Nanowires

DOI: 10.1002/anie.200806379

Ionic-Liquid-Assisted Formation of Silver Nanowires**

*Tae Young Kim, Won Jung Kim, Seung Hyun Hong, Jong Eun Kim, and Kwang S. Suh**

Anisotropic metal nanostructures, such as nanorods, nanotubes, and nanowires, exhibit optical properties of significant technological interest including enhanced fluorescence, nonlinear optical properties, optical resonances in the near infrared (NIR), and orientation-dependent plasmon excitation.[1] In particular, metal nanowires have attracted particular interest because of their potential use as interconnects for the assembly and integration of molecular-scale components into electronic devices.[2] In light of this potential, silver nanowires represent a special class of one-dimensional (1D) metal nanostructures, because bulk silver exhibits the highest electrical and thermal conductivity. Although a number of different routes to the formation of silver nanowires have been reported, a solution-based synthesis is considered as one of the most effective methods for the large-scale production of silver nanowires.[3] Sun, et al. described a soft, solution-based polyol process in which the reduction of a silver precursor is effected by a polyol in the presence of a surface-capping agent, such as poly(vinyl pyrrolidone).[4] According to this method, the formation of silver nanowires occurs around the preformed seeds from the initial reduction of a silver precursor in a polyol. The surface-capping agent serves to regulate particle growth by confining the growth of the lateral surface and encouraging the cross-section surface of the nanowire to grow, leading to the formation of nanowires with high aspect ratio. However, a common problem of the standard polyol process is the inability to effectively reproduce uniform silver nanowires, as a result a mixture of nanostructures of several shapes, such as wires, truncated cubes, and tetrahedrons, is produced in the same reaction. This mixture arises because the shapes and sizes of the products are strongly affected by the concentration, addition sequence, and rate of addition of the capping and reducing agent. Therefore, there is still a need to develop a more straightforward procedure for fabricating silver nanowires with controllable shapes and sizes in an effective and reproducible fashion.

In parallel with the development of metal nanostructures, recognition of the possibilities afforded by ionic liquids as alternatives to soft templates has recently led to a growing interest in the preparation of size- and shape-controlled nanostructures.[5] Ionic liquids (ILs), defined herein as salts that melt at or below 100 °C, can provide unique properties that can be tuned by selecting the appropriate combination of cations and anions. In particular, the imidazolium ILs associated with specific anions are known to self-organize in away that is adaptable to the fabrication of metal nanostructures.[6] A few reports describe that ILs can be used as a reaction medium for the production of metal nanostructures, though most of the products were obtained as spherical or non-spherical nanoparticles and not as long nanowires.[7] However, it is still appealing to study the relationship between the different ILs and the structures of the nanomaterials fabricated in them.

Herein, we demonstrate that ILs constitute a unique soft material capable of promoting the in situ growth of silver nanowire. To our knowledge, this is the first report of IL-assisted formation of silver nanowires, in which a metal precursor, such as silver nitrate ($AgNO_3$), is converted into elemental metal by ethylene glycol (EG) in the presence of ILs. *N*-alkyl imidazolium based ILs were explored as soft materials to control the nucleation step and to provide a hierarchical organization of the silver nanostructures. The key in this method is the use of 1-butyl-3-methylimidazolium coupled with methylsulfate (bmim-$MeSO_4$) for the synthesis of silver nanostructures and this will be discussed in terms of the formation of an ionic-liquid–silver complex and the growth of these complexes into the final nanostructures. To shed light on the growth mechanisms, we also put forward a primary experimental model and examined the effects of changing the IL anions on the shape of the nanostructures.

The first step involves the combination of two solutions, one of $AgNO_3$ in EG and one of ionic liquids in EG. The reaction mixture was stirred at room temperature for 15 min, and then refluxed at 160 °C for 60 minutes. The reaction proceeds through a self-seeding process in which heterogeneous metallic seeds not required in the entire process. When the reaction mixture turned turbid throughout, with a yellowish color, a small portion of the solution was taken from the vessel and viewed by SEM methods, this revealed that silver nanostructures had started to appear.

