氟化镧纳米粒子的原位合成及润滑机理

仝 芳,袁芳芳,吴 勇,吴现棉,唐定国,杨汉民
(中南民族大学化学与材料科学学院
催化材料科学湖北省暨国家民委—教育部共建重点实验室,湖北 武汉 430073)

摘 要:在 Tween-80/n-$C_{10}H_{21}OH$/H_2O 体系层状液晶中原位合成出粒径为 5～25 nm 氟化镧纳米粒子,用四球摩擦磨损实验机考察了氟化镧纳米粒子在 Tween-80/n-$C_{10}H_{21}OH$/H_2O 体系层状液晶中的润滑性能,并用 X-射线光电子能谱对其摩擦化学作用机理进行了研究。结果表明,氟化镧纳米粒子能提高 Tween-80/n-$C_{10}H_{21}OH$/H_2O 体系层状液晶的润滑性能,其在摩擦过程中,发生了摩擦化学反应,在摩擦表面生成了化学反应膜。

关键词:氟化镧纳米粒子;原位合成;润滑机理;吐温-80
中图分类号:TB 383 O 611.4 **文献标识码**:A **文章编号**:1672－5425(2009)06－0043－05

近几十年来,纳米粒子受到了广泛的关注。当宏观物体细分为超微颗粒(纳米级)后,显示出许多奇异的特性,其光学、热学、电学、磁学、力学以及化学方面的性质与大块固体相比会有显著的不同,在磁性材料、电子材料、光学材料、高致密度材料的烧结、催化、传感、陶瓷增韧等方面有广阔的应用前景[1~6]。

无机纳米粒子,如氧化钛[7]、氢氧化镧[8]、硼酸镧[9]、硼酸钛[10]、硼酸锌[11]、氧化铁[12]、镍[13]、碳酸钙[14]、氧化锌[15]等被广泛添加到润滑剂中以改善其摩擦学性能。但是,当无机纳米粒子暴露在空气中时,很容易发生氧化和团聚,分散性很差,且合成工艺复杂、费用昂贵,所以应用无机纳米粒子作为润滑剂的添加剂也受到了限制,这些问题得到越来越多研究者的关注[16,17]。

层状液晶是由表面活性剂、助表面活性剂、油等组成的分子有序组合体,可以作为制备纳米微粒的模板[18~20];另一方面,因其层状结构而具有一定的润滑性能。因而在层状液晶中原位合成纳米粒子[21,22],既可以简化纳米粒子的合成工艺、降低生产成本,又能够对层状液晶摩擦学性能起到改善作用。

目前已有研究表明,氟化镧(LaF_3)纳米粒子作为润滑剂添加剂能够大幅提高基础油的承载力和抗磨性[23]。基于此,作者在 Tween-80、n-$C_{10}H_{21}OH$ 和 H_2O 构成的层状液晶体系中合成出 LaF_3 纳米粒子,用 XRD 和 TEM 对其结构进行了表征,用四球摩擦磨损实验机考察了其润滑性能,并对润滑机理进行了研究。

1 实验

1.1 试剂与仪器

Tween-80(>99%,Aldrich),正癸醇、无水乙醇、硝酸镧和氟化钠均为分析纯,液体石蜡为化学纯,水为二次蒸馏水。

59X 型偏振光显微镜,上海光学仪器厂;Tecnai G20 型透射电子显微镜,FEI 公司;D8 型 X-射线衍射仪,Bruker 公司;KQ-100 型超声波清洗器,昆山超声波仪器厂;TDL80-2B 型台式离心机,上海安亭科学仪器厂;MRS-10A 型四球摩擦磨损实验机,济南实验机厂。

1.2 层状液晶单相区域的确定

按不同组成配样,充分振荡混合后,置(25 ± 0.1)℃水浴中恒温 12 h 以上,由偏振光显微镜判断为何种溶致液晶单相。

1.3 氟化镧纳米粒子的制备

在 Tween-80 和正癸醇混合溶剂中,分别逐步滴加 0.3 mol·dm^{-3} 的 NaF 水溶液和 0.1 mol·dm^{-3} 的 $La(NO_3)_3$ 水溶液,制得 Tween-80/n-$C_{10}H_{21}OH$/NaF 体系层状液晶和 Tween-80/n-$C_{10}H_{21}OH$/$La(NO_3)_3$ 体系层状液晶,然后将两种液晶混合,NaF 和

