

Morphology-Control in Microwave-Assisted Synthesis of Silver Particles in Aqueous Solutions

Tetsushi Yamamoto, Hengbo Yin,¹ Yuji Wada,* Takayuki Kitamura, Takao Sakata,² Hirotaro Mori,² and Shozo Yanagida*

Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

¹Department of Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

²Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047

Received October 7, 2003; E-mail: ywada@mls.eng.osaka-u.ac.jp

The morphologies of Ag particles can be controlled between distorted sphere and prism by employing microwave-promoted reductions of highly concentrated 0.1 M silver nitrate in aqueous solutions. We can selectively synthesize either sphere-Ag or prism-Ag particles by changing only an additive, i.e., either trisodium citrate/formaldehyde or poly(*N*-vinyl-2-pyrrolidone) (PVP). The particle sizes and size distributions of sphere-Ag particles are strongly dependent on the concentration of trisodium citrate.

Nanosized metallic materials, such as silver, gold, and other noble metals, have displayed considerable phenomena due to their strong size- and shape-dependent properties.^{1–5} Furthermore, new size-dependent properties of sub-micrometer particles, such as optical properties, may merge. The morphology control of these particles has a strong dependence on the reaction conditions. Sphere-Ag nanoparticles have been synthesized by classical Turkevich methods,^{6,7} a reversed micelle process,⁸ photoreductions,^{9,10} ultrasonic radiation,¹¹ thermal decomposition,¹² and ⁶⁰Co γ -irradiation.¹³ Recently, morphology controls of metal particles have been regarded as the next target in the preparations of nanosized metals, for example, wire-,^{4,9,14} prism-,¹⁰ and cube-Ag,¹⁵ polyhedron-, cube-, and prism-Pt,^{5,16} rod-Co,¹⁷ prism-Pd or Ni¹⁵ by using capping molecules, such as poly(*N*-vinyl-2-pyrrolidone) (PVP),^{14,15} sodium polyacrylate,^{5,16} and tetra-*n*-octylammonium carboxylate.¹⁷

Microwave (MW) dielectric loss heating is rapidly emerging as a newly accepted heating technology for a variety of organic and inorganic syntheses.¹⁸ In our MW-assisted syntheses of nanosized nickel and CdS particles, we found that MW heating can give a smaller size distribution of the nano-sized nickel and CdS in a narrower range than the conventional outside heating. We ascribe such interesting results to homogeneous and rapid heating caused by a MW (2.45 GHz)-matched dielectric loss of dipolar molecular circumstances.^{19,20} This interesting heating effect can be called “homogeneous MW-matched dielectric heating”. Keeping the concept of MW heating and these successes in mind, we decided to try applying a MW heating technique for the morphology-control of the nano-size particle shape in addition to the size and its distribution. We discuss here how sphere- or prism-silver (Ag) particles are selectively synthesized by the reduction of silver nitrate in aqueous solutions up to 0.1 M concentration under microwave irradiation in the presence such additives as trisodium citrate and poly(*N*-vinyl-2-pyrrolidone) (PVP), which may work as a heat gen-

erator in homogeneous MW-matched dielectric heating.

Experimental

A domestic MW oven (Sanyo EM-650T, having a maximum power output of 650 W and a magnetron frequency of 2.45 GHz) was modified by installing a condenser through a hole on the ceiling and a magnetic stirrer at the bottom (Shikoku Keisoku Kogyo Co., ZMW-002). A 100 mL Pyrex or quartz glass flask was placed at the center of the oven as a reaction vessel. Additives, such as trisodium citrate/formaldehyde or poly(*N*-vinyl-2-pyrrolidone) (PVP; Wako; average M_w , 40000; concentrations of PVP expressed as polymer units of PVP in Table 1), were added into a silver nitrate aqueous solution. The mixture solution in the flask was irradiated by MW at 650 W for an appropriate time. After MW irradiation, as-prepared samples were washed with 50 mL of ion-exchanged water three times to remove any unreacted additives, and separated by centrifugation, giving product samples A1 and A3–A8 (Table 1).