A representative scanning electron microscopy (SEM) image of the silver nanowires synthesized in the IL (bmim-$MeSO_4$) is shown in Figure 1. This image reveals that the sample is composed of a large quantity of silver nanowires and with lengths of up to about 15 μm with no or few nanoparticles.

In our synthesis, it was found that no apparent changes in the silver nanowire products were observed when the molar ratio of bmim-$MeSO_4$ to $AgNO_3$ was varied in the range from 0.75:1 to 2.25:1. Furthermore, the formation of silver nanowires was virtually independent of the rate of addition and sequence of the reactive components, and thus this soft, solution-based approach should be easily extended to large-scale production of silver nanowires.

---

[*] Dr. T. Y. Kim, Dr. W. J. Kim, S. H. Hong, Dr. J. E. Kim, Prof. K. S. Suh
Department of Materials Science and Engineering, Korea University
5-1 Anam-dong, Seongbuk-gu, Seoul 137-713 (Korea)
Fax: (+82) 2-929-4408
E-mail: suhkwang@korea.ac.kr

[**] Financial support from InsCon Tech, Co. Ltd is gratefully acknowledged.

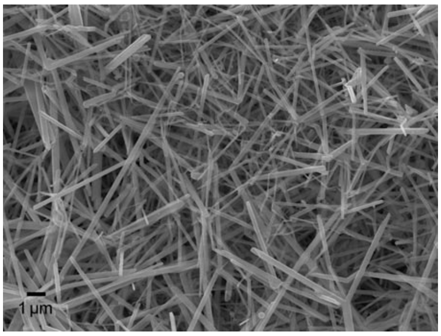

Figure 1. SEM image of silver nanowires prepared by the ionic liquid (bmim-$MeSO_4$) assisted polyol process.

The X-ray diffraction (XRD) pattern taken from the sample prepared in bmim-$MeSO_4$ indicates that the crystal structure of these nanowires is face-centered cubic (fcc) (Figure 2) and the intensity ratios of the (111) peak to the (200) and (220) peaks were 2.9 and 4.0, respectively. Compared with the intensity ratios obtained from the standard powder pattern of fcc-structured silver crystals (JCPDS; 2.1 and 4.0), these values indicate that the silver nanowires may have a preferred orientation along the (111) plane. Since the (200), (220), and (111) surfaces of fcc-structured metal particles are different in their surface atom densities, their electronic structure, and possibly even their chemical reactivity, it may be deduced that bmim-$MeSO_4$ preferentially interacts chemically with certain crystallographic orientations of silver metal to stabilize silver nanostructures with anisotropic shape.[8]

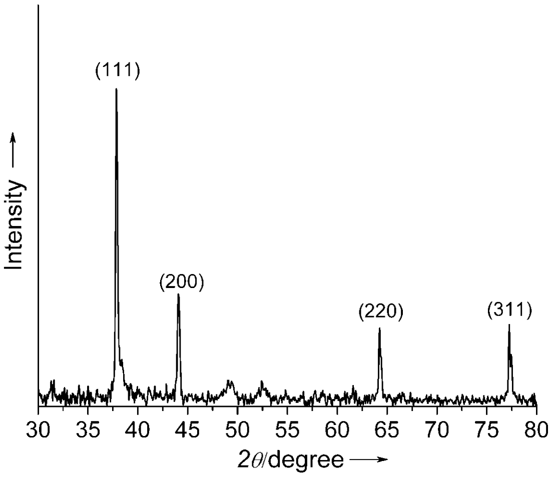

Figure 2. X-ray diffraction pattern of the silver nanowires synthesized in bmim-$MeSO_4$, indicating that the crystal structure of the nanowire is face-centered cubic (fcc) (JCPDS 4-0783).

To elucidate the role of the ILs on the wire-formation process, comparative experiments were carried out by changing the chemical structure of the ILs. The SEM images in Figure 3 reveal that the use of ILs bearing chloride (bmim-Cl) and bromide (bmim-Br) resulted well-defined nanoparticles with cubic and octahedral shape, respectively, while bmim-$MeSO_4$ afforded silver nanowires in a highly reproducible manner. These results indicate that the morphology of silver nanostructures is strongly dependent on the IL type and ILs and enabled us to systemically investigate the factors influencing the growth mechanism of silver metals. When we applied the same procedure with ILs containing cations such as 1-ethyl-3-methylimidazolium (emim-$MeSO_4$) and 1-ethyl-3-methylpyridinium (empy-$MeSO_4$), similar nanowire structures were formed preferentially (data not shown). This formation revealed the strong effect of the ILs anions on the shape control of the silver nanostructures. This anion effect could arise from the different abilities of the anions to coordinate with the silver metal, leading to different nucleation mechanisms.

