Preparation and Characterization of Monodispersed Near-sphere and Flake Gold Powders

LUO Hui, LI ShiHong, ZENG Yiming, LIU Jisong, LI Wenlin, XING Qisi, LIANG Yun, YAO Zhiqiang, ZHANG Jun

(State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Sino-Platinum Metals Co. Ltd., Kunming 650106, China)

Abstract: Monodispersed near-sphere and flake gold powders were prepared by the direct reduction of chloroauric acid tetrahydrate ($HAuCl_4·4H_2O$) in water. using ascorbic acid (VC) as the reducing agent and lineal polyethyleneimine (L-PEI) as the surfactant. SEM, XRD and laser particle sizer were used to test the morphology, size, crystal form and dispersity of obtained gold powders. The molar ratio of VC to $HAuCl_4·4H_2O$, concentration of L-PEI, temperature as well as pH value of the reaction solution were investigated, and their effects on morphology and size of near-sphere and flake gold particles were discussed. The conditions for preparing near-sphere and flake gold powders in range of one to several micrometers were optimized. Possible explanations for the nuclei formation and growth of near- sphere and flake gold particles were also proposed.

Key words: metal materials; near-sphere gold; flake gold; preparation; characterization

CLC number: TB831 **Document Code:** A **Article ID:** 1004-0676(2017)01-0015-07

单分散近球形和片状金粉的制备及表征

罗 慧，李世鸿，曾一明，刘继松，李文琳，幸七四，梁 云，姚志强，张 骏

(贵研铂业股份有限公司 稀贵金属综合利用新技术国家重点实验室，昆明 650106)

摘 要：以 $HAuCl_4·4H_2O$ 为前驱体，抗坏血酸(VC)为还原剂，线性聚乙烯亚胺(L-PEI)为表面活性剂在水相中制备了单分散的近球形和片状金粉。采用 SEM、XRD 和激光粒度分析仪对金粉的形貌、粒径、结晶和分散性进行了测试和表征。研究了还原剂和金前驱体的摩尔比、L-PEI 浓度、温度及反应溶液的 pH 对近球形和片状金粉的形貌和粒径大小的影响。给出了制备微米级近球形和片状金粉的反应条件，同时也提出了近球形和片状金粉的成核和晶核生长的可能解释。

关键词：金属材料；近球形金粉；片状金粉；制备；表征

The properties and applications of metal powders are mainly determined by their shape, size, crystallization, composition and dispersity. Mono-dispersed near-sphere and flake gold powders have demonstrated great potential for applications in many fields especially in forming various kinds of gold pastes in thick film technologies[1-4]. Flake gold powder can offer features and advantages difficult to be achieved by spherical gold powder such as rheo-logical properties, better conductivity and good sintering properties[5-8]. Gold powders with a diameter of about one to several micrometers are widely used in

Received: 2016-03-14
Foundation: The fund of the State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals (SKL-SPM-201532), Development &Industrialization of Buried Conductive and Via-Fill gold pastes used on LTCC Substrate (2015IA035) and Key Technologies of Preparing LTCC Electronic Pastes and Their Industrial Applications(2015020211).
Fist author: LUO Hui, female, graduate, engineer. Research direction: Electronic paste. E-mail: Estron@126.com

forming gold pastes suitable for low temperature co-fired ceramic technologies abroad[3, 5, 9-12].

So far, a number of experimental methods have been developed by researchers for the preparation of gold nanoparticles with various shapes including one-dimensional (1D) or 2D morphologies such as nanocubles, nanowires, nanorods, nanoribbons and nanosheets and so on[13-16]. However, it is still a challenge and an important task to produce mono-dispersed near-sphere and flake gold powders in the range of a few micrometers in an industrial way domestically[5, 7, 10, 13-17]. In this work, we developed a simple way to obtain monodispersed near-sphere and flake gold powders by reduction of chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) using ascorbic acid (VC) as reducing agent and lineal polyethyleneimine (L-PEI) as surfactant in water under mild stirring and can be easily realized for massive production.