The product samples were kept in methanol for powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. Transmission electron microscopy (TEM) was undertaken with a Hitachi H-8000 electron microscope. An electron diffraction analysis was carried out to certify the crystal phases of the Ag particles. A TEM sample was prepared by dropping a silver suspension onto an amorphous-carbon coated copper grid. The particle sizes of the silver particles were determined by directly measuring the sizes of randomly chosen particles on the TEM images. Ultraviolet–visible (UV–vis) absorption spectral measurements were carried out with a U-3300 UV–vis spectrophotometer.

Results and Discussion

Preparation of Nano-Sized Sphere-Silver Particles in Aqueous Solution. It is well known as a silver mirror reaction, where metal Ag is formed as silver metal film under a reflux of aqueous solution of silver nitrate and formaldehyde; the formaldehyde therein works as a reducing agent of $[\text{Ag}(\text{NH}_3)_2]^+$

Table 1. Preparation of Silver Particles under MW (2.45 GHz) Irradiation at 650 W

Sample	Silver nitrate /M	Trisodium citrate/M	Formaldehyde /M	PVP /M	MW irradiation time/min	Conventional heating time ^{a)} /min
A1	0.1	0.1	1.5	—	1	—
A2	0.1	0.1	1.5	—	—	8
A3	0.1	1.0	1.5	—	1	—
A4	0.1	1.5	1.0	—	1	—
A5	0.01	—	—	3	30	—
A6	0.01	—	—	3	90	—
A7	0.1	—	—	3	20	—
A8	0.1	—	—	3	75	—

a) 50 mL aqueous solution containing reactants was heated from room temperature to the boiling temperature (taking about 4 min), and kept boiling for a given time under vigorous stirring in an oil bath (150 °C). The conventional heating time was the total reaction time.

(Tollens' reagent) to metal silver. We found that MW-induced 1-min heating of aqueous solutions (up to 0.1 M) of silver nitrate gave aggregates of sphere-nanoparticles in the presence of trisodium citrate (0.1–1.5 M) and excess of formaldehyde (1.5 M) (Table 1). Conventional heating using an oil bath also gave comparable spherical particles (sample A2 in Table 1). SEM and XRD analyses revealed that all of the spherical particles were identified as face-centered-cubic (fcc) metal Ag (powder diffraction file, PDF #4-783). As shown in Fig. 1, sample A1, prepared in the presence of an equal quantity (0.1 M) of trisodium citrate to silver nitrate, resulted in the formation of sphere-Ag particles with a smaller average particle size (24 nm) and a narrower particle size distribution (10–90 nm) than sample A2 prepared by the conventional heating (average size 71 nm, size distribution 20–360 nm). Therefore, we speculated that MW irradiation should induce homogeneous and fast nucleation of silver metal from the reduction of silver cation, and their successive flash growth to nano-sized spherical particles, as observed in the MW-assisted preparation of nano-sized nickel metal.¹⁹ On the other hand, when the concentration of trisodium citrate was increased excessively from 0.1 M to 1.0–1.5 M, the average particle sizes were increased (65 nm at A3 and 132 nm at A4) and the size distributions became wider with an increase of trisodium citrate under MW flash heating.

When trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 0.1 or 1.0 M) was added into silver nitrate aqueous solutions, silver citrate ($\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$, PDF #1-30) was formed as a white powder, which was confirmed by powder XRD analysis. Therefore, the formation of sphere-Ag particles should be formed through silver citrate formation. At a low concentration of trisodium citrate (0.1 M), citrate works as an efficient stabilizer.²¹ Small sphere-silver particles were formed under microwave irradiation (Scheme 1). However, at a high concentration of trisodium citrate (1.5 M), a large excess of trisodium citrate may promote the "coalescence"¹³ of silver particles, and may affect the dielectric loss of the reaction medium, leading to rapid heating under MW irradiation. Therefore, a large excess of trisodium citrate may spontaneously promote the "coalescence"¹³ of silver particles and, subsequently, successive particle growth should occur by a localized-"super heating"²² or "hot spot"²³ induced under MW irradiation, as observed in the MW-assisted preparation of nano-sized CdS.²⁰ In addition to the MW effect, when the concentration of sodium citrate was increased, the in-