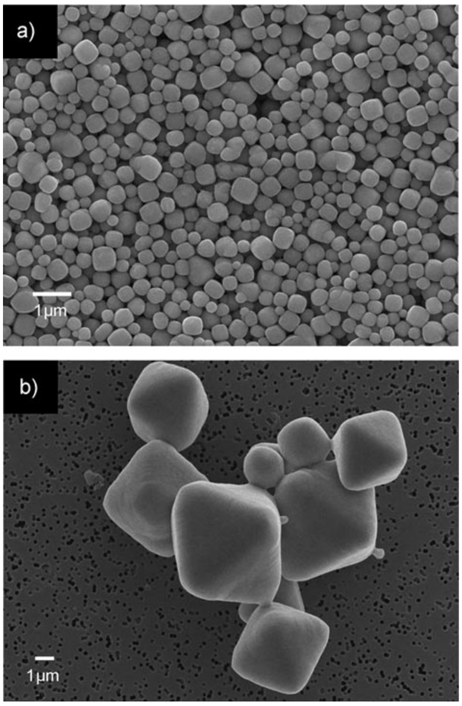

Figure 3. Selected SEM micrographs of the silver nanostructures prepared using a) bmim-Cl and b) bmim-Br.

The formation of the silver nanowires in bmim-$MeSO_4$ was monitored by in situ transmission electron spectroscopy (TEM) analysis of aliquots taken from the reaction mixture at different times (10, 20, 30, and 60 min). TEM images shown in Figure 4 can be used to understand the sequence of the nanostructure growth. At an early stage of the process (10 min), small silver nanoparticles with sizes on the range of 2–10 nm are formed through the initial reduction of $AgNO_3$ in the presence of bmim-$MeSO_4$. At $t = 20$ min, a closer inspection of selected parts shows that some of the silver nanoparticles have multiply twinned structures (Figure 4c). The selected-area electron diffraction (SAED) pattern confirms that the nanoparticles formed in this stage are not a single crystal because the diffraction spots could not be assigned to any particular simple pattern associated with fcc silver. Because these crystallographic surfaces are considered to have different chemical potential and reactivity, it is conceivable that atoms on different crystallographic facets

