ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Fabrication, Characterization, and Printing of Conductive Ink Based on Multi Core–Shell Nanoparticles Synthesized by RAPET

*Evgeny Butovsky, Ilana Perelshtein, Ifat Nissan, and Aharon Gedanken**

In the current research, conductive patterns are deposited on different substrates by direct inkjet printing of conductive inks based on metal@carbon and bimetal@carbon core–shell nanoparticles synthesized by the RAPET (reaction under autogenic pressure at elevated temperatures) technique. Various co-solvents and additives are examined for production of stable conductive ink. The morphology of the deposited layers is characterized by optical and scanning electron microscopy measurements. The stability of the prepared inks is examined by dynamic light scattering measurements. The electrical resistivity is measured by a four-point probe system and calculated using the geometric dimensions. The results obtained are very promising and indicate that the conductivity of the deposited layers is close to that of bulk metals and higher than most results published so far. Moreover, the importance and advantages of the protective carbon layer that prevents metal oxidation is demonstrated.

1. Introduction

Conductive ink printing is an area of research that has attracted great interest in recent years. In contrast to conventional methods such as vacuum deposition and photolithography,[1] inkjet printing technology's main advantages are that it is fast, simple, inexpensive, and even provides process capability at low temperatures.[2–7] One of the most important components of inkjet printing technology is the conductive material reference. Several candidate conductive materials have been studied, namely, molten metal, conductive polymers, and metallic nanoparticle suspensions,[8] which are considered to be the most promising candidate inkjet printing material. Using ink-jet printing to fabricate conductive circuits has been found to have great potential for the electronic industry.[9–14] The printed electronics can be produced by common printing equipment, such as screen, flexography, offset lithography, inkjet, and gravure.[15,16] For fabrication of high resolution printed electronics elements, ink is the most important factor in the printing process. In general, the ink is composed of filler, binder, solvent, and additives. The materials mentioned above—metallic nanoparticle suspensions, carbon materials, and conductive polymers—have been studied as potential ink fillers. Because of their high conductivity, the metallic inks are mostly used for manufacturing of printed electronics at room temperature. On the other hand, using metal nanoparticles is quite problematic due to their spontaneous oxidation at ambient conditions which does not allow receiving desirable results, particularly as their size gets smaller.[17,18]

One of the solutions to the oxidation problem lies in the protection of the outer layer of the ink material by ligands,[19] polymers,[20] silica,[21,22] or carbon,[23] in other words creating nanoparticles with core–shell structure where one or two metals constitute a core and the shell is a protective layer. There are many advantages of a core–shell structure. For example, the replacement of an expensive reactive metal in the center of the particles by another less expensive material makes it possible to substantially reduce the cost.[24,25] There are various methods for the formation of nanoparticles (NPs) with core–shell structures: sonochemistry,[26,27] electrochemistry,[28] ammonia catalysis,[29] and laser-induced fusion,[30] amongst others. Several reports on the formation of core–shell nanostructures of transition metals have already been published.[31–36] Recently, a new type of NP composed of a core and a shell of two different metals has been synthesized.[37–48] Because of the nanometer-scale size of the layers, such bimetallic materials may have better or different chemical,[37] magnetic,[38–41] optical,[42,43] and catalytic[44–48] properties compared to the pure metals. Various techniques have been used to prepare binary particles containing Pd for their strongly catalytic properties,[49] Au–Ag bimetallic particles for their unique optical behavior,[50] and Ag–Cu particles for their electrical properties. Recently, copper NPs have been proposed as a low-cost replacement for silver and gold NPs which are currently used as conductive interface materials. However, the main obstacle in using copper NPs is their spontaneous

E. Butovsky, Dr. I. Perelshtein, I. Nissan,
Prof. A. Gedanken
Department of Chemistry
Kanbar Laboratory for Nanomaterials
Institute of Nanotechnology and Advanced Materials
Bar-Ilan University
Ramat-Gan 52900, Israel
E-mail: aharon.gedanken@biu.ac.il

DOI: 10.1002/adfm.201300837

oxidation under ambient conditions.[51,52] Thus, it is necessary to protect the metal core by a shell that is resistant to relative high temperatures and oxidation; carbon could be a good candidate for this purpose.

