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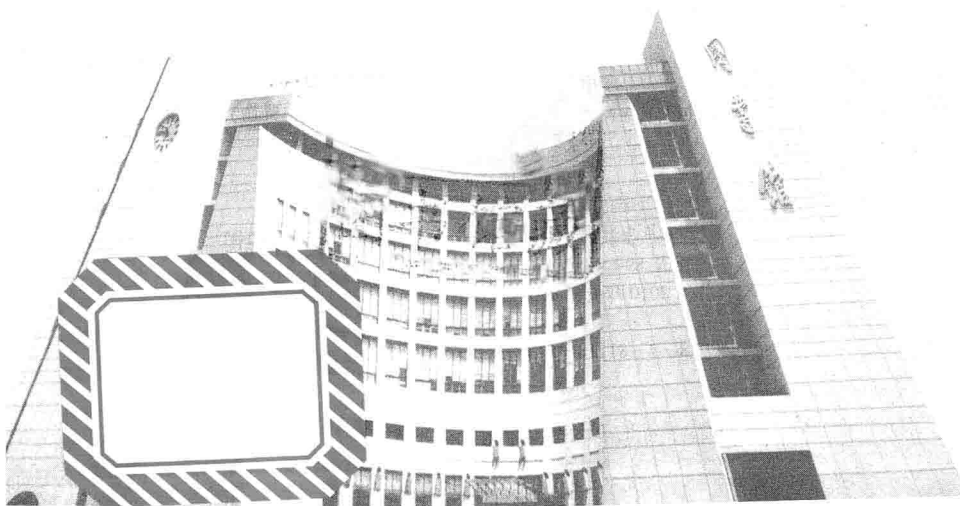

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Candidate: He Ying
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答辩委员会对论文的评语

一维 ZnO 纳米材料是当今纳米技术的研究热点之一。论文就一维 ZnO 纳米结构材料自组装合成技术、表征、形成机理、动力学和应用探索等方面开展了研究工作，该论文的主要研究成果和创新点如下：

1. 首次提出了利用高分子在亚浓溶液状态具有网络限域效应自组装 ZnO 纳米线的研究思想，构建了基于聚合物网络骨架控制 ZnO 纳米点成核和生长模型。

2. 分别采用高分子络合-气相生长法、高分子络合-溶液生长法和高分子络合-烧结法等三种工艺路线，成功地实现了 ZnO 纳米线。其晶体质量与当前文献报道的最佳结果相当。

3. 系统分析了络合材料、工艺参数和生长工艺路线等对一维 ZnO 纳米结构材料、形貌和光学性能的影响规律，并对有关机理开展了研究。

4. 研究了高长径比 ZnO 纳米线的光学特性和场致发射特性，探索了它们在光催化降解脱色、电子场发射和涂料改性等方面的应用，为其潜在的实际应用奠定了基础。

答辩委员会一致认为，该论文的研究成果具有创新性，分析合理。该论文数据可靠。答辩过程中表达清晰，能正确回答问题。反映出作者具有扎实的基础理论和跨学科的专门知识，具有独立科研能力。

答辩委员会表决结果

经答辩委员会表决，全票同意通过贺英同学的博士学位论文答辩，并认为该论文已达到博士学位论文的水平，建议授予该生工学博士学位。

答辩委员会主任：**夏义本**

2006年7月18日

摘　要

一维 ZnO 纳米材料以其新颖的物理、化学和生物学特性以及在纳米器件中的潜在用途成为当今纳米技术的研究热点。而一维纳米结构 ZnO 材料大规模、低成本和简单有效的合成与组装无论从基础研究的角度来说，还是从性能与应用的角度来看，都有着重要的意义。本文全面综述了国内外在一维 ZnO 纳米结构材料的制备、性能及应用方面的研究进展，开展了一维 ZnO 纳米结构材料自组装合成技术、表征、形成机理、动力学和应用探索等方面的研究工作，探讨了一维 ZnO 纳米结构材料的光学性能和光催化性能，得到了如下研究结果：

1. 探索出一种能在各种晶面的硅衬底上自组装取向生长 ZnO 纳米线的新方法。该方法提出了采用离子络合转换机理来制备 ZnO 纳米微晶的研究思想，建立了聚合物网络骨架控制 ZnO 纳米点成核和 ZnO 纳米线生长的新的 ZnO 纳米结构自组装生长模型——聚合物网络限域模型。该模型主要基于络合共价作用驱动 ZnO/高分子（如 PVA）自组装过程的假定，以 PVA 等均聚极性高分子作为配位体并充当自组装载体，通过高分子-金属配位络合反应，将构晶离子（Zn^{2+}）结合在高分子侧链上；而当高分子（PVA）浓度达到亚浓溶液状态时，高分子链相互穿插交叠形成网眼均匀的高分子交联网络，因而具有限制与之作用的纳米微粒尺寸和分布的网络限域效应。在 ZnO 晶体的极性生长特性和聚合物网络限域效应的双重作用下，可制