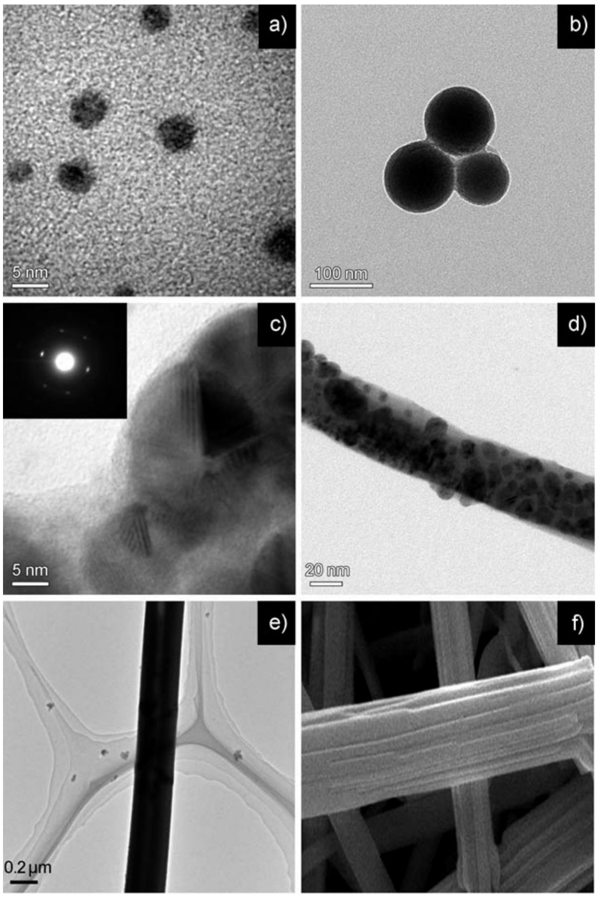

Figure 4. Selected TEM micrographs of the silver nanostructures prepared by the reduction of $AgNO_3$ precursor in the presence of bmim-$MeSO_4$ after a) 10 min, c) 20 min, d) 30 min, and e) 60 min. For comparison, TEM image of the silver nanoparticles prepared using bmim-Br at $t = 10$ min is shown in (b). The inset of (c) shows the SAED pattern indicating the nanoparticle is Ag with a twinned structure. f) SEM image showing that the as-obtained anisotropic silver is indeed composed of several nanowires, as a consequence of self-assembly into bundle-like structure.

have different interaction strengths with bmim-$MeSO_4$.[9] In this case, bmim-$MeSO_4$ can act as a capping agent to kinetically control the growth rates of different crystalline faces by interacting with these faces through adsorption and desorption. Although there is no direct evidence for the capping action of ILs, it is possible that ILs have a selective adsorption ability which predominately depends on the anions of the ILs, such that bmim-$MeSO_4$ preferentially adsorbs to certain face of the primary silver nanoparticles. On the basis of the different reactivity of crystallographic surfaces, the primary nanoparticles can grow further into anisotropic nanostructure as a result of the continuous surface deposition of solvated ions, which generally applies in most cases involving silver nanowires grown by standard polyol process.[4] However, this nanoparticle-to-nanowire transition through ion-by-ion attachment cannot be considered responsible for the particle-based aggregation into a 1D array, as shown in Figure 4 d.

Figure 4 d presents a clear evidence of the intermediate step in the nanowire formation, where the nanowire-like arrangements were indeed composed of a continuous string of silver nanoparticles. This result indicates that the main pathway of silver-nanowire growth in bmim-$MeSO_4$ involves the spontaneous self-organization of adjacent particles in an anisotropic fashion. With increasing reaction time, a silver nanowire with smooth surfaces was observed as shown in Figure 4 e, in which the joints between the aggregated silver nanoparticles had completely disappeared. It appears that the silver nanoparticles assembled in particle chains, fused together to reduce the surface area and are transformed into a single crystal, which is consistent with the SAED and XRD data. In addition, this assembly process continues further to form a well-defined bundle structure comprising several nanowires stacked upon one another (Figure 4 f), resembling the way in which the particle aggregation occurred. These observations corroborate the mesocrystal transformation features in recent reports, in which primary nanoparticles are the building units that assemble into larger structures, which transform into a single crystal by oriented attachment and fusion.[10] Kotov and co-workers demonstrated that the nanoparticles of CdTe assemble to form nanowires, the growth pathway of which is not through point-initiated vectorial growth but rather by the recrystallization of multiple nanoparticles in a linear aggregate.[11] Kotov and co-workers suggested that the driving force for such an arrangement is the dipole–dipole interaction of the nanoparticles.[11] Our findings also demonstrate the collective behavior of silver nanoparticles through self-assembly in such a way to enhance the long-range and mesoscopic order. It is apparent that ILs can be an important contributor in this assembly process because bmim-$MeSO_4$ supports the 1D alignment of silver nanoparticles whereas bmim-Cl and bmim-Br stimulate three-dimensional (3D) arrangements. Prior work has demonstrated the potential use of imidazolium-based ILs as an entropic driver for the extended ordering of nanoscale structures since they possess pre-organized structures through an extended hydrogen-bond network and thus can be described as supramolecular fluids with segregated polar and nonpolar domains.[12] In our cases, it is quite probable that bmim-based ILs form a complex with silver nanoparticles at an early stage by anion coordination of ILs to the surface of nanoparticles. We believe that the ILs distributed over the nanoparticle surface play an important role in the determination of interparticle interactions, leading different assembly processes with respect to the types of ILs employed. Since the most favorable location of anions around the cations in bmim-based ILs differs as the type of anions changes, the directional polarizability of ILs bound to the surface of nanoparticles may also vary.[13] It is speculated that bmim-$MeSO_4$ provides a higher degree of directional polarizability than either bmim-Cl or bmim-Br, as a result of the bulky and delocalized charge state of the anions. This feature of bmim-$MeSO_4$ may be responsible for the 1D assembly of nanoparticles, although other possibilities, such as unequal adsorption abilities of ILs to the nanoparticle surface, cannot be ruled out. The details of the interplay between the IL and the formation of silver nanostructures within it remain to be determined, but our results raise the possibility of controlling the morphology by careful selection of the ILs.