Dispersing metallic NPs having a relatively high specific gravity in a fluid base is challenging, and typically requires a polymeric stabilizing ligand which will hinder interparticle contact. Most direct-write technologies require stable, concentrated dispersions of metal NPs in the conductive ink. Wet chemical approaches for the synthesis of colloidal silver nanoparticles have been used to generate such particles; however, producing large quantities of metal nanoparticle using a simple synthesis method is also a challenge. Many colloidal processes for the surfactant stabilized synthesis of silver NPs have been reported.[53–58] The choice of ligand is important in conductive ink formulation because these ligands need to be removed after the printing in order to form high purity metallic films. For example, ligands with stronger affinity for silver such as alkanethiolates are less desirable when compared to ligands such as alkyl amines or carboxylates which usually show weak affinity for silver.[51–54] The most successful syntheses used for conductive ink formulation are mainly based on the polyol method;[59,60] however, producing NPs with easily removable capping agents is difficult using this method. Weaker affinity of ligands may allow lower curing temperatures for the ink which is attractive for printing electronic devices on flexible substrates like paper or polymers.[61,62]

The present work demonstrates the use of metal@carbon and bimetal@carbon core–shell nanoparticles for the formation of stable conductive ink for inkjet printing. Samples of Ag@C, Cu@C, Ag@Cu@C and Cu@Ag@C were fabricated by a rapid, one-step, straightforward, solvent-, surfactant- and catalyst-free technique called RAPET (reaction under autogenic pressure at elevated temperatures).[23,63–70] RAPET has already been shown to be an excellent method for the fabrication of spherical core-shell structures. Different co-solvents (water, iso-propanol, propanol, ethylene glycol mono butyl ether (EGBE) and ethylene glycol mono methyl ether (EGME)), additives (Disperbyk-198, Disperbyk-190, Bykjet-9132) in various quantities have been examined for obtaining the appropriate results in terms of ink stability and conductivity of the deposited layer. The characterization of the prepared inks has revealed high conductivity and stability to oxidation at relative high temperatures of the products. In addition, physical properties of the newly formed inks have been examined and shown to be in good agreement with the required specifications for inks. To the best of our knowledge there is no previously published data on using carbon coated multilayer nanoparticles for ink production.

2. Results and Discussion

2.1. Structural Characterization

Core–shell (Ag@C and Cu@C) and bimetal core–shell (Ag@Cu@C and Cu@Ag@C) nanoparticles were synthesized by a RAPET method.[23,70] The detailed mechanism of the multilayer particles' formation was described in our previous publication[70] and will only be mentioned briefly here. One of the possible explanations for the formation of bi-metallic@carbon structures is as follows: when $Cu(Ac)_2$ is added to Ag@C particles, no separate particles of Cu@C are found, but rather the particles are composed of two metals in the core and carbon in the shell. The formation of the Ag@Cu@C structure is explained as follows. The copper layer which is kinetically deposited first on the Ag@C composite dissolves in the carbon layer and when it reaches its solubility limit, it is deposited around the silver core. This mechanism is similar to the explanation provided for the catalytic effect of Ni, Co, and Fe in the formation mechanism of carbon nanotubes.[71–73] These metals are also dissolved in the carbon until they reach their solubility limit. A second possible interpretation is that during the heating the Ag@C particles serve as nucleic centers for the formation of the Cu layer, and this process is much faster than the formation of individual copper particles. During the cooling, the bi-metallic particles are coated by a carbon shell. The original carbon shell of Ag@C is not removed and stays intact and a possible structure of the obtained material is being Ag@C@Cu@C. These two suggested mechanisms also apply for Cu@C on the addition of AgAc.

The morphologic and structural characterizations of the mono core@ shell materials are presented in **Figure 1**a,b. TEM analysis clearly shows that the particles have a core–shell structure (Figure 1a). The shape of the core–shell NPs is spherical and their size varies between 30 and 250 nm (Figure 1b). The bi-metal@carbon nanoparticles were analyzed by HRTEM and the existence of the multilayer structure was proved by using the line-scan mode. For the Ag@Cu@C (Figure 1c), it is clearly seen that the core layer of silver is covered by a 15 nm layer of Cu. The shell layer of the particles consists of carbon.

The thermal gravimetric coupled with mass spectroscopy analysis (TGA/MS) was carried out to examine the stability to oxidation at high temperatures of all the synthesized materials. The results indicate that the core shell particles consist of a carbon shell which is decomposed at around 300 °C. The amount of C is estimated to be 1.5 wt% by elemental analysis. It has been shown that carbon shell plays a very important role in protecting the metal from oxidation.

