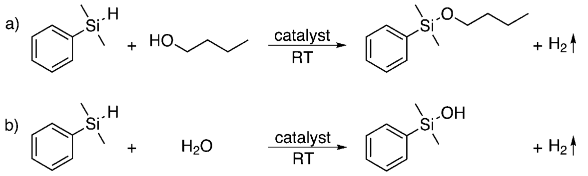


Figure 3. Electron micrographs before, during, and after the TUFT process: a) SEM image of electrospun composite nanofibers and b) TEM image of the fibers. c) SEM image of the PPX-coated composite fibers. d) SEM image of the gold-containing PPX tubes after template removal and subsequent freeze-fracturing. e) TEM image of the PPX tubes.

After the composite fibers had been coated with PPX, the resulting fibers had an average diameter of (711 ± 46) nm (Figure 3c). These core–shell fibers were annealed under reduced pressure at 280 °C, in order to remove the template PLLA material, which resulted in PPX tubes with an average diameter of (730 ± 83) nm. IR spectroscopy confirmed the quantitative removal of the PLLA (Supporting Information, Figure S3). The tubular structure was clearly proven by SEM (Figure 3d). Further, TEM analysis also confirmed the tubular structure and indicated the presence of gold nanoparticles inside the PPX tubes (Figure 3e). Subsequent TGA measurements confirmed a gold content of 9 wt%. The encapsulated particles were found to be immobilized when in contact with organic solvents, such as di- or trichloromethane (see the Supporting Information for UV/Vis spectra, Figure S4). Due to the absence of leaching, these gold nanoparticle PPX tubes should be suitable for various applications, for example as novel reusable tea-bag-like catalyst systems.

To study the applicability of this tea-bag-like catalyst, the alcoholysis of dimethylphenylsilane with *n*-butanol,[26] as well as the well-studied hydrolytic oxidation of dimethylphenylsilane,[27] were used as model reactions (Scheme 1). Even at room temperature the catalyst system showed high catalytic activity, which also proved the reactants' ready access to the inside of the PPX nanotubes. The gold-catalyzed alcoholysis of dimethylphenylsilane (Scheme 1a, 6.6 mol% gold with respect to the silane) yielded the adduct butoxydimethylphenylsilane in quantitative yield after 26 h, whereas the reaction catalyzed by non-immobilized PLLA@Au nanoparticles required 5 h for quantitative conversion. At 100 °C, the same reaction (based on 0.05 mol% immobilized gold) required 5 h for complete conversion of the silane. In comparison, for non-encapsulated gold nanoparticles on an aluminum oxide support (3–5 nm mean diameter, 0.05 mol% gold with respect to the silane), quantitative conversion required only 3 h (at 100 °C).[26] However, the cited catalyst system was only used at 100 °C, whereas the prepared PPX tubes were also suitable for catalysis at room temperature, as mentioned above. Further, we speculate that the semipermeable PPX tubes[7] can be used for selective catalysis. Since the gold nanoparticles are fully encapsulated rather than surface-immobilized, a second catalyst could be attached to the shell of the PPX tubes[28] allowing for site-isolated tandem catalysis.[29]



Scheme 1. Model reactions for the non-immobilized PLLA@Au nanoparticles as well as for the gold-containing PPX nanoreactors. a) Alcoholysis of dimethylphenylsilane with *n*-butanol. b) Hydrolytic oxidation of dimethylphenylsilane.

Using the PPX-encapsulated gold catalyst system, we observed excellent catalytic activity for the hydrolytic oxidation of dimethylphenylsilane (Scheme 1b). At room temperature, the corresponding adduct, dimethylphenylsilanol, was formed in quantitative yield after 3.5 h (0.87 mol% gold with respect to the silane), whereas at 80 °C the same reaction (with 0.83 mol% gold) required 1.5 h for complete conversion. In comparison, alternative gold-based catalyst systems, such as nanograined metallic glass[30] and hydroxyapatite-supported gold nanoparticles,[31] required 24 h for 93% conversion (RT, 0.87 mol% nanograined gold with respect to the silane) and 3 h at 80 °C for quantitative conversion (2 nm mean particle diameter, 0.83 mol% nanoparticulate gold with respect to the silane), respectively. In both cases, neither disiloxanes nor other by-products could be found, and in the absence of gold nanoparticles, no product was formed. Upon removal of the tea-bag-like catalyst during the reaction, product formation stopped immediately, confirming that the catalyst does not leach. When the removed catalyst was then added to the reaction mixture, conversion recommenced until quantitative conversion was achieved. Further, in order to study the reusability of the catalyst system, the silane alcoholysis was repeated 18 times using the same sample of PPX-encapsulated gold nanoparticles. Even after 18 cycles, the reaction time required for complete conversion did not increase. Moreover, the weight of the PPX catalyst system remained constant, hence the nanoparticle-based PPX nanoreactors demonstrated excellent reusability.