得分布均匀、尺寸均一、定向性好的 ZnO 纳米线。此技术成功地克服了以往气相法定向生长中通常要求 ZnO 晶体晶面须与衬底表面匹配的限制，使得纳米线的生长对衬底不具有选择性，同时还可以实现在低温环境下的制备。

2. 利用离子络合转换机理和聚合物网络限域生长模型，分别采用高分子络合-气相生长法、高分子络合-溶液生长法和高分子络合-烧结法等三种自组装合成方法，在半导体硅衬底上自组装出了分布均匀、粒度单一性好的取向生长 ZnO 纳米线/棒等一维纳米结构材料。ZnO 纳米线/棒的直径约为 20～150 nm，长度为 0.5～6 μm，具有六方纤锌矿晶体结构，沿[0001]方向取向生长，其晶体质量与当前文献报道的最佳结果相当。

3. 分析研究了所制备 ZnO 纳米结构材料的尺寸、形貌、排列间距和晶体质量的控制影响因素。研究发现，ZnO 纳米结构的自组装生长是由其极性生长特征和高分子网络骨架限域模型决定的，各种生长条件对 ZnO 纳米结构的影响主要是通过控制 ZnO 形核和生长基元在先驱体溶液中的比例来实现的。采用不同的络合材料会影响 ZnO 纳米结构的形貌，利用 PVA、PAM 等高分子材料作为络合剂可以得到均匀直径的 ZnO 纳米线，而利用氨水、柠檬酸钠(TSC)和六亚甲基四胺(HMTA)等小分子材料作为络合剂，则分别得到 ZnO 纳米花、ZnO 纳米片和棒槌状 ZnO 纳米棒；调节所用高分子亚浓溶液浓度，可控制 ZnO 纳米材料的粒径和分布；控制适度弱碱性的络合溶液 pH 值有利于 ZnO 纳米结构沿[0001]取向生长，在弱碱性溶液中易得到长柱状 ZnO 纳米线，而在强碱性溶液中易形成短的 ZnO

纳米棒以至颗粒。此外，分析比较了高分子络合法三种工艺对ZnO晶体形貌的影响，发现采用高分子络合-溶液生长法和高分子络合-烧结法得到的ZnO纳米线柱面光滑均匀，且高分子络合-烧结法制备的纳米线端面更平滑并呈现明显六角柱形结构；而采用高分子络合-气相生长法制得的纳米线呈现不等径生长的层(台阶)状结构，并应用晶体生长界面运动学和界面动力学理论解释了ZnO纳米结构晶体表面台阶的成因。

4. 研究了一维ZnO纳米结构的光致发光性能、紫外吸收性能和光催化性能。典型的ZnO纳米线室温下在325 nm激发光下的光致发光谱主要有两个峰：一个是383 nm附近的近带边强紫外发射峰，半高宽为30.82 nm；另一个是445 nm处较弱的蓝光发射峰或506 nm处的弱绿光发射峰。紫外发射峰与ZnO的带间跃迁相关，主要来自ZnO材料中电子和空穴的直接复合，而蓝-绿光发射峰可能由ZnO中的氧空位或锌填隙等结构缺陷引起。所制备的样品晶体完整性较高，其光学性能与当前文献报道的最佳结果相当。

同ZnO体材料(紫外吸收峰373 nm)相比，所制备的一维ZnO纳米结构材料的紫外吸收峰在～360 nm处，蓝移了～13 nm；且其紫外光吸收性能与粒径大小有关，随着ZnO粒径的减小，紫外吸收峰出现蓝移，呈现出室温量子尺寸效应。

一维ZnO纳米结构材料在太阳光的照射下对染料甲基红具有较好的光催化降解作用，在光照120 min后，对甲基红的降解率几乎可达100%。一维ZnO纳米结构较好的光催化性能，使其能够直接利用太阳光和普通光源来净化环境，降解有毒有机物。

5. 采用差示扫描量热法(DSC)测试了高分子络合-烧结法制备 ZnO 纳米线的结晶曲线，对其结晶动力学进行了研究，推导出结晶动力学方程为：$1-X_t=\exp(-7.475\times10^{-2}t^{1.9})$，并利用热重(TG)测试结果，通过热分解反应，导出了反应动力学方程：$\frac{d\alpha}{dT}=\frac{3.76\times10^{23}}{\phi}e^{-21\,340.8/T}(1-\alpha)^{2.8}$，从而得到了化学反应速度随时间、浓度和温度变化的关系。