The reduction of chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) to produce various shapes of nano-meter scale gold powders by VC is a simple process which has been studied at detail by many previous researchers[6, 18-23]. The reaction only requires the mixing of the agents at suitable external conditions. As we know reaction parameters such as the reactant concentrations, temperature and pH value of reacting solution all have an influence on the final morphology and size of the particles. This study concentrated on molar ratio between VC and Au, L-PEI concentration, temperature and pH value of the reacting solution and their influence on the morphology and size of the final particles. The selected conditions for preparing near-sphere and flake gold powders in range of one to several micrometers were concluded and presented.

1 Experimental

1.1 Chemicals and materials

Chemical purity of ascorbic acid (VC), HCl and NaOH, were purchased from Sinopharm Chemical Reagent Co. Ltd.; Lineal polyethyleneimine (L-PEI), chemical pure, was purchased from Airly Chemistry Co. Ltd.; Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) came from Sino-platinum Ltd.. 0.05 mol/L HCl and NaOH solution were prepared and used to adjust pH value of the reaction solution. The water used in the whole process was ultra-pure deionized water.

1.2 Preparations of monodispersed near-sphere and flake gold powders

A typical procedure to prepare gold powder was as follows: 300 mL reducing solution containing VC and L-PEI was heated to a certain temperature and mildly stirred by a waterbath magnetic stirrer. Adjust pH value of the reducing solution by adding drops of 0.05 mol/L HCl or NaOH solution. Then, 25 mL $HAuCl_4 \cdot 4H_2O$ solution (0.1 mol/L) was added into the reducing solution dropwise. The mixed solution was heated and kept at a certain temperature and magnetically stirred for reaction for at least one hour. After reaction, gold powder was collected by pouring out the upper solution and washed with deionized water several times to remove the remaining reactants. Finally the purified product was collected and freeze-dried for further test and characterization.

1.3 Characterization

Hitachi scanning electron microscope X-650 was used to analyze the morphology and measure particle size of prepared gold powders. The XRD pattern of prepared gold powders were conducted on a diffractometer (Ultima-III, Rigaku) with Cu K_α radiation. Characterization of size distribution of gold powders were dispersed in deionized water and taken on a Malvern 3000 Master Sizer.

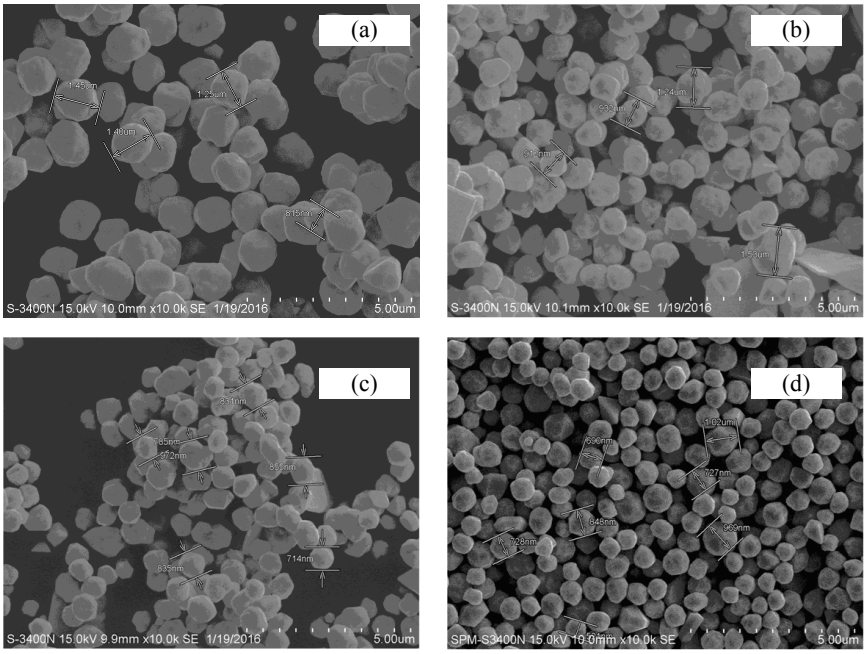
2 Results and discussions

2.1 Preparation of near-sphere gold powder

Sphere is the lowest-energy shape, simple reduction generally results in the formation of spherical particles. Each one of these parameters (reducing agent to gold ratio, concentration of surfactant, temperature and pH value of reducing solution the way of adding and so on) has a substantial influence on the final shape of the particle[6, 9, 21-22]. Although the exact role of these parameters in determining the morphologies is not yet fully understood, it is not difficult to get sphere or near-sphere shaped particles by controlling the experiment parameters.