2.2. Preparation of Ink Solution

In the current research, the prepared nanoparticles of Ag@C, Cu@C, Ag@Cu@C and Cu@Ag@C were used as filler for

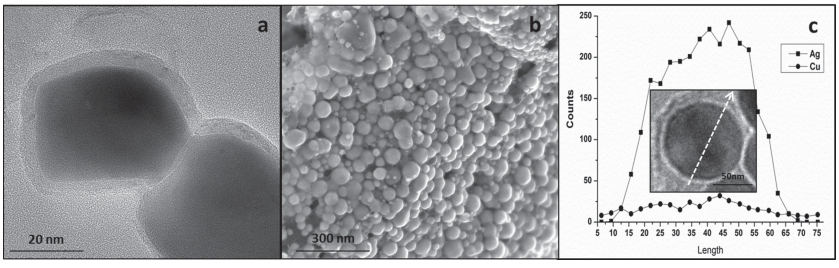

Figure 1. a) TEM micrograph of Ag@C nanoparticles at high resolution; b) SEM micrograph of Cu@C NPs; c) line scan profile of Ag@Cu@C particle.

Table 1. Formulation of three selected ink solutions.

	Sample A			Sample B			Sample C	
Material	Weight [g]	Percentage [wt%]	Material	Weight [g]	Percentage [wt%]	Material	Weight [g]	Percentage [wt%]
Cu@C	1	25	Ag@Cu@C	1	25	Cu@Ag@C	1	25
H_2O	1	25	H_2O	1	25	H_2O	1	25
iso-Propanol	1	25	n-Propanol	1	25	iso-Propanol	1	25
EGME	1	25	EGME	1	25	EGME	1	25
Disperbyk198	0.1	10 (on NPs)	Disperbyk190	0.1	10(on NPs)	Byk-Jet 9132	0.1	10 (on NPs)
Carbon Black	0.01	1 (on NPs)	Carbon Black	0.01	1(on NPs)	Carbon Black	0.01	1 (on NPs)
Conductivity, S cm^{-1}		2.6×10^3	Conductivity, S cm^{-1}		2.8×10^3	Conductivity S cm^{-1}		4.4×10^3

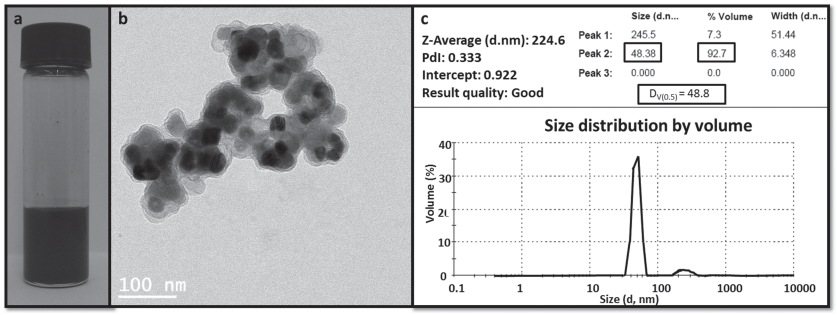

Figure 2. a) Cu@Ag@C nanoparticles dispersed in Byk-Jet 9132 after 2 weeks; b) TEM image of the particles after 2 weeks; c) DLS of the dispersion after 2 weeks.

conductive ink. Various co-solvents and dispersing additives of different amounts were added to improve the stability and physical properties of the inks, such as fluid jetting and layer formation. However, obtaining a stable colloidal solution of core–shell nanoparticles was extremely challenging and the most appropriate combinations for preparing a conductive ink are summarized in **Table 1**. Cu@Ag@C NPs form a stable colloidal solution and give the highest conductive values. Therefore, all the following characterization and printing tests were carried out with Cu@Ag@C dispersion.

As mentioned above, the most stable dispersion was obtained when Cu@Ag@C NPs were dispersed in Byk-Jet 9132. The stability of the solution was examined by TEM and DLS measurements and the results are presented in **Figure 2**. The dispersion solution has a deep black color which remains stable for at least two weeks (Figure 2a). The DLS measurements of a solution that was stored for two weeks indicate that almost a monodispersion solution was achieved with individual particle size of around 50 nm (Figure 2b). Most of the nanoparticles (93%) in the prepared solution are 50 nm in size and only small amount (7%) is 245 nm in size. In order to confirm the DLS results, TEM measurements were performed (Figure 2c). From the image it can be seen that the average size of the dispersed particles is around 50 nm which is in a good agreement with DLS results. In addition, it can be clearly seen from the TEM image that the core–shell structure has been retained and that each particle is covered by a carbon shell. The latter point indicates that the structure of the particles was not destroyed during the preparation of the dispersion.

