Nanoscale Res Lett (2009) 4:465–470
DOI 10.1007/s11671-009-9264-3

NANO EXPRESS

Synthesis and Characterization of Monodispersed Copper Colloids in Polar Solvents

**Wei Yu · Huaqing Xie · Lifei Chen ·
Yang Li · Chen Zhang**

Received: 5 November 2008 / Accepted: 27 January 2009 / Published online: 19 February 2009

Abstract A chemical reduction method for preparing monodispersed pure-phase copper colloids in water and ethylene glycol has been reported. Owing to the reduction property of ethylene glycol, the reaction rate in ethylene glycol is higher than that in water. In addition, the amount of reducing agent can be reduced largely. Ascorbic acid plays roles as reducing agent and antioxidant of colloidal copper, due to its ability to scavenge free radicals and reactive oxygen molecules. Thermogravimetric results reveal that the as-prepared copper nanoparticles have good stability, and they begin to be oxidized at above 210 °C. Polyvinyl pyrrolidone works both as size controller and polymeric capping agents, because it hinders the nuclei from aggregation through the polar groups, which strongly absorb the copper particles on the surface with coordination bonds.

Keywords Chemical synthesis · Monodispersed · Copper colloid · Polyvinyl pyrrolidone

Introduction

In recent years, there is an increasing interest in the research on metal colloids due to the multiple applications involving their physical and chemical properties [1–3]. For example, the magnetic fluids made of Fe metal particles have higher magnetization in comparison with the fluids containing magnetic-iron oxide (Fe_3O_4 or γ-Fe_2O_3) [4]. Co nanoparticles in a colloidal solution can assemble into highly constrained linear chains along the direction of the magnetic field, and the magnetic-field-induced chains become floppy after removal of the field, folding into three-dimensional coiled structures upon gentle agitation [5]. Co nanoparticles dispersed in monopolar solvents are effective for enhancing the heating rates of xylene by microwaves, and the smaller particles exhibits greater levels of microwave absorption enhancement than nanoparticles of larger diameters [6]. Pt and Ag colloids in aqueous solution and organic solvents can be effectively used for the hydrogenation of *cis*, *cis*-1,3-cyclooctadiene [7]. The colloidal solution of PtRu nanoparticles has catalytic activity for methanol oxidation [8]. Colloidal silver and copper nanoparticles exhibit characteristic spectra due to surface plasmon resonance [9]. Copper colloids embedded in oxide glasses strongly modify their optical properties, making these composite materials useful for resonant-type nonlinear optical materials for photonic devices [10]. Copper nanoparticles are good additive of nanofluid, which is produced by dispersing nanoparticles into conventional heat transfer fluids, and nanofluids are proposed as the next generation heat transfer fluids due to the fact that their thermal conductivities are significantly higher than those of the base liquids [11–13].

During the past few decades, many methods have been developed for the synthesis of metal colloids, such as laser ablation technique [14], photochemical route [15], microwave dielectric heating [16], and thermal decomposition method [17]. In contrast with noble metals, such as Ag, Au, and Pt, pure metallic copper usually cannot be obtained easily via the reduction of simple copper salts in aqueous solution. Despite zero valence copper initially forming the polar solvents ultimately, it has been found that the zero valence copper can easily transform into oxides in those

---

W. Yu · H. Xie (✉) · L. Chen · Y. Li · C. Zhang
School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China
e-mail: hqxie@eed.sspu.cn

solvents with high dipole moments under ambient conditions [18]. So a simple chemical reduction strategy for the synthesis of copper colloids at mild conditions is highly desired. However, nanoparticles tend to be fairly unstable in solution and therefore, special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such colloidal particles in solution. To obtain stable colloids, the most effective and common strategy is the introduction of a protective agent in the reaction system [19]. Here, we report a facial chemical reduction method to synthesize monodispersed copper colloids in polar solvent without protective gas. Two reaction media, water and ethylene glycol, were used as solvents, and the influences of solvents on reaction rate, the amount of reducing agent and reaction mechanism were discussed. The roles of polyvinyl pyrrolidone (PVP) and ascorbic acid were investigated.