Fig.1 showed the gold powders prepared with 0.4 g/L L-PEI concentration at 20℃, pH=4.0 were near-

sphere in shape, the average particle size (Tab.1) gradually decreased from 1.2~1.4 μm to 0.7~1.0 μm with increasing molar ratio (*n*(VC)/*n*(Au)) from 4:1, 6:1 to 8:1, and remained about the same when *n*(VC)/*n*(Au) ratio was 10:1.



(a). S-1: *n*(VC)/*n*(Au)=4:1; (b). S-2: *n*(VC)/*n*(Au)=6:1; (c). S-3: *n*(VC)/*n*(Au)=8:1; (d). S-4: *n*(VC)/*n*(Au)=10:1

Fig.1 SEM images of near-sphere gold powders prepared with different *n*(VC)/*n*(Au) ratios

图 1 不同 *n*(VC)/*n*(Au)比例制备的近球形金粉的扫描电镜图像

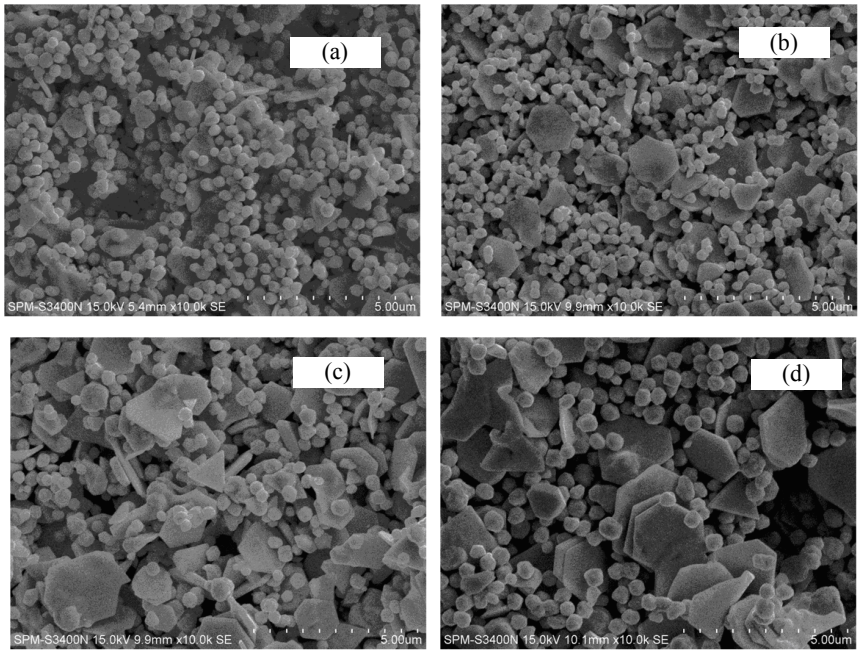
Tab.1 Experiment parameters and size of prepared gold powders

表 1 制备的金粉的实验参数和粒径

No.	*n*(VC)/*n*(Au)	Average sphere particle size/μm
S-1	4:1	1.2~1.4
S-2	6:1	0.9~1.2
S-3	8:1	0.7~1.0
S-4	10:1	0.7~1.0