One of the physical parameters that may indicate the quality of the prepared ink is the viscosity of the dispersion. The ideal viscosity of inkjet ink is known to be in the range 2 to 8 cP. The viscosity of the Cu@Ag@C in Byk-Jet 9132 was measured at room temperature and the value of 2.9 cP was recorded and is in the required range. An additional parameter which may indicate the quality of interaction between the ink and the substrate is the contact angle. The Cu@Ag@C dispersion was dropped on various substrates such as glass, glass coated by kapton and impermeable paper. In all cases the drop was almost completely flat and a contact angle of less than 50 was measured (**Figure 3**). The result indicates a good interaction between the liquid phase and the substrate which is an important parameter in printing process.

2.3. Conductivity Measurements and Printing

The prepared ink solutions were printed on impermeable paper. One of the results is presented in **Figure 4**a and relates to Cu@Ag@C nanoparticles dispersed in water, EGME, iso-Propanol and with Byk-jet 9132 as a dispersant agent. Very similar results in terms of conductivity were obtained when the core–shell nanoparticles of Ag@Cu@C were used. After drying the samples their conductivity was measured. The layer resistivity was calculated from the measured resistance taking into account the following geometric parameters of the layers:

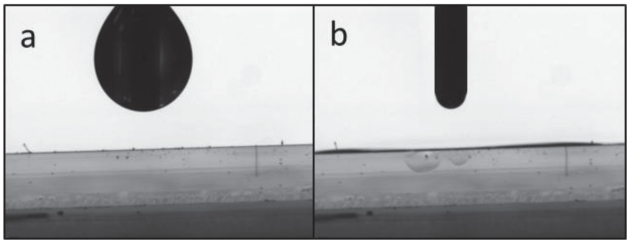

Figure 3. Image of ink drop; a) before and b) after contact with the substrate.

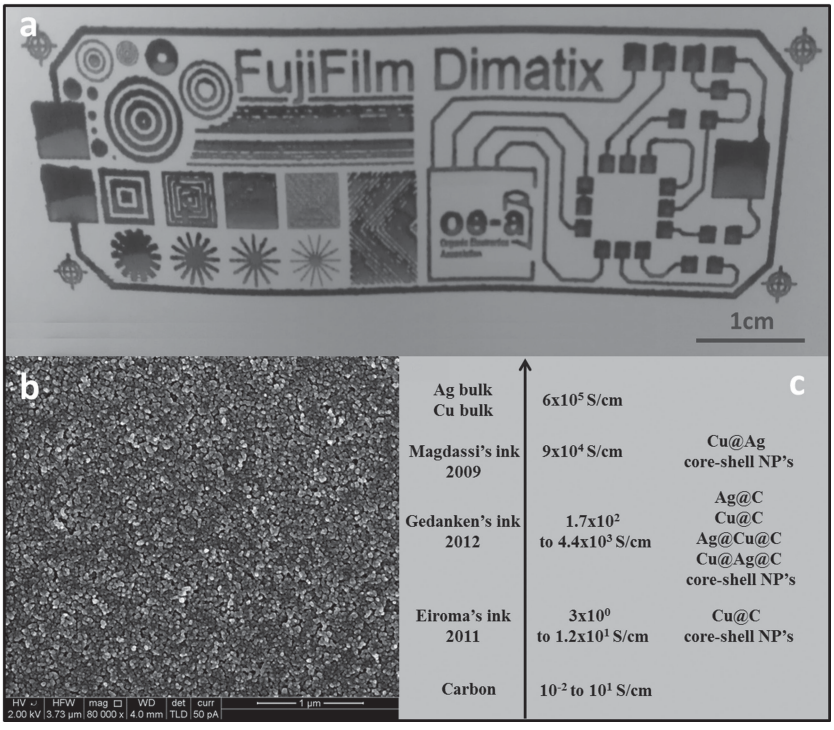

Figure 4. a) The printed template of Cu@Ag@C nanoparticles on impermeable paper; b) SEM image of the printed layer; c) comparison of conductivities.

length (about 9 cm), width (about 0.1 cm) and thickness (about 1 µm). The conductivity values range from 1.7×10^2 to 4.4×10^3 S cm^{-1}. The high conductivity values could be explained by a very dense deposited layer of core–shell NPs as presented in the SEM micrograph (Figure 4b). The quality of inks is based on the conductivity of the deposited pattern.