Experimental

Preparation of Copper Colloids

Copper sulfate, ascorbic acid, PVP-K30 (Mw = 40,000), and ethylene glycol (E.G) were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. All the chemicals were analytical grade and used as purchased without further purification. In the experiments, copper colloids were synthesized by two procedures, using deionized water and E.G as reaction solvents, respectively. In a typical procedure, a certain amount of PVP and ascorbic acid was dissolved in the 200 mL 0.2 mmol/L $CuSO_4$ aqueous (or E.G) solution under mechanical stirring, and the reaction mixture was kept at 80 °C for some time. The colloidal suspension was then taken out from the oil bath and cooled to room temperature. For further characterization, the colloid was diluted by ethanol and centrifuged at 8000 rpm for 15 min to separate the particles from the suspension. The particles separated were then resuspended in ethanol and the centrifugation was repeated 3 times so as to remove the surfactant. After that, the precipitates were dried under vacuum overnight and then collected. The experimental parameters are listed in Table 1, and the corresponding XRD patterns of the products prepared at different experimental parameters are shown in Fig. 2.

Characterization of Copper Nanoparticles

XRD measurements were recorded using a (D8-Advance, Germany) X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source ($\lambda = 0.154$ nm). XRD patterns were recorded from 20° to 80° (2θ) with a scanning step of 0.01. The size and morphology of the Cu nanoparticles were examined by using transmission electron microscopy (TEM, JEOL 2100F). The TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping the suspension onto a holey carbon film supported on a copper grid, and drying it in air. A thermogravimetric (TG-DTG, Netzsch STA 449C) analyzer (sample mass: about 15.0 mg; atmosphere, flowing dry oxygen; heating rate, 10 K/min) was used for thermogravimetric analysis.

Results and Discussion

The Influences of Solvents on Reaction Process

Sample 1 and sample 2 were synthesized using water as solvent, and the reaction time was 6 and 8 h, respectively. Because ascorbic acid is a weak reducing agent, the reaction rate using water as solvent is slow. The color change of the reaction process is shown in Fig. 1a. The light blue reaction system turned to cloudy yellow in 3 h, and then it became brick red, and after 2 h it became red colloidal. Figure 2 shows the XRD patterns of samples prepared by different procedures. When the reaction time was less than 6 h, the product was impure, and it was the mixture of face-centered cubic (fcc) phase of copper (JCPDS 04-836) and cubic phase of Cu_2O (JCPDS 05-0667), and copper was the main product. The XRD analysis results coincided with the experimental phenomena. When the reaction time was over 8 h, the product was pure-phase copper.

Comparing to the reaction rate using water as solvent, the rate using E.G was higher, and the color change of the

Table 1 Comparison of results from the two reaction systems and different experimental parameters

Sample No.	Solvent	$CuSO_4$ (mmol/L)	PVP-K30 (mmol/L)	Product	Ascorbic acid/Cu^{2+} (mol/mol)	Reaction time	Mean size (nm)
1	Water	0.2	0.5	$Cu_2O + Cu$	20	6 h	–
2	Water	0.2	0.3	Cu	20	8 h	7 ± 3
3	Water	0.2	0.5	Cu	20	8 h	4 ± 1
4	E.G	0.2	0.3	Cu	8	1 h	6 ± 3
5	E.G	0.2	0.5	Cu	8	1 h	3 ± 1