In summary, we have demonstrated that the simple reduction of a silver precursor in the presence of ILs preferentially affords various nanostructures including silver nanowires, depending on the type of ionic liquids used and the reaction conditions. The morphology of the as-obtained silver nanostructures is apparently related to the stabilization and self-organization of the ionic liquids and thus can be tuned by modulating the type of ionic liquid and the reaction conditions. In addition, our procedure does not require exotic metallic seeds or an additional capping agent during the reaction, thereby facilitating its use as a versatile and straightforward approach for the development of silver nanowires.

Experimental Section

Silver nanowires were synthesized by reducing $AgNO_3$ with ethylene glycol (EG) in the presence of Ionic liquids (ILs). ILs were selected to have different anions such as chloride (Cl), bromide (Br), and methylsulfate ($MeSO_4$) coupled with the cation of 1-butyl-3-methylimidazolium (bmim). In a typical synthesis, the reactions were carried out by initially mixing $AgNO_3$ solution (5 mL; 0.625 mM, in EG) with IL solution (5 mL; 0.94 mM, in EG) at room temperature and stirring at this temperature for 15 min. The reaction mixtures were then heated to approximately 160 °C for 60 min under vigorous stirring until all $AgNO_3$ had been completely reduced. Typically, nanowires were formed rapidly after a brief induction period of 15 min. The growth of the silver nanowires was monitored by sampling small portions of the reaction mixture at various reaction times, The samples were cooled in an ice bath to halt the growth of nanostructures, and observed with a scanning electron microscope (SEM). The reaction product was collected on a Teflon filter with pore size of 0.2 μm, washed with propylene carbonate, and dried in a vacuum oven.

The SEM measurements were carried out with a field-emission microscope (FE-SEM, JEOL JSM-700F) at an acceleration voltage of 15 kV. XRD patterns were obtained on a Philips X′Pert Pro diffractometer at a scanning rate of $0.2^\circ s^{-1}$ in 2θ ranging from 30 to 80°. The transmission electron microscopic (TEM) images were taken on a JEOL JEM-2000 EX operated at 200 kV. The TEM samples were prepared by placing small droplets of the diluted reaction solution (with water and isopropyl alcohol) on copper grids. The diffraction patterns were also recorded through selected-area electron diffraction (SAED) on an individual nanostructure.

Received: December 30, 2008
Revised: March 3, 2009

Keywords: ionic liquids · nanostructures · nanowires · self-assembly · silver

---

[1] a) M. B. Mohamed, V. Volkov, S. Link, M. A. El-Sayed, *Chem. Phys. Lett.* **2000**, *317*, 517 – 523; b) G. Schider, J. R. Krenn, W. Gotschy, B. Lamprecht, H. Ditlbacher, A. Leitner, F. R. Aussenegg, *J. Appl. Phys.* **2001**, *90*, 3825 – 3830.

[2] a) D. I. Gittins, D. Bethell, D. J. Schiffrin, R. J. Nichols, *Nature* **2000**, *408*, 67 – 69; b) Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science* **2001**, *293*, 1289 – 1292.

[3] a) Y. Sun, Y. Xia, *Adv. Mater.* **2002**, *14*, 833 – 837; b) J. Q. Hu, Q. Chen, Z. X. Xie, G. B. Han, R. H. Wang, B. Ren, Y. Zhang, Z. L. Yang, Z. Q. Tian, *Adv. Funct. Mater.* **2004**, *14*, 183 – 189; c) K. K. Caswell, C. M. Bender, C. J. Murphy, *Nano Lett.* **2003**, *3*, 667 – 669.