In order to confirm the stability of the carbon shell, the conductivity measurement was carried out on the heated pattern. The printed pattern was placed in an oven and heated at 150 °C for 1 h. The resistance was measured immediately after the heating and similar values as before heating were obtained. If the carbon layer was damaged, the exposure of the metals might lead to the increase in the conductivity. However, the fact that the conductivity was not changed after heating indicates that the carbon was not removed from the surface even after exposure to 150 °C and that it protects the metal from oxidation.

Numerous works have been published on the current topic show different levels of achievements. Grouchko et al.[74] succeeded in synthesizing and printing by inkjet a core–shell nanocomposite of Cu@Ag. However, they noted that Ag which was used as the outer shell undergoes destruction at high temperatures, which is followed by oxidation of the copper. Undoubtedly, this can dramatically change the conductivity. Eiroma et al.[75] reported the synthesis and use of Cu@C NPs for printing conductive patterns, but high conductivity was not achieved. Figure 4c presents comparison of conductivity values of different materials–bulk of the relevant metals (Ag and Cu), carbon and various core–shell materials that were examined in previous works.[74,75] The results obtained by our group have two main advantages. On the one hand, we obtained higher (up to three orders of magnitude) conductivity compared to that of ref. [75]. On the other hand, we succeeded in overcoming the problem of oxidation, mentioned in ref. [74] by forming a stable carbon shell on the multilayer metal core.

3. Conclusions

We have demonstrated the use of bimetal@carbon core–shell nanoparticles for the preparation of conductive inks. The NPs were synthesized by the RAPET method. Physicochemical characterization of the nanoparticles have revealed the existence of the carbon shell which prevents the metal core from oxidation even up to 300 °C. The formulation of a stable colloidal solution of Cu@Ag@C NPs was achieved by using Byk-Jet 9132 as a dispersant. The prepared solution was further used for printing on various substrates. The physical properties of the obtained ink were measured and found to be in good agreement with the specification for inks. The advantages of using carbon coated bimetal nanoparticles for production of conductive inks lies in their ability to provide high conductivity levels and withstand oxidation even at high temperatures.

4. Experimental Section

Synthesis of Core–Shell Metal@Carbon Nanoparticles: The synthesis of metal@carbon core–shell nanoparticles is described in our previous work.[23] Briefly, a few grams of acetate of Ag (Cu) were inserted into a Swagelok Union at room temperature under nitrogen in a glove box. The filled cell was placed inside the furnace and kept at 850 °C for 3 h. At the end of reaction, the Swagelok was cooled to room temperature, opened and a black powder of Ag@C (Cu@C) was obtained. All the products were characterized by various techniques and analyzed to examine their morphological and crystal structure, elemental content, stability at high temperature and other properties.[23]

Synthesis of Multilayer Bimetallic Core–Shell Nanoparticles: The synthesis of multilayer bimetallic core–shell nanoparticles was performed as follows: the products of the previous syntheses (Ag@C or Cu@C) constitute the precursors for the fabrication of Ag@Cu@C and Cu@Ag@C core–shell multilayer structures. Acetates of Ag (Cu) were added to as-prepared Cu@C and Ag@C NPs and introduced into a Swagelok cell at room temperature in a nitrogen-filled glove box. The filled reactors were closed, placed in the tube furnace and kept at 850 °C for 3 h. At the end of process, the Swagelok was cooled to room temperature, opened and a black powder of Ag@Cu@C (Cu@Ag@C) was collected. All the products were characterized by structural, morphological and compositional measurements.[70]

Preparation of Ink: The conductive inks were prepared as follows: 1 g of the synthesized material (Ag@C, Cu@C, Ag@Cu@C and Cu@Ag@C) was mixed with 0.1 g of dispersing additive and 1 g of co-solvent. Three co-solvents were used for preparation: double distilled water DDW (18.2 Ω cm); iso-propanol (Gadot, ≥99.8%) or n-propanol (Sigma-Aldrich, ACS reagent, ≥99.5%); ethylene glycol butyl ether (EGBE, Sigma-Aldrich, ≥99.0%) or ethylene glycol methyl ether (EGME, Sigma-Aldrich, anhydrous, 99.8%). All the dispersants

were purchased from BYK Chemie Gmbh and have pigment affinic groups: Disperbyk-190, Disperbyk-198, Disperbyk-2012 and Bykjet-9132. Formulations of a few selected samples are shown in the Results section. All the co-solvents were added for improving the fluid jetting of the ink and the layer forming properties. 0.01 g of carbon black pigment was added in order to emphasize the black color. The prepared suspension was sonicated for 5 min in an ice-water ultrasonic bath at 60% intensity (MRC, CLEAN-01). Before printing, the ink was filtered through a 0.5 µm syringe filter.