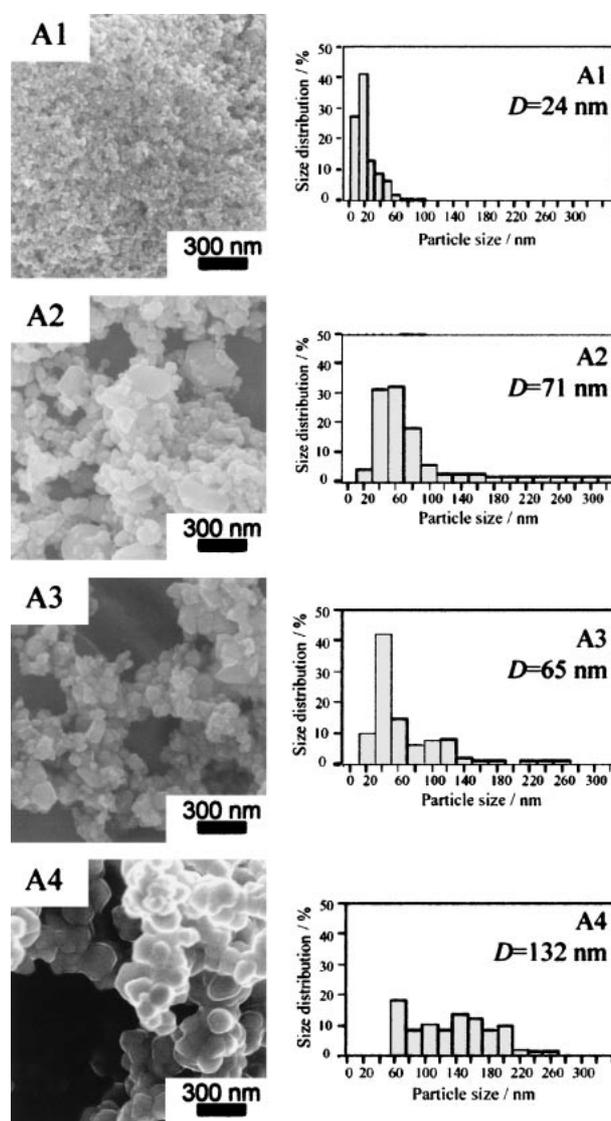
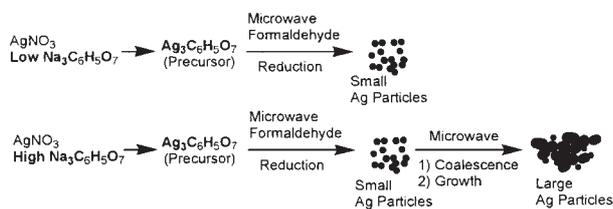


Fig. 1. SEM images and size distributions of sphere-Ag particles synthesized in silver nitrate (0.1 M) aqueous solution under MW irradiation by changing trisodium citrate at 0.1 M (A1), 1.0 M (A3), and 1.5 M (A4) or by a conventional heating in trisodium citrate at 0.1 M (A2). In size distributions, D is average particle size.



Scheme 1.

ter-molecule hydrogen bonding of the citrate moieties associated with silver particles should enhance the collision probability of the particles, resulting in the coalescence of silver nanoparticles. As a result, large Ag particles with a wide particle distribution were produced in the presence of a larger amount of trisodium citrate under MW irradiation. In other words, the nucleation and growth of Ag particles is dependent on the concentration of citrate ion as a MW-matched heating source; thus, the heating speed should be properly controlled for the MW-assisted synthesis of sphere-Ag particles having a narrow size distribution.