[4] a) Y. Sun, Y. Yin, B. T. Mayers, T. Herricks, Y. Xia, *Chem. Mater.* **2002**, *14*, 4736 – 4745; b) Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett.* **2002**, *2*, 165 – 168.

[5] a) C. S. Consorti, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, D. H. Farrar, A. J. Lough, W. Loh, L. H. M. da Silva, J. Dupont, *J. Phys. Chem. B* **2005**, *109*, 4341 – 4349; b) T. Gutel, J. Garcia-Anton, K. Pelzer, K. Philippot, C. C. Santini, Y. Chauvin, B. Chaudret, J. Basset, *J. Mater. Chem.* **2007**, *17*, 3290 – 3292; c) G. S. Fonseca, G. Machdo, S. R. Teixeira, G. H. Fecher, J. Morais, M. C. M. Alves, J. Dupont, *J. Colloid Interface Sci.* **2006**, *301*, 193 – 204; d) E. Redel, R. Thomann, C. Janiak, *Inorg. Chem.* **2008**, *47*, 14 – 16; e) F. C. Gozzo, L. S. Santos, R. Augusti, C. S. Consorti, J. Dupont, M. N. Eberlin, *Chem. Eur. J.* **2004**, *10*, 6187 – 6193.

[6] a) Y. Wang, H. Yang, *J. Am. Chem. Soc.* **2005**, *127*, 5316 – 5317; b) D. B. Zhao, Z. F. Fei, W. H. Ang, P. J. Dyson, *Small* **2006**, *2*, 879 – 883; c) B. G. Trewyn, C. M. Whitman, V. S. Y. Lin, *Nano Lett.* **2004**, *4*, 2139 – 2143; d) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096 – 5100.

[7] a) M. Scariot, D. O. Silva, J. D. Scholten, G. Machado, S. R. Teixeira, M. A. Novak, G. Ebeling, J. Dupont, *Angew. Chem.* **2008**, *120*, 9215 – 9218; *Angew. Chem. Int. Ed.* **2008**, *47*, 9075 – 9078; b) J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, *J. Am. Chem. Soc.* **2002**, *124*, 4228 – 4229; c) Y. Gao, A. Voigt, M. Zhou, K. Sundmacher, *Eur. J. Inorg. Chem.* **2008**, 3769 – 3775; d) L. Ren, L. Meng, Q. Lu, Z. Fei, P. J. Dyson, *J. Colloid Interface Sci.* **2008**, *323*, 260 – 266.

[8] Z. L. Wang, *J. Phys. Chem. B* **2000**, *104*, 1153 – 1175.

[9] K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, T. Torimoto, *Chem. Commun.* **2008**, 691 – 693.

[10] a) H. Cölfen, M. Antonietti, *Angew. Chem.* **2005**, *117*, 5714 – 5730; *Angew. Chem. Int. Ed.* **2005**, *44*, 5576 – 5591; b) S. Wohlrab, N. Pinna, M. Antonietti, H. Cölfen, *Chem. Eur. J.* **2005**, *11*, 2903 – 2913; c) M. Niederberger, H. Cölfen, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3271 – 3287.

[11] Z. Tang, N. A. Kotov, M. Giersig, *Science* **2002**, *297*, 237 – 240.

[12] a) C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos, J. Dupont, *J. Phys. Chem. B* **2006**, *110*, 13011 – 13020; b) A. Mele, G. Romano, M. Giannone, E. Ragg, G. Fronza, G. Raos, V. Marcon, *Angew. Chem.* **2006**, *118*, 1141 – 1144; *Angew. Chem. Int. Ed.* **2006**, *45*, 1123 – 1126; c) J. Dupont, P. A. Suarez, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2441 – 2452; d) Y. Zhou, J. H. Schattka, M. Antonictti, *Nano Lett.* **2004**, *4*, 477 – 481; e) E. Redel, R. Thomann, C. Janiak, *Chem. Commun.* **2008**, 1789 – 1791.

[13] a) S. M. Urahata, M. C. C. Ribeiro, *J. Chem. Phys.* **2004**, *120*, 1855 – 1863; b) T. Yan, C. J. Burnham, M. G. D. Pópolo, G. A. Voth, *J. Phys. Chem. B* **2004**, *108*, 11877 – 11881.