基金项目:湖北省自然科学基金资助项目(2006ABA369),中南民族大学自然科学基金资助项目(YZZ06028)
收稿日期:2009－03－09
作者简介:仝芳(1984－),女,重庆人,硕士研究生,研究方向:功能纳米材料与纳米结构;通讯联系人:唐定国,博士。E-mail:yanghanmin@sina.com。

万方数据

$La(NO_3)_3$在层状液晶的溶剂层中反应,生成白色LaF_3纳米微粒沉淀,取出一定量沉淀用乙醇洗涤,离心,反复操作,充分洗涤,并在超声波清洗器中振荡分散,用于电子显微镜分析;其余不经分离,洗涤,直接进行摩擦学性能测试。

1.4 摩擦磨损实验

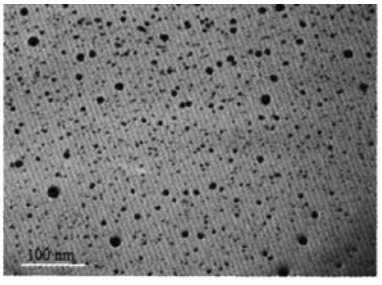
用四球摩擦磨损实验机考察层状液晶及分散有LaF_3纳米粒子的层状液晶的极压抗磨性能。在环境温度为25℃条件下,(1200±10)r·min^{-1}、1800 s对其进行摩擦磨损实验。用读数显微镜测出钢球的磨斑直径,取3次平均值。

1.5 表面分析

将摩擦磨损实验后的钢球在石油醚和丙酮中超声清洗2次,各15 min,然后用PHI-5702型多功能X-射线光电子能谱仪(XPS)进行表面分析。以Mg$K\alpha$线($h\nu$=1253.6 eV)为发射源,功率250 W,通过能量29.35 eV,被测元素电子结合能的精确度为±0.3 eV,以污染碳的C_{1s}结合能284.60 eV作为内标。

2 结果与讨论

2.1 氟化镧纳米粒子在层状液晶中的原位合成、表征及分散稳定性



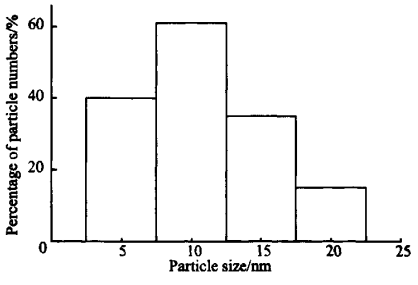


图2 氟化镧纳米粒子的透射电子显微镜图及其粒径分布图

Fig. 2 TEM micrographs of LaF_3 nanoparticles and the corresponding particle size distribution histograms

透射电子显微镜图(图2)表明,LaF_3纳米粒子粒径分布比较均匀,为5～25 nm的类球状颗粒。将LaF_3样品的XRD图谱(图3)与标准图谱比较,各衍射峰的晶面间距d、强度I都一致,由此可推断所得样品为LaF_3纳米粒子。

LaF_3纳米粒子在层状液晶中的分布图见图4。

由图4可见,所析出微粒的大小受到了层状液晶两亲双分子层的限制,所得LaF_3纳米粒子的粒径在纳米级范围内。LaF_3纳米粒子是在层状液晶两亲双分子层之间的溶剂层原位合成的,相互之间碰撞的几率较小,基本上不存在团聚现象,且具有好的分散稳定性。

图1为Tween-80/n-$C_{10}H_{21}OH$/H_2O体系的部分相图。其中实线表示Tween-80/n-$C_{10}H_{21}OH$/H_2O体系的层状液晶区域,虚线分别表示0.3 mol·dm^{-3} NaF水溶液和0.1 mol·dm^{-3} $La(NO_3)_3$水溶液代替组分水形成的液晶区域。