In conclusion, PLLA-SH was synthesized and subsequently used for the stabilization of gold nanoparticles. Electrospun gold-containing nanofibers were coated with PPX using the CVD process, and the template PLLA material was then removed quantitatively. The resulting PPX tubes were obtained as macroscopic nonwovens and successfully immobilized the encapsulated gold nanoparticles. Despite the insoluble PPX shell, the inside of the gold-loaded tubes was shown to be accessible to the reactants and was used for both the catalytic hydrolytic oxidation of dimethylphenylsilane and for the corresponding silane alcoholysis with *n*-butanol. The tea-bag-like catalyst system featured solid performance in the alcoholysis and excellent catalytic activity with regard to the hydrolytic oxidation even at room temperature. No disiloxanes were formed, and no catalyst leaching occurred. The catalyst system was reused 18 times with no decrease in activity. Since PPX membranes have been shown to be size selective,[7] these novel catalyst-confining systems obtained by the highly flexible TUFT process have huge potential for the preparation of other catalysts based on nanoparticles, bacteria, enzymes, and dendrimers. The combination of different catalysts in one system and the potential for substrate selectivity are as yet unexplored and are topics of current research.

Received: February 10, 2014
Published online: April 2, 2014

Keywords: catalysis · electrospinning · gold · nanostructures · poly(*p*-xylylene)

---

[1] a) N. A. Kotov, J. O. Winter, I. P. Clements, E. Jan, B. P. Timko, S. Campidelli, S. Pathak, A. Mazzatenta, C. M. Lieber, M. Prato, R. V. Bellamkonda, G. A. Silva, N. W. S. Kam, F. Patolsky, L. Ballerini, *Adv. Mater.* **2009**, *21*, 3970–4004; b) D. T. Thompson, *Nano Today* **2007**, *2*, 40–43.

[2] G.-M. Kim, A. Wutzler, H.-J. Radusch, G. H. Michler, P. Simon, R. A. Sperling, W. J. Parak, *Chem. Mater.* **2005**, *17*, 4949–4957.

[3] W. Caseri, *Macromol. Rapid Commun.* **2000**, *21*, 705–722.

[4] a) C. Lourenco, M. Teixeira, S. Simões, R. Gaspar, *Int. J. Pharm.* **1996**, *138*, 1–12; b) J. Hang, L. Shi, X. Feng, L. Xiao, *Powder Technol.* **2009**, *192*, 166–170.

[5] a) M. K. Corbierre, N. S. Cameron, M. Sutton, S. G. J. Mochrie, L. B. Lurio, A. Rühm, R. B. Lennox, *J. Am. Chem. Soc.* **2001**, *123*, 10411–10412; b) D.-H. Han, C.-Y. Pan, *J. Polym. Sci. Part A* **2008**, *46*, 341–352.

[6] a) M. Gaab, S. Bellemin-Laponnaz, L. Gade, *Chem. Eur. J.* **2009**, *15*, 5450–5462; b) M. Stratakis, H. Garcia, *Chem. Rev.* **2012**, *112*, 4469–4506.

[7] a) M. Stasiak, A. Studer, A. Greiner, J. H. Wendorff, *Chem. Eur. J.* **2007**, *13*, 6150–6156; b) J.-P. Lindner, C. Röben, A. Studer, M. Stasiak, R. Ronge, A. Greiner, J. H. Wendorff, *Angew. Chem.* **2009**, *121*, 9035–9038; *Angew. Chem. Int. Ed.* **2009**, *48*, 8874–8877.

[8] a) Z. Xie, Z. Liu, Y. Wang, Q. Yang, L. Xu, W. Ding, *Int. J. Mol. Sci.* **2010**, *11*, 2152–2187; b) A.-H. Lu, F. Schüth, *Adv. Mater.* **2006**, *18*, 1793–1805; c) M. Graeser, E. Pippel, A. Greiner, J. H. Wendorff, *Macromolecules* **2007**, *40*, 6032–6039.

[9] a) S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. Yang, G. A. Somorjai, *Nat. Mater.* **2009**, *8*, 126–131; b) S. Ikeda, Y. Ikoma, H. Kobayashi, T. Harada, T. Torimoto, B. Ohtani, M. Matsumura, *Chem. Commun.* **2007**, 3753–3755.