2.2 Preparation of flake gold powder

Generally, preferential and directional growth of particles result in anisotropic growth which finally leads to flake or other anisotropic morphologies although the exact mechanisms for the formation of these morphologies has not been fully understood yet. Researches pointed out that referential adsorption of some molecules to specific facets can hinder or enhance the crystal growth in some directions[7, 19, 21-22], however reacting conditions such as temperature, pH value of reacting solution and other parameters may also contribute to anisotropic growth of crystals. By continuously increasing concentration of L-PEI, anisotropic growth of gold particle was observed. By increasing L-PEI concentration from 0.6 to 1.5 g/L, the prepared gold powders were a mixture of near-sphere and flake with about the same diameter. However, the ratio of gold flake tend to rise as L-PEI concentration increased from 0.4 to 1.0 g/L. Although the exact mechanisms for the formation and increase of these flake was not clear, we could conclude that the increasing concentration of L-PEI enhanced the anisotropic growth of gold into flake. When L-PEI concentration was 1.5 g/L the ratio of flake did not show obvious increase. Fig.2 indicated that with an increasing concentration of L-PEI, the average particle size of near-sphere gold decreased slightly from 0.7~1.0 μm to 0.5~0.6 μm, but the diameter of gold flake remained unchanged. Therefore L-PEI concentration 1.0 g/L was chosen and fixed for further experiments.

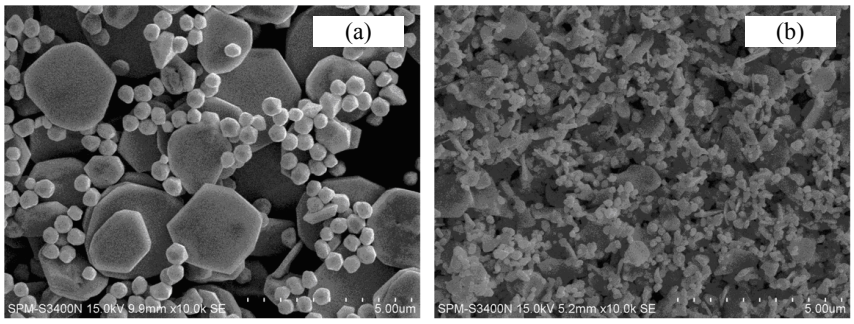


(a). S-5: ρ(L-PEI)=0.6 g/L; (b). S-6: ρ(L-PEI)=0.8 g/L; (c). S-7: ρ(L-PEI)=1.0 g/L; (d). S-8: ρ(L-PEI)=1.2 g/L

Fig.2 SEM images of gold powder prepared with different L-PEI concentrations

图 2 不同 L-PEI 浓度下制备的金粉的扫描电镜图像

Our target was to reduce the percentage of near-sphere particles and prepare gold powder with over 90% flake. Fig.3 showed the gold powders prepared at lower pH values, 3.0 and 2.0, while L-PEI concentration=1.0 g/L, n(VC)/n(Au)=8:1 and the temperature remained 20℃.



(a). S-9: pH=3.0; (b). S-10: pH=2.0

Fig.3 SEM images of gold powder prepared at low pH values

图 3 低 pH 溶液中制备的金粉的扫描电镜图像

The SEM showed that when pH value of reaction solution reached 2.0 although the ratio of near-sphere gold in prepared gold reduced, deformed flakes and agglomeration was observed, the results indicated decreased particle size of near-sphere and diameter of gold flake as well (Tab.2). So pH=3.0 is appropriate for the reaction solution.