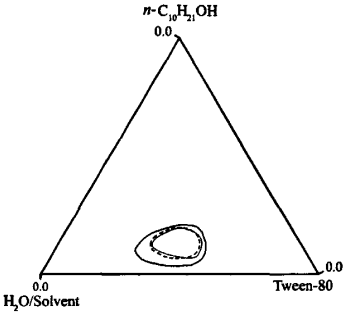


图1 Tween-80/n-$C_{10}H_{21}OH$/H_2O体系层状液晶的部分相图

Fig. 1 Partial phase diagram of Tween-80/n-$C_{10}H_{21}OH$/H_2O system [NaF solution or $La(NO_3)_3$ solution]

由图1可见,NaF和$La(NO_3)_3$的存在降低了层状液晶的稳定性,使得Tween-80/n-$C_{10}H_{21}OH$/H_2O体系的层状液晶区域缩小。

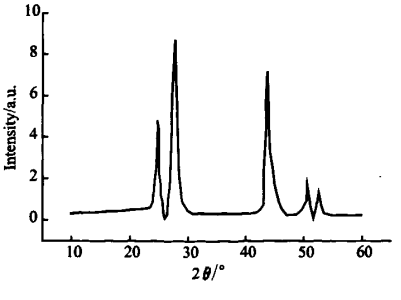


图3 氟化镧纳米粒子的XRD图谱

Fig. 3 X-ray diffraction pattern of LaF_3 nanoparticles

万方数据

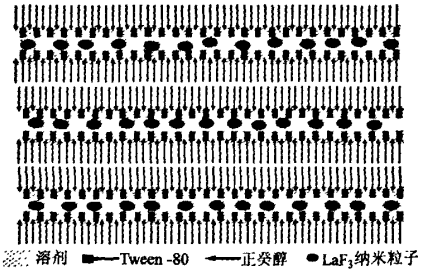


图 4 氟化镧纳米粒子在层状液晶中的分布图

Fig. 4 The distribution of LaF_3 nanoparticles in lamellar liquid crystal

2.2 氟化镧纳米粒子在 Tween-80/n-$C_{10}H_{21}OH/H_2O$ 层状液晶中的润滑性能

LaF_3 纳米粒子与 Tween-80/n-$C_{10}H_{21}OH/H_2O$ 体系层状液晶混合体在不同负荷下钢球的磨斑直径见图 5。

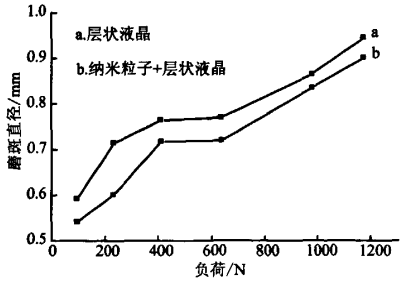


图 5 不同负荷下钢球的磨斑直径变化曲线

Fig. 5 Wear scar diameter curve versus applied load

由图 5 可见,LaF_3 纳米粒子的存在使相同负载下钢球的磨斑直径降低,说明在 Tween-80/n-$C_{10}H_{21}OH/H_2O$ 体系层状液晶中,LaF_3 纳米粒子的存在能够比较有效地提高层状液晶的抗磨性能。LaF_3 纳米粒子与 Tween-80/n-$C_{10}H_{21}OH/H_2O$ 体系层状液晶混合体在不同负荷下的摩擦系数见图 6。

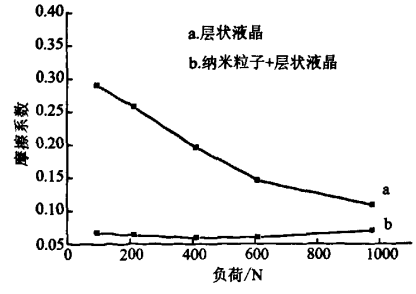


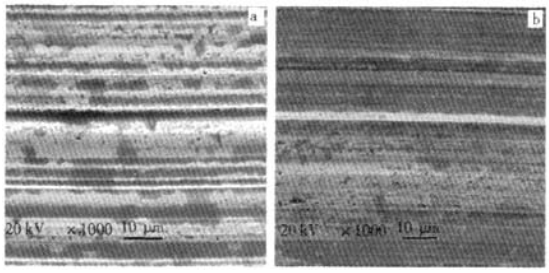
图 6 不同负荷下的摩擦系数变化曲线

Fig. 6 Friction coefficient curve versus applied load

由图 6 可见,LaF_3 纳米粒子的存在提高了层状液晶润滑性能,使各压力下的摩擦系数均降低,并且较稳定,特别是在低负荷下效果更为明显。

2.3 表面分析及 LaF_3 纳米粒子的润滑机理

在四球摩擦磨损实验机上,以钢一钢为摩擦副、负荷为 412 N、转速 1200 r·min^{-1}、时间为 30 min 的条件下,LaF_3 纳米粒子不存在和存在时钢球表面磨损形貌图见图 7。