Printing: Inkjet printing of the prepared fluids was carried out with the Dimatix DMP-2800 laboratory-scale piezoelectric drop-on-demand printer (Fujifilm Dimatix). The printer uses single-use cartridge has 16 nozzles linearly spaced at 254 µm with typical drop sizes of 1 and 10 pL. Cartridges producing a nominal drop volume of 10 pL were used. Printing was performed at a jetting frequency of 1 kHz and the substrate was heated to 60 °C during the printing. Layers were deposited on impermeable paper, microscopic glass slides (Thermo Scientific) and the glass slides coated by kapton. Polyimide film (Kapton) was obtained from Du Pont Co. The glass slides were cleaned by immersion in acetone under ultra-sonication for 5 min followed by immersion in isopropanol under ultra-sonication for 5 min and drying under nitrogen flow. A single layer for inkjet printing was applied.

Characterization: Various analytical techniques have been used for the characterization of the as-prepared inks and the deposited layers. The morphologies and nanostructures of the NPs dispersed in the ink were characterized with a transmission electron microscope (TEM) Model JEM-1200EX, working at an acceleration voltage of 120 keV. Samples for TEM analyses were prepared by placing a drop of the ink on a gold grid coated with an amorphous carbon film, and then drying in air. The contact angle between the ink and the substrates was measured with KRÜSS GmbH Germany device model FM40Mk2. The topography of the printed layers was characterized by optical microscopy (LEXT OLS4000, Olympus). The overall morphology of the printed layers was investigated by high-resolution scanning electron microscopy (HR-SEM, JSM, 7000 F). The particle size of the prepared colloidal solution was measured by dynamic light scattering (DLS), model Zetasizer Nano SZ (Malvern Instruments). The viscosity of the prepared inks was measured by Viscolite VL7-100B-d15 with a measuring range 1 to 5000 cP. Electrical characterization of the deposited layers was performed by home-made four-point probe resistance measurement device. Layer conductivity was calculated using measured values for resistance, electrode gap length and width and layer thickness.

Acknowledgements

We would like to thank Landa Labs for their kind support in performing printing experiments.