[10] a) A. La Torre, G. A. Rance, J. El Harfi, J. Li, D. J. Irvine, P. D. Brown, A. N. Khlobystov, *Nanoscale* **2010**, *2*, 1006–1010; b) Y.-J. Gu, W.-T. Wong, *J. Nanosci. Nanotechnol.* **2009**, *9*, 2066–2071.

[11] K. Shin, Y. Jun, G. Y. Han, J. H. Park, *J. Nanosci. Nanotechnol.* **2009**, *9*, 7436–7439.

[12] H. Kong, J. Song, J. Jang, *Macromol. Rapid Commun.* **2009**, *30*, 1350–1355.

[13] Z. Sun, J. Zeng, H. Hou, H. Wickel, J. H. Wendorff, A. Greiner, *Prog. Colloid Polym. Sci.* **2005**, *130*, 15–19.

[14] a) M. Bognitzki, H. Hou, M. Isahaque, T. Frese, M. Hellwig, C. Schwarte, A. Schaper, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2000**, *12*, 637–640; b) H. Hou, Z. Jun, A. Reuning, A. Schaper, J. H. Wendorff, A. Greiner, *Macromolecules* **2002**, *35*, 2429–2431.

[15] a) X. Zong, K. Kim, D. Fang, S. Ran, B. S. Hsiao, B. Chu, *Polymer* **2002**, *43*, 4403–4412; b) E.-R. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, D. G. Simpson, E. H. Sanders, G. W. Wnek, *J. Controlled Release* **2002**, *81*, 57–64; c) J. Zeng, H. Hou, A. Schaper, J. H. Wendorff, A. Greiner, *e-Polym.* **2003**, *3*, 102–110.

[16] A. Greiner, S. Mang, O. Schäfer, P. Simon, *Acta Polym.* **1997**, *48*, 1–15.

[17] H. Abe, N. Takahashi, K. J. Kim, M. Mochizuki, Y. Doi, *Biomacromolecules* **2004**, *5*, 1606–1614.

[18] S. Aryal, K. C. R. Bahadur, N. Bhattarai, B. M. Lee, H. Y. Kim, *Mater. Chem. Phys.* **2006**, *98*, 463–469.

[19] C. K. Yee, R. Jordan, A. Ulman, H. White, A. King, M. Rafailovich, J. Sokolov, *Langmuir* **1999**, *15*, 3486–3491.

[20] S. Bokern, J. Getze, S. Agarwal, A. Greiner, *Polymer* **2011**, *52*, 912–920.

[21] R. P. Andres, J. D. Bielefeld, J. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, *Science* **1996**, *273*, 1690–1693.

[22] N. Ogata, S. Yamaguchi, N. Shimada, G. Lu, T. Iwata, K. Nakane, T. Ogihara, *J. Appl. Polym. Sci.* **2007**, *104*, 1640–1645.

[23] a) P. Jiang, S. Xie, J. Yao, S. Pang, H. Gao, *J. Phys. D* **2001**, *34*, 2255–2259; b) J. I. Langford, A. J. C. Wilson, *J. Appl. Crystallogr.* **1978**, *11*, 102–113.

[24] G. A. Rance, D. H. Marsh, A. N. Khlobystov, *Chem. Phys. Lett.* **2008**, *460*, 230–236.

[25] See Ref. [15a].

[26] P. Raffa, C. Evangelisti, G. Vitulli, P. Salvadori, *Tetrahedron Lett.* **2008**, *49*, 3221–3224.

[27] T. Y. Lee, L. Dang, Z. Zhou, C. H. Yeung, Z. Lin, C. P. Lau, *Eur. J. Inorg. Chem.* **2010**, 5675–5684.

[28] J. A. M. Hepperle, F. Mitschang, A. K. Bier, B. K. Dettlaff, A. Greiner, A. Studer, *RSC Adv.* **2013**, *3*, 25976–25981.

[29] S. L. Poe, M. Kobašlija, D. T. McQuade, *J. Am. Chem. Soc.* **2006**, *128*, 15586–15587.

[30] N. Chen, R. Frank, N. Asao, D. V. Louzguine-Luzgin, P. Sharma, J. Q. Wang, G. Q. Xie, Y. Ishikawa, N. Hatakeyama, Y. C. Lin, M. Esashi, Y. Yamamoto, A. Inoue, *Acta Mater.* **2011**, *59*, 6433–6440.

[31] T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 5302–5304.