a. 层状液晶润滑的钢球表面　　b. LaF_3 纳米粒子和层状液晶润滑的钢球表面

图 7 钢球表面磨损形貌图

Fig. 7 Morphologies of the worn surface of steelball

由图 7 可见,不存在 LaF_3 纳米粒子的层状液晶润滑下的钢球表面磨损较为严重,出现大而深的犁沟,擦伤比较严重,磨斑直径比较大(图 7a);而含 LaF_3 纳米粒子的层状液晶润滑下的钢球磨损表面较为光滑平整,擦痕都比较浅,磨斑直径比较小(图 7b)。说明 LaF_3 纳米粒子的存在有效地提高了层状液晶的润滑性能。

用 XPS 分析了在 LaF_3 纳米粒子和层状液晶混合体系润滑下钢球磨痕表面的元素组成和化学状态,着重对磨痕表面的 La 和 F 元素进行了分析,结果见图 8。

由图 8 可见,La 元素 3d 的电子结合能为 835.3 eV,表明在摩擦表面 La 元素以三价镧的形式存在;F 元素 1s 的电子结合能为 684.4 eV,表明 F 元素以氟化物的形式存在于钢球的摩擦表面,由此可推测 LaF_3 纳米粒子经过摩擦,发生了摩擦化学反应,在摩擦表面可能生成了由 La^{3+} 和 F^- 的无机化合物组成的化学反应膜。另外,Tween-80 和正癸醇有机分子吸附在钢表面,起到了减摩抗磨的作用。层状液晶中因存在大量的 Tween-80(>45%)和正癸醇(>10%),它们是两亲分子,极性端可吸附在钢球表面,起到润滑作用;LaF_3 纳米粒子在负荷比较低时,在摩擦副的摩擦表面起到类似滚珠作用;负荷比较高和转速比较高时,可能会在摩擦副的高温接触面融化,起到流体润滑的作用。这

万方数据

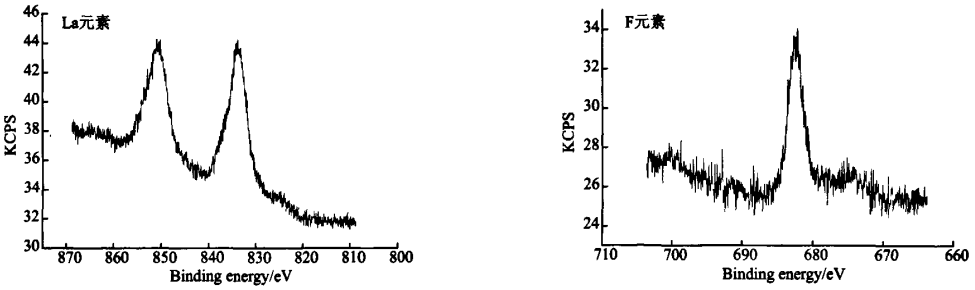


图 8 钢球表面典型元素 XPS 图

Fig. 8 XPS pictures of typical elements in steelball surface

样,生成的无机反应膜与有机吸附膜的协同作用使得 LaF_3 纳米粒子和层状液晶混合体系具有比较优良的润滑性能。

3 结论

在 Tween-80/n-$C_{10}H_{21}OH$/H_2O 层状液晶中可合成平均粒径为 5～25 nm 的 LaF_3 纳米粒子。LaF_3 纳米粒子可提高 Tween-80/n-$C_{10}H_{21}OH$/H_2O 体系层状液晶的润滑性能。LaF_3 纳米粒子在摩擦表面生成了由 La^{3+}、F^- 的无机化合物组成的化学反应膜。无机反应膜与有机吸附膜的协同作用使得 LaF_3 纳米粒子和层状液晶混合体系具有比较优良的润滑性能。

参考文献:

[1] Gittins D I, Bethell D, Schiffrin D J, et al. A nanometre-scale electronic switch consisting of a metal cluster and redox-addressable groups[J]. Nature, 2000, 408(6808): 67-69.