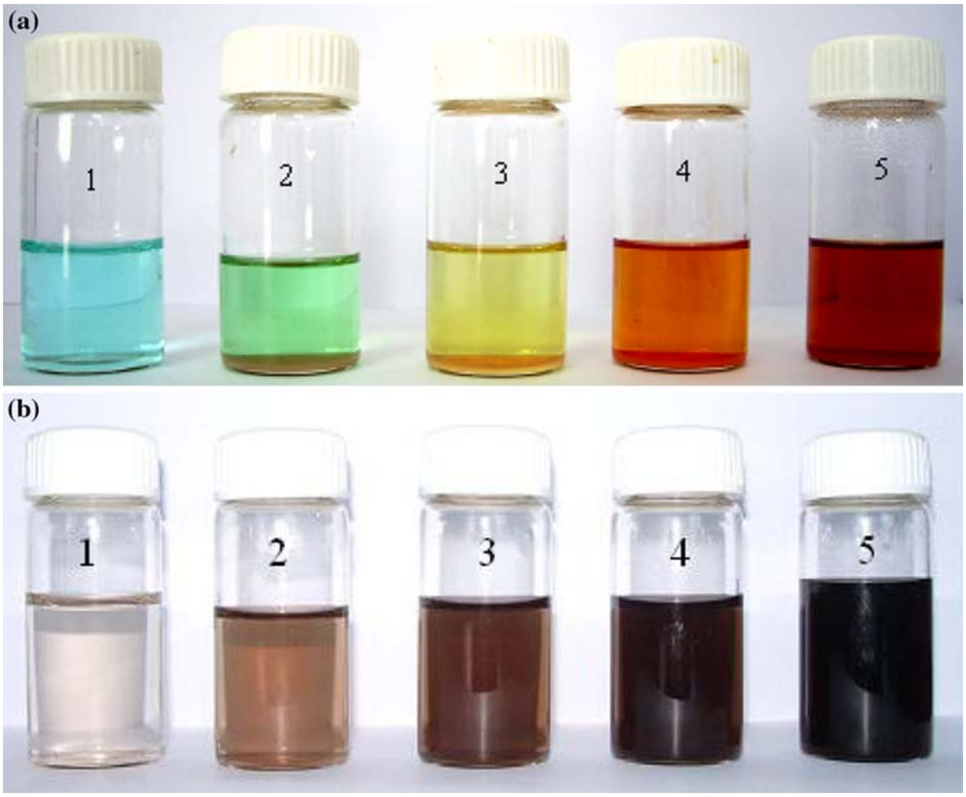
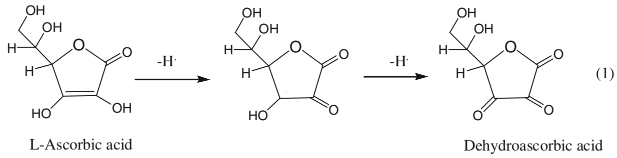


Fig. 1 The color change of the reaction process in water medium (**a**) and E.G medium (**b**)

reaction process is shown in Fig. 1b. In 15 min, the initial precursor solution with light blue color changed to light brown, red, and black. The reaction could complete in 1 h, and the product was phase-pure. The higher rate using E.G attributed to the reduction property of E.G. E.G was a weak reducing agent, and it could reduce Cu^{2+} to Cu^{+}, which was confirmed by some experimental facts [16, 20]. Due to the united deoxidization of ascorbic acid and E.G, the reaction using E.G was fast, and Cu_2O was not detected in the procedure. In addition, the amount of reducing agent ascorbic acid could be reduced largely. When water was solvent, the molar ratio of ascorbic acid/Cu^{2+} was up to 20. For E.G reaction system, the molar ratio of ascorbic acid/Cu^{2+} was 8.

The Role of Ascorbic Acid as Reducing Agent and Antioxidant of Colloidal Copper

To prevent oxidation, the reaction solutions were carefully deoxygenated and the entire processes were performed under rigorous protection of inert gas in many reported studies [21]. During the synthesis process, ascorbic acid plays a role as reducing agent, and in the storage, excessive ascorbic acid is essential to avoid oxidation of copper nanoparticles. The antioxidant properties of ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules [22], accompanying the donation of electrons to give the semi-dehydroascorbate radical and dehydroascorbic acid (Eq. 1). Therefore, ascorbic acid plays dual roles of reducing agent and antioxidant of copper nanoparticles. The reaction can complete without protective gas. The TG-DTG curves of the prepared copper nanoparticles using E.G as solvent are shown in Fig. 3. The results show that copper nanoparticles begin to be oxidized at above 210 °C, indicating that copper nanoparticles have good stability. From 210 to 400 °C, the oxidation rate is slow. When temperature is further increased, the oxidation rate becomes higher. When the temperature reaches 650 °C, the oxidation is completed with the weight increment of 25.10%, and the oxidation product is CuO (the theoretical weight increment 25.0%). The TG-DTG curves of the prepared copper nanoparticles using water is similar to that using E.G.