Tab.2 Morphologies and diameter of gold powder prepared at low pH values

表 2 低 pH 溶液中制备的金粉的形貌和粒径

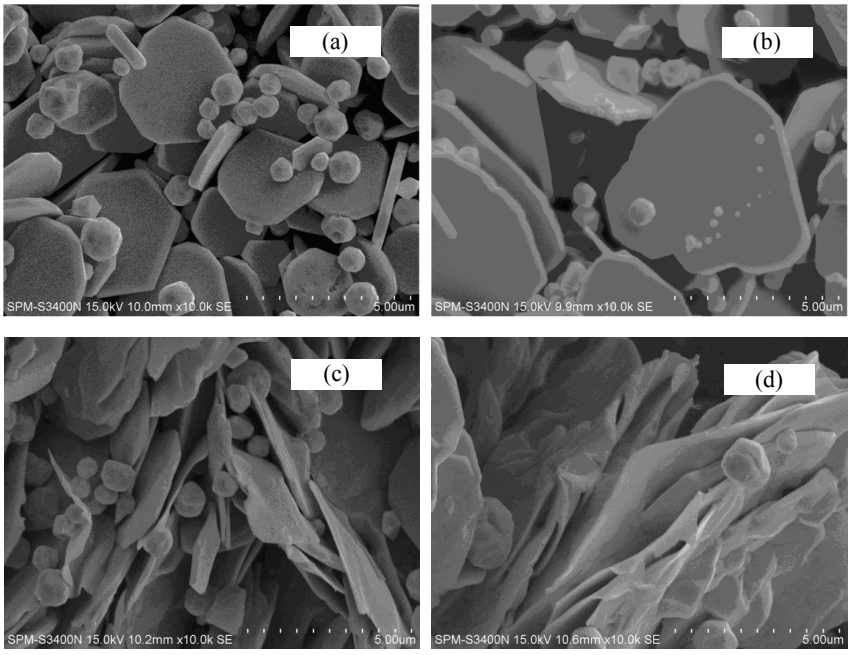
No.	pH	Average size/μm		Morphology
		Sphere particle	Flake diameter	
S-9	3.0	0.5~0.6	2~3	near-sphere and flake
S-10	2.0	0.2~0.4	0.9~1.5	near-sphere and deformed flake

Tab.3 showed experiment parameters, average particle size and morphologies of gold powder prepared at different temperatures. Average particle size and diameter of flake increased with rising temperature, the percentage of flake increased as well which could be seen from Fig.4. However, when temperature of reaction solution reached 50℃ the flake stacked together due to rapid nuclei formation and crystal growth which could be observed from experiment (Fig.4(c) and (d)). So the appropriate temperature for preparing gold flake powder was 30~40℃.

Tab.3 Morphology of gold powder prepared at different temperatures

表 3 不同温度溶液下制备的金粉的形貌

No.	*T*/℃	Average size/μm		Morphology
		Sphere particle	Flake diameter	
S-11	30	0.5~0.8	2~4	near-sphere and flake
S-12	40	0.5~0.8	4~6	flake
S-13	50	0.6~1.0	4~8	near-sphere and stacked flake
S-14	60	0.6~1.0	7~10	stacked flake



(a). S-11: *T*=30℃; (b). S-12: *T*=40℃; (c). S-13: *T*=50℃; (d). S-14: *T*=60℃

Fig.4 SEM images of gold powder prepared at different temperatures　图 4 不同温度溶液下制备的金粉的扫描电镜图像

Fig.5 showed powders prepared under the selected condition as: *n*(VC)/*n*(Au)=8:1, L-PEI concentration =1.0 g/L, pH=3.0, temperature 40℃. It can be seen the powder was over 90% gold flake with a few near-sphere particles, and the thickness was about 290 nm.