[2] Henglein A. Small-particle research: Physicochemical properties of extremely small colloidal metal and semiconductor particles[J]. Chem Rev, 1989, 89(8):1861-1873.

[3] Whetten R L, Khoury J T, Alvarez M M, et al. Nanocrystal gold molecules[J]. Adv Mater, 1996, 8(5): 428-433.

[4] Lü C L, Cui Z C, Wang Y, et al. Preparation and characterization of ZnS/polymer nanocomposite films with high refractive index [J]. Mater Chem, 2003, 13(9): 2189-2195.

[5] Brust M, Walker M, Bethell D, et al. Synthesis of thiol-derivatised gold nanopartilces in a two-phase liquid-liquid system[J]. J Chem Soc Chem Commun, 1994,16(7): 801-802.

[6] Tian N, Zhou Z Y, Sun S G, et al. Synthesis of tetrahexahedral platinum nanocrystals with high-index facets and high electro-oxidation activity [J]. Science, 2007,316(5825): 732-735.

[7] Hu Z S, Dong J X. Study on antiwear and reducing friction additive of nanometer titanium oxide[J]. Wear, 1998, 216(1): 92-96.

[8] Zhang Z, Liu W, Xue Q. Study on lubricating mechanisms of $La(OH)_3$ nanocluster modified by compound containing nitrogen in liquid paraffin[J]. Wear, 1998, 218(2): 139-144.

[9] Hu Z S, Dong J X, Chen G X, et al. Preparation and tribological properties of nanoparticle lanthanum borate [J]. Wear, 2000, 243(1-2): 43-47.

[10] Hu Z S, Dong J X. Study on antiwear and reducing friction additive of nanometer titanium borate [J]. Wear, 1998, 216(1): 87-91.

[11] Dong J X, Hu Z S. A study of the anti-wear and friction-reducing properties of the lubricant additive, nanometer zinc borate [J]. Tribol Int, 1998, 31(5): 219-223.

[12] Hu Z S, Dong J X, Chen G X. Study on antiwear and reducing friction additive of nanometer ferric oxide [J]. Tribol Int, 1998, 31(7): 355-360.

[13] Qiu S Q, Zhou Z R, Dong J X, et al. Preparation of Ni nanoparticles and evaluation of their tribological performance as potential additives in oils[J]. Tribol, 2001, 123(3): 441-443.

[14] Qiu S Q, Dong J X, Chen G X. Wear and friction behaviour of $CaCO_3$ nanoparticles used as additives in lubricating oils [J]. Lubr Sci, 2000, 12(2): 205-212.

[15] Battez A Hernandez, Rico J E Fernandez, Arias A Navas, et al. The tribological behaviour of ZnO nanoparticles as an additive to PAO_6[J]. Wear, 2006, 261(3-4): 256-263.

[16] Chen S, Liu W M, Yu L G. Preparation of DDP-coated PbS nanoparticles and investigation of the antiwear ability of the prepared nanoparticles as additive in liquid paraffin[J]. Wear, 1998, 218 (2):153-158.

[17] Chen S, Liu W M. Characterization and antiwear ability of non-coated ZnS nanoparticles and DDP-coated ZnS nanoparticles[J]. Mater Res Bull, 2001, 36(1-2): 137-143.

[18] Guo R, Yang J, Friberg S E. Complex lamellar structure of polyoxyethylene 20 sorbitan oleate and a fatty acid/lecithin lamellar liquid crystal [J]. Langmuir, 1996, 12(17): 4286-4291.

[19] Sun Z W, Chen X, Wang L Y, et al. Synthesis of gold nanoplates in lamellar liquid crystal [J]. Colloids and Surface A, 2008, 326 (1-2): 23-28.

[20] Ding Y H, Chen L P, Guo R. Preparation of zinc gluconate nanostructures with different shapes by lamellar liquid crystal template [J]. Colloids and Surface A, 2007, 295 (1-3): 85-90.

万方数据

[21] Yang H M, Yang M, Zhang Y, et al. In situ synthesis and lubrication of PbS nanoparticles in lamellar liquid crystal[J]. Colloid J, 2004, 66(5): 635-641.