Preparation of Prism-Silver Particles in Aqueous Solution. Prism-Ag particles were synthesized under MW irradiation in silver nitrate aqueous solutions when PVP was added instead of trisodium citrate/formaldehyde. When a sample containing a low concentration of silver nitrate (0.01 M) was irradiated under MW irradiation for 30 min, the formation of sphere-Ag particles having an average particle size of 25 nm with a size distribution of 10–35 nm was observed (Fig. 2, A5). The selected-area-electron diffraction showed that the sphere-particle can be assigned to fcc metal silver. By prolonging the MW irradiation time for up to 90 min, the average particle size of the sphere-Ag particles was increased to 50 nm with a size distribution of 40–60 nm, accompanying the formations of several two-dimensional triangles with edge sizes of 70–250 nm (Fig. 2, A6). When the concentration of silver nitrate was increased to 0.1 M, both sphere-Ag particles with an average particle size of 70 nm and triangular Ag particles with edge lengths of 200–380 nm were formed under MW irradiation for only 20 min (Fig. 2, A7). After MW irradiation for 75 min, nearly all of the initial spherical particles were converted to prismatic structures with edge lengths of 230–420 nm (Fig. 2, A8). At low concentrations of silver nitrate (0.01 M) and PVP (0.3 M) after 120 min under MW irradiation, we could not obtain prism-Ag particles. The prismatic particles were composed of both perfectly triangular and truncated triangular prisms. Triangular prisms were ascribed to fcc structures by electron-diffraction analysis (Fig. 2, inset A8). From $\{220\}$ Bragg reflections at a lattice spacing of 1.44 Å, the top crystal face of a prism-Ag particle must be (111). An additional weak diffraction spot corresponding to $\frac{1}{3}\{422\}$ Bragg reflections at a lattice spacing of 2.50 Å was observed due to the local hexagonal-like structure in an automatically-flat silver.¹⁰ We concluded that high-concentrated silver nitrate (0.1 M) was favorable for the formation of prism-Ag particles.

From a UV–vis spectroscopy measurement we observed an absorption peak at ca. 410 nm due to a characteristic surface plasmon resonance of a sphere-silver particle synthesized at the low concentrations of silver nitrate (0.01 M) and PVP (Fig. 3a). With a longer MW irradiation time, the plasmon ab-

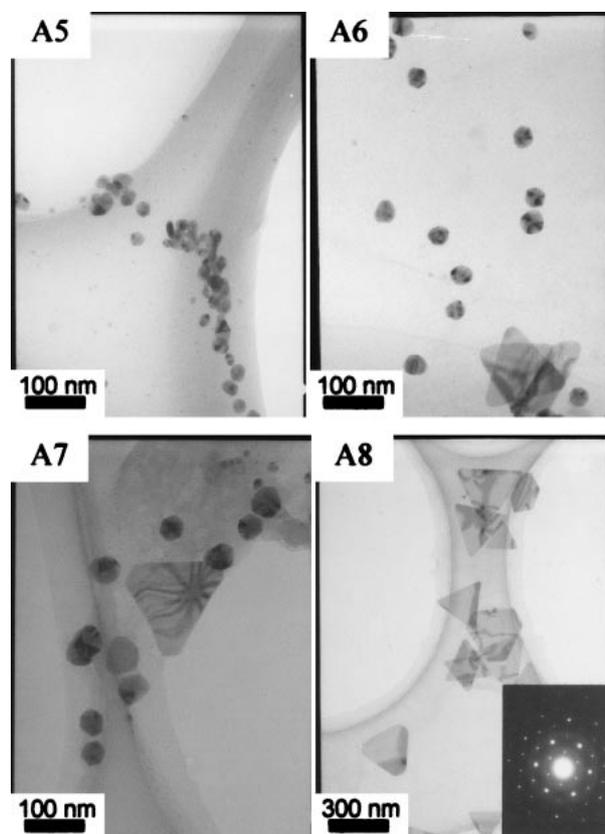


Fig. 2. TEM images of Ag particles synthesized in the presence of PVP (3 M) under MW irradiation for 30 min (A5) and 90 min (A6) in silver nitrate (0.01 M) aqueous solution or for 20 min (A7) and 75 min (A8) in silver nitrate (0.1 M) aqueous solution, respectively. Inset of A8 shows an electron diffraction analysis of a prism-Ag particle.

sorption maximum peak shifted slightly towards longer wavelengths as the particles became larger. However, in the case of prismatic particles composed of both perfectly triangular and truncated triangular prisms, we observed another absorption shoulder-peak at ca. 470 nm in addition to a ca. 420-nm peak for the sample synthesized at a high concentration of silver nitrate (0.1 M) and PVP (Fig. 3b). The shoulder-peak at ca. 470 nm may be due to an in-plane quadrupole resonance caused by a prism shape, as reported previously.¹⁰ However, we could not detect a strong peak at 670–770 nm, which was observed in previous work as being due to an in-plane dipole plasmon resonance.¹⁰ This difference can be explained as being due to the presence of large-size prism-Ag particles with edge sizes of 230–420 nm in the present case.