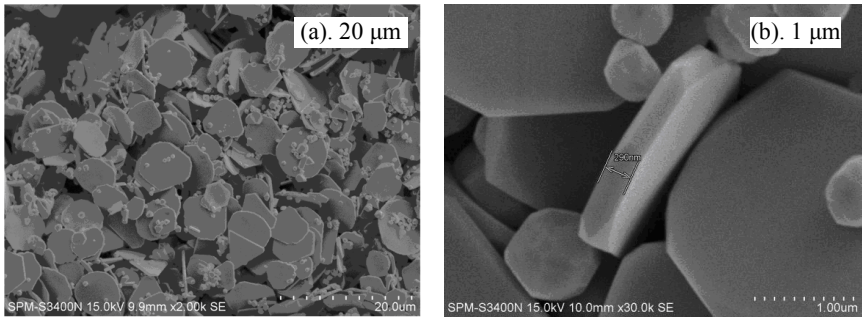


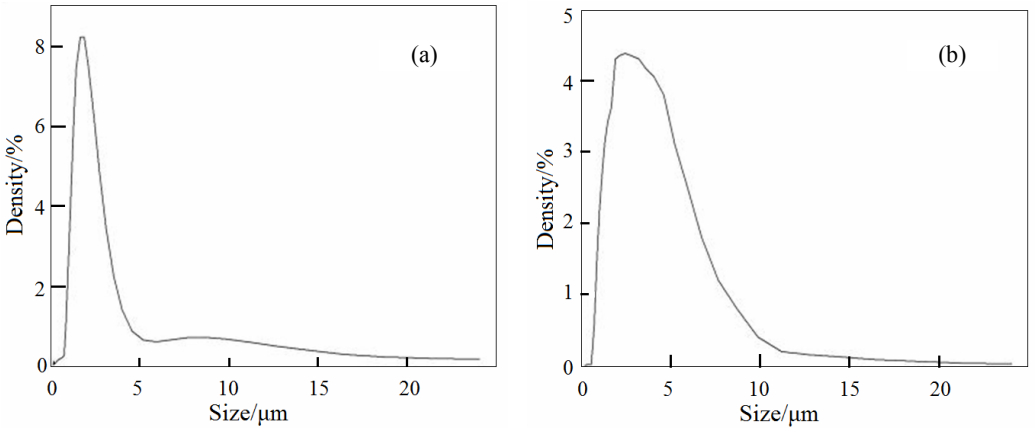
Fig.5 Different magnification SEM images of powder samples (S-12) prepared under the selected condition

图 5 选定条件下制备的片状金粉样品(S-12)的不同放大倍数扫描电镜图像

2.3 Size distribution of the prepared powders

Both of the XRD patterns (omitted in this article) of near-sphere gold powder and flake gold powder are the same, and showed strong diffraction peak at 38.9°, which is ascribed to the {111} facet of face-centered cubic metal gold structure. It means that the existing status of gold powder is crystal.

Characterization of size distribution of two gold powders was conducted and shown in Fig.6.



(a). S-1; (b). S-12

Fig.6 Size distributions of (a) near-sphere gold powders and (b) flake gold powder

图 6 近球形金粉(a)及片状金粉(b)的粒度分布图

The results indicated that both the near-sphere gold powder and flake gold were monodispersed, D_{90} of each powder is 3.99 and 6.24 μm, respectively.

3 Conclusions

1) Gold powders prepared at a relatively low L-PEI concentration (0.4 g/L) were near-sphere in shape, and the average particle size can be adjusted by n(VC)/n(Au) under these reduction conditions.

2) Gold powders prepared at different L-PEI concentration (0.4, 0.6, 0.8 and 1.0 g/L) were a mixture of near-sphere and flake in shape, the increasing concentration of L-PEI enhanced the anisotropic growth of gold into flake. The percentage and diameter of flake increased with L-PEI concentration as well.

3) pH value and temperature of the reduction solution also have an influence on the formation and percentage of gold flake. The flake deformed and agglomerated when pH=2.0 and stacked together at high temperature due to rapid nuclei formation and crystal growth.

4) The selected condition of preparing near-sphere gold powder was n(VC)/n(Au)=4:1, L-PEI concentration=0.4 g/L, pH=4.0 and temperature=20℃, the powder was monodispersed and good crystallization of pure gold with a diameter of 1.2~1.4 μm.

5) The selected condition of preparing gold flake was n(VC)/n(Au)=8:1, L-PEI concentration 1.0 g/L, pH=3.0 and temperature 40℃, the prepared gold flake was monodispersed and good crystallization of pure gold with a diameter of 4~6 μm and 290 nm in thickness.

Reference:

[1] 张济祥, 谢宏潮, 阳岸恒, 等. 高纯金制备技术研究现状与展望[J]. 贵金属, 2015, 36(3): 81-86.
ZHANG J X, XIE H C, YANG A H, et al. Status and prospect of preparative methods for high-purity gold[J]. Precious metals, 2015, 36(3): 81-86.

[2] THELEMANN T, THUST H, HINTZ M. Using LTCC for microsystems[J]. Microelectronics international, 2002, 19(3): 19-23.

[3] LENKKERI J, JAAKOLA T, KAUTIO K, et al. Prospects and limits of LTCC technology[J]. Advances in micro-electronics, 2005, 32(3): 9-12.