[22] Yang H M, Yang M, Guo R. Tribology properties of CdS nanoparticles in situ synthesized in lamellar liquid crystal system of Triton X-100/$C_{10}H_{21}OH/H_2O$ [J]. J Disper Sci Technol, 2005, 26(4): 477-482.

[23] Zhou J F, Wu Z S, Zhang Z J, et al. Study on an antiwear and extreme pressure additive of surface coated LaF_3 nanoparticles in liquid paraffin[J]. Wear, 2001, 249(5-6): 333-337.

In-situ Synthesis and Lubricating Mechanism of LaF_3 Nanoparticles

TONG Fang, YUAN Fang-fang, WU Yong, WU Xian-mian, TANG Ding-guo, YANG Han-min

(Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430073, China)

Abstract: The LaF_3 nanoparticles were prepared in Tween-80/n-$C_{10}H_{21}OH/H_2O$ lamellar liquid crystal. The size of LaF_3 nanoparticles was about 5～25 nm. The friction and wear behaviors of LaF_3 nanoparticles as an additive in lamellar liquid crystal were studied by wear and tear test machine. It had been found that the LaF_3 nanoparticles could improve the lubrication performance of lamellar liquid crystal. The XPS analysis of the worn surfaces indicated that tribochemically reaction film was generated during the friction process.

Keywords: LaF_3 nanoparticles; in-situ synthesis; lubricating mechanism; Tween-80

(上接第 6 页)

[16] Kiel J H A, Edelaar A C S, Prins W, et al. Performance of silica-supported copper oxide sorbents for SO_x/NO_x-removal from flue gas. Ⅱ. Selective catalytic reduction of nitric oxide by ammonia [J]. Appl Catal B: Environ, 1992, 1(1): 41-60.

[17] Curtin T, Regan F O, Deconinck C, et al. The catalytic oxidation of ammonia: Influence of water and sulfur on selectivity to nitrogen over promoted copper oxide/alumina catalysts[J]. Catal Today, 2000, 55(2): 189-195.

[18] Palomares A E, López-Nieto J M, Lázaro F J, et al. Reactivity in the removal of SO_2 and NO_x on Co/Mg/Al mixed oxides derived from hydrotalcites[J]. Appl Catal B: Environ, 1999, 20(4): 257-266.

[19] Van der Wal, Willem J J Kuijpers, Euqene G M Geus, et al. Process for the removal of sulfur dioxide from gases[P]. USP 5 516 498, 1996-05-14.

[20] 侯相林, 高荫本, 陈诵英. 热煤气净化技术的研究进展[J]. 环境科学动态, 1996, (1): 14-16.

[21] 李存儒, 刘世斌. 复合金属氧化物脱硫剂脱除 SO_2 的研究[J]. 燃料化学学报, 1998, 26(4): 381-384.

[22] 阮桂色, 冯先进, 宫为民. 负载型金属氧化物烟气脱硫剂的研究[J]. 矿冶, 2000, 9(1): 99-102.

[23] Hedges S W, Yeh J T. Kinetics of sulfur dioxide uptake on supported cerium oxide sorbents[J]. Environ Prog, 1992, 11(2): 98-103.

Research Progress of Metal Oxide Sorbent/Catalyst for Combined Removing SO_2 and NO_x from Flue Gas

HU Li-song, WANG Yan, LIU Xi-wen, LU Yun-ping

(Key Laboratory for Green Chemical Process of Ministry of Education, School of Environment and Civil Engineering, Wuhan Institute of Technology, Wuhan 430073, China)

Abstract: There is an increasing probability that flue gas cleanup for NO_x removal will be required at some installations in China. Integrated systems that combine control functions in a single process offer a number of advantages for retrofit and new stations. This paper presents studies, prospects of some integrated process for simultaneous removal of SO_2 and NO_x using different metal oxides sorbent/catalyst, and points out some problems during its practical operation.