Received: March 7, 2013
Revised: April 8, 2013
Published online: June 10, 2013

[1] I. Jung, Y. Hwan Jo, I. Kim, H. M. Lee, *J. Electron. Mater.* **2012**, *41*, 115.
[2] M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, *Adv. Mater.* **2010**, *22*, 673.
[3] B. J. de Gans, P. C. Duineveld, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 203.
[4] D. J. Lee, J. H. Oh, *Thin Solid Films* **2010**, *518*, 6352.
[5] S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Frechet, D. Poulikakos, *Nanotechnology* **2007**, *18*, 345202.
[6] J. Park, D. J. Lee, S. J. Kim, J. H. Oh, *J. Micromech. Microeng.* **2009**, *19*, 095021.
[7] H. M. Dong, W. W. Carr, J. F. Morris, *Phys. Fluids* **2006**, *18*, 072102.
[8] P. Calvert, *Chem. Mater.* **2001**, *13*, 3299.
[9] A. C. Arias, J. Daniel, B. Krusor, S. Ready, V. Sholin, R. Street, *J. Soc. Inf. Disp.* **2007**, *15*, 485.
[10] D. Kim, S. H. Lee, S. Jeong, J. Moonz, *Electrochem. Solid State Lett.* **2009**, *12*, 195.
[11] T. Takenobu, N. Miural, S. Y. Lu, A. H. T. Okimoto, M. Shiraishi, Y. Iwasa, *Appl. Phys. Express* **2009**, *2*, 025005.
[12] S. Gamerith, A. Klug, H. Scheiber, U. Scherf, E. Moderegger, E. J. W. List, *Adv. Funct. Mater.* **2007**, *17*, 3111.
[13] R. Amin, Y. Li, V. Rushi, M. Manos, *IEEE Antennas Propag. Mag.* **2009**, *51*, 13.
[14] N. A. Luechinger, E. K. Athanassiou, W. J. Stark, *Nanotechnology* **2008**, *19*, 445201.
[15] P. Harrop, D. Lawrence, *Masterclass 3: Printed Electronics Active RFID Summit* **2005**.
[16] N. K. Lim, S. Lee, N. Kim, G. Cho, *IEEE Trans. Adv. Packag.* **2009**, *32*, 72.
[17] S. Gangopadhyay, G. C. Hadjipanayis, B. Dale, C. M. Sorenson, K. J. Klabunde, V. Papaefthymiou, A. Kostikas, *Phys. Rev. B* **1992**, *45*, 9778.
[18] R. Seshadri, R. Sen, G. N. Subbanna, K. R. Kannan, C. N. R. Rao, *Chem. Phys. Lett.* **1994**, *231*, 308.
[19] P. Kanninen, C. Johans, J. Merta, K. Kontturi, *J. Colloid Interface Sci.* **2008**, *318*, 88.
[20] N. Shpaisman, S. Margel, *Chem. Mater.* **2006**, *18*, 396.
[21] W. Fu, H. Yang, L. Chang, M. Li, H. Bala, Q. Yu, G. Zou, *Colloids Surf., A* **2005**, *262*, 71.
[22] M. Aslam, S. Li, V. P. Dravid, *J. Am. Ceram. Soc.* **2007**, *90*, 950.
[23] E. Butovsky, A. Irzh, B. Markovsky, A. Gedanken, *New J. Chem.* **2012**, *36*, 155.
[24] K. Sasaki, J. X. Wang, J. Hanson, R. R. Adzic, *J. Phys. Chem. B* **2005**, *109*, 22701.
[25] J. Zhang, Y. Mo, M. B. Vukmirovic, R. Klie, K. Sasaki, R. R. Adzic, *J. Phys. Chem. B* **2004**, *108*, 10955.
[26] V. G. Pol, H. Grisaru, A. Gedanken, *Langmuir* **2005**, *21*, 3635.
[27] Y. Koltypin, N. Perkas, A. Gedanken, *J. Mater. Chem.* **2004**, *14*, 2975.
[28] X. Li, Chem. *J. Chin. Univ.* Hong Kong **2005**, *26*, 1869.
[29] P. Wang, D. Chen, F. Tang, *Langmuir* **2006**, *22*, 4832.
[30] V. Prashant, *J. Phys. Chem. B* **2002**, *106*, 7729.
[31] S. V. Pol, V. G. Pol, A. Gedanken, *Chem.–Eur. J.* **2004**, *10*, 4467.
[32] V. G. Pol, G. Seisenbaeva, V. G. Kessler, A. Gedanken, *Chem. Mater.* **2004**, *16*, 1793.
[33] S. Tang, S. Vongehr, Z. Zheng, H. Liu, X. Meng, *J. Phys. Chem. C* **2010**, *114*, 18338.
[34] L. S. Wang, D. B. Buchholz, Y. Li, J. Li, C. Y. Lee, H. T. Chiu, R. P. H. Chang, *Appl. Phys. A: Mater. Sci. Process.* **2007**, *87*, 1.
[35] L.-B. Luo, S.-H. Yu, H.-S. Qian, J.-Y. Gong, *Chem. Commun.* **2006**, 793.
[36] E. K. Athanassiou, R. N. Grass, W. J. Stark, *Nanotechnology* **2006**, *17*, 1668.
[37] C. J. Murphy, A. M. Gole, S. E. Hunyadi, J. W. Stone, P. N. Sisco, A. Alkilany, B. E. Kinard, P. Hankins, *Chem. Commun.* **2008**, 544.
[38] M. B. Mohamed, V. Volkov, S. Link, M. A. El-Sayed, *Chem. Phys. Lett.* **2000**, *317*, 517.
[39] D. Yang, D. Cui, *Chem.–Asian J.* **2008**, *3*, 2010.
[40] C. Z. Li, K. B. Male, S. Hrapovic, J. H. T. Luong, *Chem. Commun.* **2005**, 924.
[41] C. J. Orendorff, L. Gearheart, N. R. Jana, C. Murphy, *Phys. Chem. Chem. Phys.* **2006**, *8*, 165.
[42] D. Zhao, B. Q. Xu, Angew. *Chem., Int. Ed.* **2006**, *45*, 4955.
[43] H. Lee, S. E. Habas, S. Kweskin, D. Butcher, G. A. Somorjai, P. D. Yang, Angew. *Chem., Int. Ed.* **2006**, *45*, 7824.
[44] R. Narayanan, M. A. El-Sayed, *J. Am. Chem. Soc.* **2004**, *126*, 7194.