(1)

The Role of PVP as Size Controller and Protective Agent of Copper Colloid

PVP is always used as the dispersant to prepare nanomaterials and the stabilizer of metal colloids, and the size and

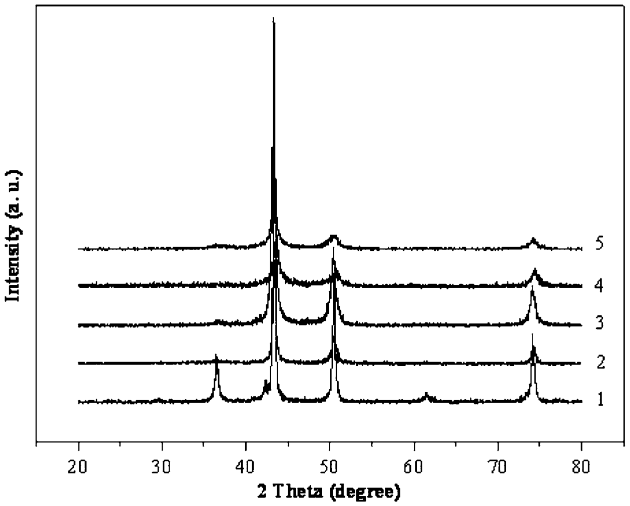


Fig. 2 XRD pattern of the products prepared at different experimental parameters

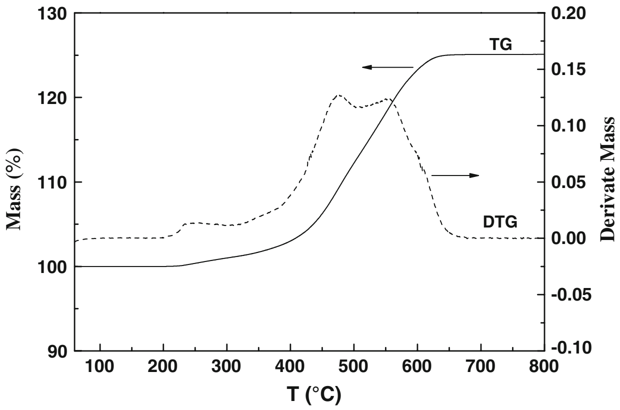


Fig. 3 Typical TG-DTG curves of Cu nanoparticles obtained in E.G medium

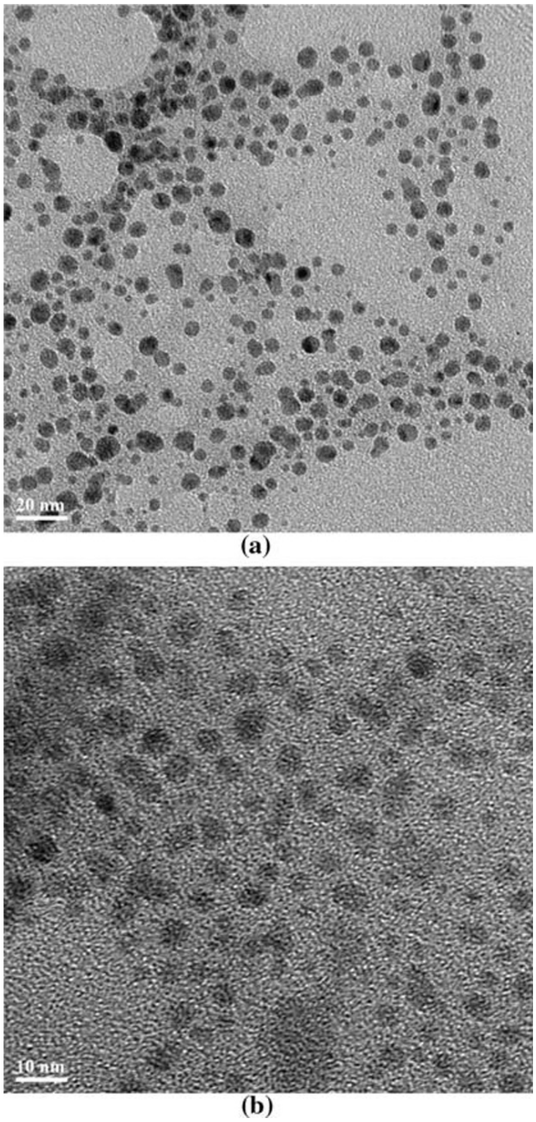


Fig. 4 Typical TEM images of Cu nanoparticles obtained in water medium. **a** Sample 2, **b** Sample 3