PVP is a homopolymer having an individual unit containing an aprotic polar imide group. The oxygen atoms of the imide groups should have a strong affinity to silver cations,²⁴ supplying electrons to silver cations, causing the thermal reduction and stabilizing the resulting silver particles through surface adsorption of the PVP chain. When the concentration of silver nitrate is increased to 0.1 M, sphere-Ag particles are converted to prisms with increasing the MW irradiation time, but no small prismatic embryos can be found, even at the initial stage of crystallization (Scheme 2). The prism-Ag particles should be formed by a shape-transformation from a sphere to a prism dur-

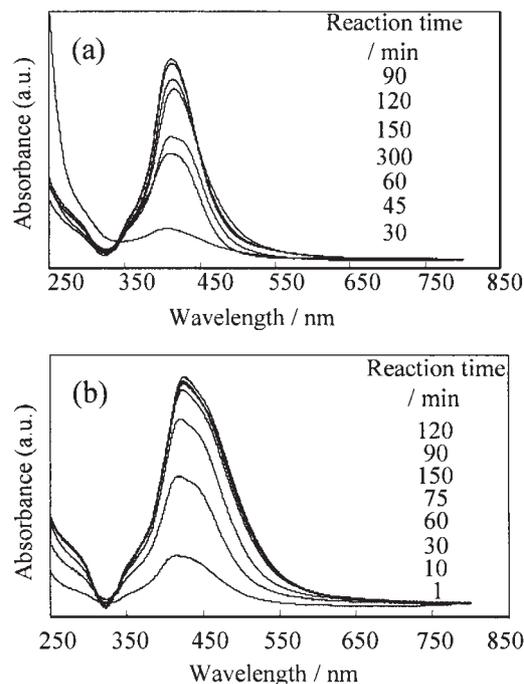
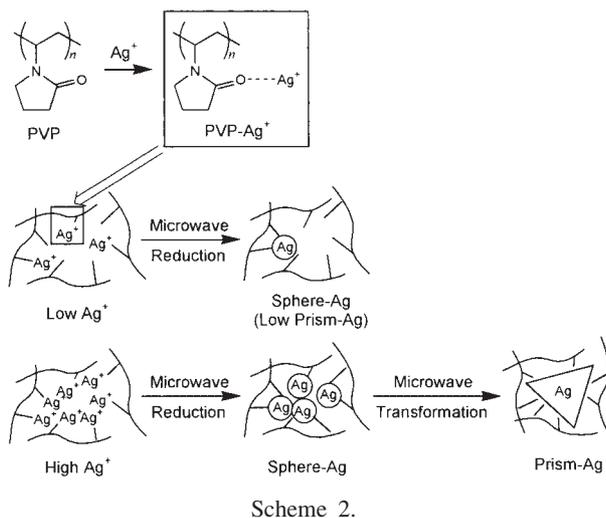


Fig. 3. UV-vis spectra of silver particles synthesized under MW irradiation for a certain time in silver nitrate aqueous solutions at (a) 0.01 M and (b) 0.1 M in the presence of PVP (3 M).



ing the crystal-growth process under MW irradiation. *N*-Methylpyrrolidone (NMP) as an aprotic polar molecule is known to have a large dipole moment (32.2) at room temperature and a large dielectric loss (8.855) under MW of 2.45 GHz.²⁵ Since the heating power of MW is proportional to the dielectric loss of the polar molecular media, MW irradiation should accelerate the coherent heating of PVP as a polymer of NMP and PVP-stabilized silver surfaces, resulting in a shape transformation from spherical silver particles to the large prism silver in the prolonged MW-promoted heating system, in which a reconstruction of the crystallites may occur, such as Ostwald ripening.²⁶

Conclusions

The size and size distribution of sphere-Ag particles can be controlled by changing the concentration of trisodium citrate. Furthermore, we have succeeded to switch the shape of Ag particles between sphere and prism by changing the concentration of a polar polymer, PVP. The synthesis shown in the present work was carried out in water under a high concentration of Ag by 100 times compared to the previously reported methods. These findings should open a new area of size- and morphology-controlled synthesis of nano metals under homogeneous MW-matched dielectric heating.