Keywords: flue gas; metal oxide; combined removal of SO_2 and NO_x

万方数据

氟化镧纳米粒子的原位合成及润滑机理

万方数据 WANFANG DATA 文献链接

作者： 仝芳， 袁芳芳， 吴勇， 吴现棉， 唐定国， 杨汉民， TONG Fang， YUAN Fang-fang， WU Yong， WU Xian-mian， TANG Ding-guo， YANG Han-min

作者单位： 中南民族大学化学与材料科学学院,催化材料科学湖北省暨国家民委-教育部共建重点实验室,湖北,武汉,430073

刊名： 化学与生物工程 ISTIC

英文刊名： CHEMISTRY & BIOENGINEERING

年，卷(期)： 2009，26(6)

被引用次数： 0次

参考文献(23条)

1. Gittins D I. Bethell D. Schiffrin D J A nanometre-scale electronic switch consisting of a metal cluster and redox-addressable groups 2000(6808)

2. Henglein A Small-particle research:Physicochemical properties of extremely small colloidal metal and semiconductor particles 1989(08)

3. Whetten R L. Khoury J T. Alvarez M M Nanocrystal gold molecules 1996(05)

4. Lü C L. Cui Z C. Wang Y Preparation and characterization of ZnS/polymer nanocomposite films with high refractive index 2003(09)

5. Brust M. Walker M. Bethell D Synthesis of thiol-derivatised gold nanopartilces in a two-phase liquid-liquid system 1994(07)

6. Tian N. Zhou Z Y. Sun S G Synthesis of tetrahexahedral platinum nanocrystals with high-index facets and high electro-oxidation activity 2007(5825)

7. Hu Z S. Dong J X Study on antiwear and reducing friction additive of nanometer titanium oxide 1998(01)

8. Zhang Z. Liu W. Xue Q Study on lubricating mechanisms of La(OH)3 nanocluster modified by compound containing nitrogen in liquid paraffin 1998(02)

9. Hu Z S. Dong J X. Chen G X Preparation and tribological properties of nanoparticle lanthanum borate 2000(1-2)

10. Hu Z S. Dong J X Study on antiwear and reducing friction additive of nanometer titanium borate 1998(01)

11. Dong J X. Hu Z S A study of the anti-wear and friction-reducing properties of the lubricant additive,nanometer zinc borate 1998(05)

12. Hu Z S. Dong J X. Chen G X Study on antiwear and reducing friction additive of nanometer ferric oxide 1998(07)

13. Qiu S Q. Zhou Z R. Dong J X Preparation of Ni nanoparticles and evaluation of their tribological performance as potential additives in oils 2001(03)

14. Qiu S Q. Dong J X. Chen G X Wear and friction behaviour of CaCO3 nanoparticles used as additives in lubricating oils 2000(02)

15. Battez A Hernandez. Rico J E Fernandez. Arias A Navas The tribological behaviour of ZnO nanoparticles as an additive to PAO6 2006(3-4)

16. Chen S. Liu W M. Yu L G Preparation of DDP-coated PbS nanoparticles and investigation of the

antiwear ability of the prepared nanoparticles as additive in liquid paraffin 1998(02)

17. Chen S. Liu W M Characterization and antiwear ability of non-coated ZnS nanoparticles and DDP-coated ZnS nanoparticles 2001(1-2)

18. Guo R. Yang J. Friberg S E Complex lamellar structure of polyoxyethylene 20 sorbitan oleate and a fatty acid/lecithin lamellar liquid crystal 1996(17)

19. Sun Z W. Chen X. Wang L Y Synthesis of gold nanoplates in lamellar liquid crystal 2008(1-2)

20. Ding Y H. Chen L P. Guo R Preparation of zinc gluconate nanostructures with different shapes by lamellar liquid crystal template 2007(1-3)

21. Yang H M. Yang M. Zhang Y In situ synthesis and lubrication of PbS nanoparticles in lamellar liquid crystal 2004(05)

22. Yang H M. Yang M. Guo R Tribology properties of CdS nanoparticles in situ synthesized in lamellar liquid crystal system of Triton X-100/C10H21OH/H2O 2005(04)

23. Zhou J F. Wu Z S. Zhang Z J Study on an antiwear and extreme pressure additive of surface coated LaF3 nanoparticles in liquid paraffin 2001(5-6)

本文链接：http://d.g.wanfangdata.com.cn/Periodical_hbhg200906012.aspx
授权使用：沈阳理工大学(sylgdx)，授权号：fdb114a5-e263-4cab-b3c0-9dd20118e3db
下载时间：2010年8月14日