shape of nanomaterials depends strongly on the solution concentration of PVP [23, 24]. Figure 4 shows that when water was the reaction solvent and the concentrations of PVP were 0.3 or 0.5 mmol/L, the copper nanoparticles were approximately spherical with the mean diameter about 7 or 4 nm, respectively. The influence of PVP on the size of copper nanoparticles in E.G was similar to that in water. When the concentration of PVP was 0.3 or 0.5 mmol/L, the copper nanoparticles were monodispersed in E.G reaction system, and the mean diameters were about 6 or 3 nm, respectively, indicating that the increasing of PVP concentration attributes to the smaller dimension particles (Fig. 5).

The mechanism of the effect of PVP on size and shape of nanomaterials has been discussed in some literatures [25–27]. PVP has the structure of a polyvinyl skeleton with nitrogen and oxygen polar groups, and the polar group donates lone-pair electrons forming a coordinative interaction with copper ions, thus creating the Cu^{2+}–PVP complex compound (Eq. 2) in the solution [15, 27]. When water was the reaction medium, the reaction time was not over 6 h, according to the XRD analysis, the product was impure. The fact indicated that Cu^{2+}–PVP complex was reduced to Cu^{+}–PVP firstly, and then Cu^{+} reacted with OH^{-} to form Cu_2O, due to the existence of enough OH^{-}, so the color of reaction system was yellow when the reaction time was 3 h. The further reduction of Cu^{+} formed the pure copper nanoparticle. The coordination action between PVP and Cu^{+} prevented the agglomeration of the copper nanoparticles (Eq. 3). Due to the higher rate using E.G as reaction medium, no intergradation product Cu_2O was detected. According to the above analysis, PVP acted as the polymeric capping agents and size controller. It hinders the nuclei from aggregation through the polar