[4] RUAN C Y, MUROOKA Y, RAMAN R K, et al. Dynamics of size-selected gold nanoparticles studied by ultrafast electron nanocrystallography[J]. Nano letter,

2007, 7(5): 1290-1296.

[5] NIU W X, ZHENG S L, ZHENG D W, et al. Selective synthesis of single-crystalline rhombic dodecahedral, octahedral, and cubic gold nanocrystals[J]. Journal of The American Chemistry Society, 2009, 131(2): 697-703.

[6] KANG H, KIM, B G, NA H B, et al. Anti-galvanic reduction of silver ion on gold and its role in anisotropic growth of gold nanomaterials[J]. American Ceramic Society, 2015 119 (46): 25974-25982.

[7] SUN Y G, XIA Y N. Shape controlled synthesis of gold and silver nanoparticles[J]. Science, 2002, 34(10): 2176.

[8] DARKO B, MARKO H, HOLC J, et al. The application of thick-film technology in CMEMS[J]. Electroceramic 2009, 19: 353-368.

[9] RAUSCHER M, ROOSEN A. Effect of particle shape on anisotropic packing and shrinkage behavior of tape-cast glass-ceramic composites[J]. Applied ceramic technology, 2009, 6(1): 24-34.

[10] SHUI A, ZENG L, UEMATSU K. Relationship between sintering shrinkage anisotropy and particle orientation for alumina powder compacts[J]. Science material, 2006, 55(9): 831-834.

[11] BESENDOROFER G, ROOSEN A. Particle shape and size effects on anisotropic shrinkage in tape-cast ceramic layers[J]. American Ceramic Society, 2008, 91(8): 2515-2520.

[12] BRUST M, WALKER M, BETHEL D, et al. Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system[J]. Journal of the chemical society chemical communications, 1994, 7(7): 801-802.

[13] SANJANLAL P R, SREEPRASAD T S, SAMAL A K, et al. Anisotropic nanomaterials structure, growth, assembly and functions[J]. Nano reviews, 2011, 2(24): 5883-5945

[14] SAU T K , MURPHY C J. Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution[J]. Journal of The American Chemical Society, 2004, 126(28): 8648-8649.

[15] TAKAHASHI H, NIIDOME T, KAWANO T, et al. Surface modification of gold nanorods using layer-by-layer technique for cellular uptake[J]. Journal of nanoparticle research, 2007, 10(1): 221-228.

[16] HIRAMATSU H, OSTERLOH F E. A simple large-scale synthesis of nearly monodisperse gold and silver nanoparticles with adjustable sizes and with exchangeable surfactants[J]. Chemistry of materials. 2004, 16(13): 2509-2511.

[17] NIKOOBAKHT B, ELSAYED M A. Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method[J]. Chemistry of materials. 2003, 15(10): 1957-1962.

[18] AMALU E H , EKERE N N, MALLIK, S. Evaluation of rheological properties of lead free solder pastes and their relationship with transfer efficiency during stencil printing process[J]. Materials and design, 2011, 32: 3189-3197.

[19] PILENI M P. Control of the size and shape of inorganic nanocrystals at various scales from nano to macro-domains[J]. Journal of physical chemistry C, 2007, 111(26): 9019-9038.

[20] PEREZ J J, PASTORIZA S I, MARZAN L M, et al. Gold nanorods: synthesis, characterization and applications[J]. Coordination chemistry reviews, 2005, 249(17/18): 1870-1901.

[21] JANA N R, GEARHEART L, MURPHY C J. Seed-mediated growth approach for shape-controlled synthesis of spheroidal and rod-like gold nanoparticles using a surfactant template[J]. Advanced materials, 2001, 13(18): 1389-1393.

[22] SUN X D, WANG E. High-yield synthesis of large single-crystalline gold nanoplates through a polyamine process[J]. Langmuir, 2005, 21(10): 4710-4712.

[23] GUO Z R, ZHANG Y, MU D Y. Facile synthesis of micrometer-sized gold nanoplates through an anlline-assisted route in ethylene glycol solution[J]. Colloids and surfaces A: physicochemical and engineering aspects, 2006, 278(1/3): 33-38.