The present study was mainly supported by “21st Century Center of Excellence Program”. A part of this work was supported by “Nanotechnology Support Project” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References

- 1 Y. Shiraishi and N. Toshima, *J. Mol. Catal. A: Chem.*, **141**, 187 (1999).
- 2 W. P. McConnell, J. P. Novak, L. C. Brousseau, III, R. R. Fuierer, R. C. Tenent, and D. L. Feldheim, *J. Phys. Chem. B*, **104**, 8925 (2000).
- 3 J. Zheng, X. Li, R. Gu, and T. Lu, *J. Phys. Chem. B*, **106**, 1019 (2002).
- 4 S. Liu, J. Yue, and A. Gedanken, *Adv. Mater.*, **13**, 656 (2001).
- 5 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. El-Sayed, *Science*, **272**, 1924 (1996).
- 6 J. Turkevich and G. Kim, *Science*, **169**, 873 (1970).
- 7 L. Rivas, S. S.-Cortes, J. V. G.-Ramos, and G. Morcillo, *Langmuir*, **17**, 574 (2001).
- 8 E. M. Egorova and A. A. Revina, *Colloids Surf., A: Physicochemical and Engineering Aspects*, **168**, 87 (2000).
- 9 Y. Zhou, L. Hao, Y. Hu, Y. Zhu, and Z. Chen, *Chem. Lett.*, **2001**, 1192.
- 10 R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, and J. G. Zhang, *Science*, **294**, 1901 (2001).
- 11 Y. Xiong, Y. Xie, G. Du, X. Liu, and X. Tian, *Chem. Lett.*, **2002**, 98.
- 12 K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, and K. Yase, *Thin Solid Films*, **327–329**, 524 (1998).
- 13 A. Henglein and M. Giersig, *J. Phys. Chem. B*, **103**, 9533 (1999).
- 14 Y. Sun and Y. Xia, *Adv. Mater.*, **14**, 833 (2002).
- 15 Y. Sun and Y. Xia, *Science*, **298**, 2176 (2002).
- 16 J. M. Petroski, Z. L. Zhang, T. C. Green, and M. A. El-Sayed, *J. Phys. Chem. B*, **102**, 3316 (1998).
- 17 J. S. Bradley, B. Tesche, W. Busser, M. Maase, and M. T. Reetz, *J. Am. Chem. Soc.*, **122**, 4631 (2000).
- 18 K. J. Rao, B. Vaidyanathan, M. Ganguli, and P. A. Ramakrishnan, *Chem. Mater.*, **11**, 882 (1999).
- 19 Y. Wada, H. Kuramoto, T. Sakata, H. Mori, T. Sumita, T. Kitamura, and S. Yanagida, *Chem. Lett.*, **1999**, 607.
- 20 Y. Wada, H. Kuramoto, J. Anand, T. Kitamura, T. Sakata, H. Mori, and S. Yanagida, *J. Mater. Chem.*, **11**, 1936 (2001).
- 21 H. Yin, Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H.

Mori, T. Sakata, and S. Yanagida, *J. Mater. Chem.*, **11**, 1694 (2001).

22 D. R. Baghurst and D. M. P. Mingos, *Chem. Commun.*, **1992**, 674.

23 S. A. Galema, *Chem. Soc. Rev.*, **26**, 233 (1997).

24 B. Yin, H. Ma, S. Wang, and S. Chen, *J. Phys. Chem. B*, **107**, 8898 (2003).

25 B. L. Hayes, "Microwave Synthesis: Chemistry at the Speed of Light," CEM, North Carolina (2002).

26 A. R. Roosen and W. C. Carter, *Physica A*, **261**, 232 (1998).