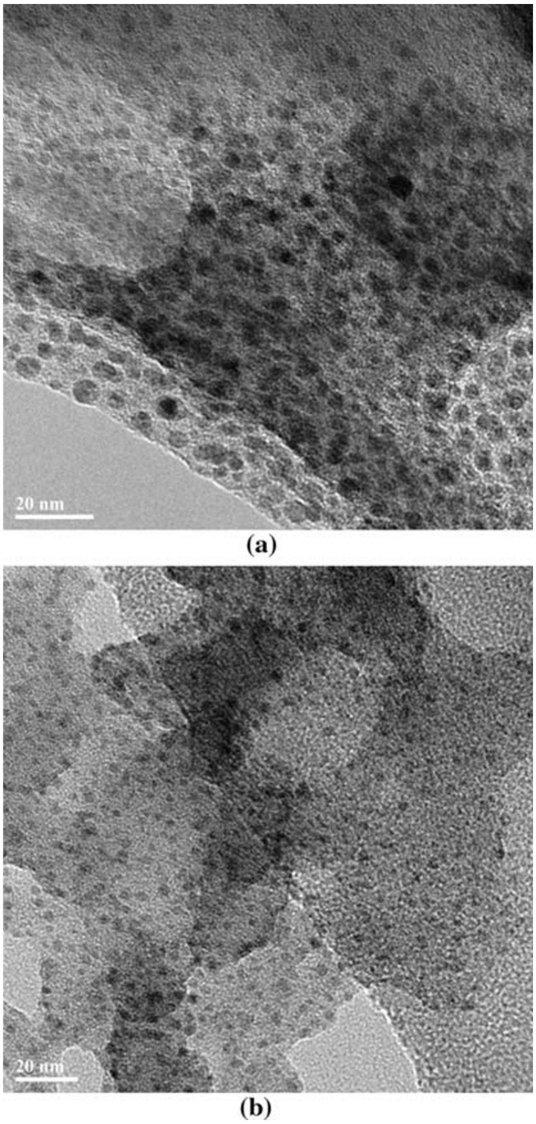


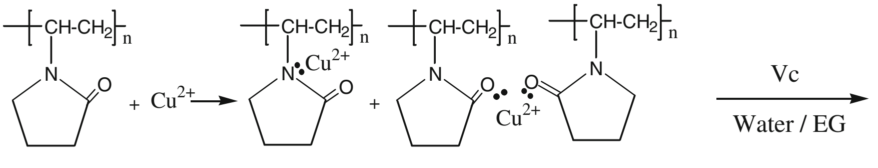
Fig. 5 Typical TEM images of Cu nanoparticles obtained in E.G medium. **a** Sample 4, **b** Sample 5

groups, which strongly absorb the copper particles on the surface with coordination bonds.

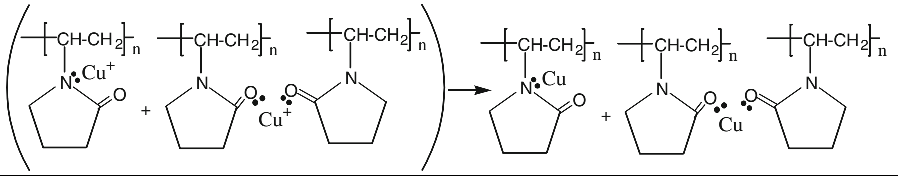
Conclusions

In this letter, two monodispersed copper colloids in water and E.G have been prepared. In order to obtain pure-phase copper colloid in water, the reaction time of 8 h is essential; otherwise the products will be the mixture of face-centered cubic phase of copper and cubic phase of Cu_2O. Comparing to the reaction rate using water, the rate in E.G was higher, due to the reduction property of E.G. In addition, the amount of reducing agent ascorbic acid could reduce largely. Ascorbic acid plays roles as reducing agent and antioxidant of colloidal copper, due to its ability to scavenge free radicals and reactive oxygen molecules. The TG-DTG curves of the prepared copper nanoparticles show that copper nanoparticles have good stability, and they begin to be oxidized at above 210 °C, and the oxidation product is CuO. The size of copper particles depended on the concentration of PVP, and the increasing of PVP concentration attributed to the smaller dimension particles. PVP works both as size controller and polymeric capping agents, because it hinders the nuclei from aggregation through the polar groups, which strongly absorb the copper particles on the surface with coordination bonds. The work proves that it is possible to obtain monodispersed pure-phase copper colloids in polar solvents through carefully selecting experimental conditions.

Acknowledgments The work was supported by the National High Technology Research and Development Program of China (2006AA05Z232), Shanghai Educational Development Foundation and Shanghai Municipal Education Commission (08CG64), the Excellent Young Scholars Research Fund of Shanghai (No.RYQ307007) and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.



(2)



(3)