[45] A. Q. Wang, C. M. Chang, C. Y. Mou, *J. Phys. Chem. B* **2005**, *109*, 18860.
[46] M. Eghtedari, A. Oraevsky, J. A. Copland, N. A. Kotov, A. Conjusteau, M. Motamedi, *Nano Lett.* **2007**, *7*, 1914.
[47] B. J. Wiley, Z. H. Wang, J. Wei, Y. D. Yin, D. H. Cobden, Y. N. Xia, *Nano Lett.* **2006**, *6*, 2273.
[48] C. Loo, A. Lowery, N. Halas, J. West, R. Drezek, *Nano Lett.* **2005**, *5*, 709.
[49] N. Toshima, T. Yonezawa, *New J. Chem.* **1998**, *22*, 1179.
[50] S. Link, Z. L. Wang, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 3529.
[51] X. Xia, C. Xie, S. Cai, Z. Yang, X. Yang, *Corros. Sci.* **2006**, *48*, 3924.
[52] P. Kanninen, C. Johans, J. Merta, K. Kontturi, *J. Colloid Interface Sci.* **2008**, *318*, 88.
[53] H. Hiramatsu, F. E. Osterloh, *Chem. Mater.* **2004**, *16*, 2509.
[54] S. Murthy, T. P. Bigioni, Z. L. Wang, J. T. Khoury, R. L. Whetten, *Mater. Lett.* **1997**, *30*, 321.
[55] C. Hao, D. Wang, W. Zheng, Q. Peng, *J. Mater. Res.* **2009**, *24*, 352.
[56] M. Chen, Y. G. Feng, X. Wang, T. C. Li, J. Y. Zhang, D. J. Qian, *Langmuir* **2007**, *23*, 5296.
[57] A. B. Smetana, K. J. Klabunde, C. M. Sorensen, *J. Colloid Interface Sci.* **2005**, *284*, 521.
[58] N. A. Luechinger, N. Booth, G. Heness, S. Bandyopadhyay, R. N. Grass, W. J. Stark, *Adv. Mater.* **2008**, *20*, 3044.
[59] B. Wiley, T. Herricks, Y. Sun, Y. Xia, *Nano Lett.* **2004**, *4*, 1733.
[60] S. Chen, D. L. Carroll, *Nano Lett.* **2002**, *2*, 1003.
[61] E. Ide, S. Angata, A. Hirose, K. F. Kobayashi, *Acta Mater.* **2005**, *53*, 2385.
[62] D. Wakuda, K. S. Kim, K. Suganuma, *IEEE Trans. Compon. Packag. Technol.* **2009**, *32*, 627.
[63] A. Gedanken, E. Luvchik, *Eur. J. Inorg. Chem.* **2008**, 2471.
[64] V. G. Pol, M. Motiei, A. Gedanken, J. Calderon-Moreno, M. Yoshimura, *Carbon* **2004**, *42*, 111.
[65] S. V. Pol, V. G. Pol, A. Gedanken , *J. Phys. Chem. C* **2007**, *111*, 13309.
[66] V. G. Pol, S. V. Pol, J. Calderon-Moreno, A. Gedanken, *Carbon* **2006**, *44*, 3285.
[67] S. V. Pol, V. G. Pol, A. Gedanken, *Chem.–Eur. J.* **2004**, *10*, 1–8.
[68] S. V. Pol, V. G. Pol, I. Felner, A. Gedanken, *Eur. J. Inorg. Chem.* **2007**, 2089.
[69] E. Holodelshikov, I. Perelshtein, A. Gedanken, *Inorg. Chem.* **2011**, *50*, 1288.
[70] E. Butovsky, I. Perelshtein, A. Gedanken, *J. Mater. Chem.* **2012**, *22*, 15025.
[71] A. Kukovecz, Z. Konya, N. Nagaraju, I. Willems, A. Tamasi, A. Fonseca, J. B. Nagy, I. Kiricsi, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3071.
[72] C. J. Lee, J. Park, J. A. Yu, *Chem. Phys. Lett.* **2002**, *360*, 250.
[73] B. K. T. Kenneth, C. Singh, M. Chhowalla, W. I. Mine, *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publishers **2004**, *1*, 665–686.
[74] M. Grouchko, A. Kamyshny, S. Magdassi, *J. Mater. Chem.* **2009**, *19*, 3057.
[75] K. Eiroma, *Society for Imaging Science and Technology*, Springfield, VA, USA **2011**, 458.