References

1. S.U. Son, S.L. Lee, Y.K. Chung, S.W. Kim, T. Hyeon, Org. Lett. **4**, 277 (2002). doi:10.1021/ol017043k
2. A. Lagunas, C. Jimeno, D. Font, L. Sola, M.A. Pericas, Langmuir **22**, 3823 (2006). doi:10.1021/la053016h
3. Y.J. Song, H. Modrow, L.L. Henry, C.K. Saw, E.E. Doomes, V. Palshin, J. Hormes, C.S.S.R. Kumar, Chem. Mater. **18**, 2817 (2006). doi:10.1021/cm052811d
4. X.X. Zhang, B.X. Qin, G.H. Wen, Y.S. Kwok, K.K. Fung, Mater. Sci. Eng. C **16**, 119 (2001). doi:10.1016/S0928-4931(01)00285-5
5. G.J. Cheng, D. Romero, G.T. Fraser, A.R. Hight Walker, Langmuir **21**, 12055 (2005). doi:10.1021/la0506473
6. A. Holzwarth, J.F. Lou, T.A. Hatton, P.E. Laibinis, Ind. Eng. Chem. Res. **37**, 2701 (1998). doi:10.1021/ie970819u
7. S.H. Choi, Y.P. Zhang, A. Gopalan, K.P. Lee, H.D. Kang, Colloids Surf. A Physicochem. Eng. Asp. **256**, 165 (2005). doi:10.1016/j.colsurfa.2004.07.022
8. Y. Shimazaki, Y. Kobayashi, S. Yamada, T. Miwa, M. Konno, J. Colloid Interface Sci. **292**, 122 (2005). doi:10.1016/j.jcis.2005.05.052
9. G. Suyal, Thin Solid Films **426**, 53 (2003). doi:10.1016/S0040-6090(02)01294-4
10. B. Macalik, L. Krajczyk, T. Morawska-Kowal, Phys Status Solidi **4**, 761 (2007). doi:10.1002/pssc.200673837
11. X.F. Li, D.S. Zhu, X.J. Wang, N. Wang, J.W. Gao, H. Li, Thermochim. Acta **469**, 98 (2008). doi:10.1016/j.tca.2008.01.008
12. M.S. Liu, M.C.C. Lin, C.Y. Tsai, C.C. Wang, Int. J. Heat Mass Transf. **49**, 3028 (2006). doi:10.1016/j.ijheatmasstransfer.2006.02.012
13. H. Bonnemann, S.S. Botha, B. Bladergroen, V.M. Linkov, Appl. Organomet. Chem. **19**, 768 (2005). doi:10.1002/aoc.889
14. T. Tsuji, K. Iryo, Y. Nishimura, M. Tsuji, J. Photochem. Photobiol. A **145**, 201 (2001)
15. S. Giuffrida, L.L. Costanzo, G. Ventimiglia, C. Bongiorno, J. Nanopart. Res. **10**, 1183 (2008). doi:10.1007/s11051-007-9343-2
16. K. Patel, S. Kapoor, D.P. Dave, T. Mukherjee, J. Chem. Sci. **117**, 53 (2005). doi:10.1007/BF02704361
17. D.K. Lee, Y.H. Kim, X.L. Zhang, Y.S. Kang, Curr. Appl. Phys. **6**, 786 (2006). doi:10.1016/j.cap.2005.04.040
18. J.G. Yang, Y.L. Zhou, O. Takeshi, R. Ichino, M. Okido, J. Mater. Sci. **42**, 7638 (2007). doi:10.1007/s10853-007-1899-9
19. Y.L. Luo, Mater. Lett. **61**, 1873 (2007). doi:10.1016/j.matlet.2006.07.166
20. L.J. Fu, J. Gao, T. Zhang, Q. Cao, L.C. Yang, Y.P. Wu, R. Holze, H.Q. Wu, J. Power Sources **174**, 1197 (2007). doi:10.1016/j.jpowsour.2007.06.030
21. X.Y. Song, S.X. Sun, W.M. Zhang, Z.L. Yin, J. Colloid Interface Sci. **273**, 463 (2004). doi:10.1016/j.jcis.2004.01.019
22. C.W. Wu, B.P. Mosher, T.F. Zeng, J. Nanopart. Res. **8**, 965 (2006). doi:10.1007/s11051-005-9065-2
23. L. Huang, F. Peng, H. Yu, H.J. Wang, Mater. Res. Bull. **43**, 3047 (2008). doi:10.1016/j.materresbull.2007.11.011
24. A. Gniewek, A.M. Trzeciak, J.J. Ziółkowski, L. Kepi'nski, J. Wrzyszcz, W. Tylus, J. Catal. **229**, 332 (2005). doi:10.1016/j.jcat.2004.11.003
25. X. Zhang, Y. Xie, F. Xu, X.H. Liu, D. Xu, Inorg. Chem. Commun. **6**, 1390 (2003). doi:10.1016/j.inoche.2003.09.002
26. Z. Zhang, B. Zhao, L. Hu, J. Solid State Chem. **121**, 105 (1996). doi:10.1006/jssc.1996.0015
27. I. Haas, S. Shanmugam, A. Gedanken, J. Phys. Chem. **110**, 16947 (2006). doi:10.1021/jp064216k