6. 采用 ZnO 纳米线/棒作为阴极发射体制作了纳米 ZnO 场发射器件，考察了其电子场发射性能。研究表明，这种 ZnO 纳米结构具有优良的场发射性能，在开启电场为 $2.2\ V\cdot\mu m^{-1}$ 时，可测到 $10\ \mu A\cdot cm^{-2}$ 的发射电流密度，接近目前有关 ZnO 纳米结构场发射报道的最佳结果，可应用于场发射纳米光电子器件。

7. 采用纳米改性涂料技术，首次制备了掺杂 ZnO 纳米线/棒的苯丙乳胶漆改性涂料，研究了掺杂量对改性性能的影响。结果表明，这种由纳米 ZnO 改性的涂料具有良好的耐水性、耐碱性、耐洗刷性和硬度，尤其在杀菌防霉性能方面有所提高，比未掺杂前抗菌性提高 21.2%。当苯丙涂料中纳米 ZnO 的添加量为单体质量的 0.06%时，纳米功能性苯丙涂料的耐水性可提高 40.3%、耐碱性可提高 32.6%、耐洗刷性可提高 18.3%、涂料硬度可提高 47.2%，使涂料综合性能达到最佳。

关键词 一维氧化锌纳米结构，自组装，高分子络合，光致发光，场发射，抗菌性，光催化降解

Abstract

One-dimensional (1D) zinc oxide (ZnO) nanomaterials have received intensive interests due to their novel physical, chemical, and biological properties as well as the potential applications in nanodevices. Large-scale, cost-effective, simple and practical synthesis and assembly of one-dimensional ZnO nanomaterials are of importance for the fundamental research and application. In this thesis, the research progress in the preparation, property and applications of one-dimensional nanomaterials of ZnO was comprehensively reviewed. The self-assembling preparation, characterization, formation mechanism, kinetics and application attempt of 1D ZnO nanostructures were throughly studied. Moreover, their unique photoelectricity and photocatalysis have been discussed. A series of new results are obtained:

1. A novel process was reported for preparing oriented ZnO nanowires on various planes of silicon substrates by using polar polymer (such as PVA) as self-assembling complex medium. Well-distributed and uniform-diameter ZnO nanowires on a (111) or (100) planes of Si substrate have been successfully self-assembled and an ion complex transformation mechanism and polymer grid backbone

localization model have been proposed. The self-assembling growth behavior of ZnO nanowires was well explained by polymer-controlled nucleation and crystal growth based on polymer grid backbone localization model. The key of the method allows us to synthesize highly regular stable nanoscale quantum dots because of PVA containing well-distributed ligand radicals on chain and the polymer chain with winding mesh structure in PVA subconcentrated solution, which limits impacting and growing scale of ZnO nanowires core. The well-oriented ZnO nanowires self-assembling grew on Si substrates by itself polar growth peculiarity and the polymer localized ZnO growth model. This technique has the advantages over the other reported methods because it solved the lattice mismatch problem of the ZnO to silicon, and was more economically feasible.

2. Based on the ion complex transformation mechanism and polymer grid backbone localization model, well-distributed and uniform-diameter ZnO nanowires/nanorods on a Si substrate have been successfully self-assembled by using polymer as the medium via polymer complexation-vapour growth, polymer complexation-liquid growth and polymer complexation-sintering respectively. The ZnO nanowires/nanorods, with diameter in range of from 20 to 150 nm and the length from 0.5 to 6 μm, evenly distribute on Si substrate and possess a hexagonal wurtzite structure which is consistent with the better results reported in the literatures.

3. The influence of preparation condition on the growth

behavior of ZnO nanostructures has been systematically investigated in detail. The investigation on the self-assembling formation mechanism of ZnO nanostructures revealed that the growth of ZnO nanostructures was in well accordance with the polar growth behavior and polymer grid backbone localization model. The effects of process conditions on the ZnO nanostructures were achieved by controlling the ratio of ZnO nuclei to growth units, as well as the sizes of ZnO nuclei in the precursor solution. The ZnO nanostructures can be tailored by using different complexing materials. The regular wire-like, flower-like, flake-like and club-like ZnO nanostructures were obtained by using polymer (such as PVA and PAM), ammonia, trisodium citrate (TSC) and hexamethylene tetraamine (HMTA) as complexing media, respectively. Polymer kind and concentration are the key factors controlling the size and spacing of the 1D ZnO nanostructures. The weak base of the complexing solution at suitable pH value promoted the [0001] oriented growth of ZnO in the self-assembling process thus leading to the ZnO nanorods/nanowires. And the morphology of the ZnO nanocrystal prepared at different experimental conditions is different. It is found that only in polymer complexation-sintering and polymer complexation-liquid growth process, especially the polymer complexation-sintering process, the top of the ZnO nanowires appears smooth and the wires show hexagon columnar structure. Apparently, these nanowires show no layered structure compared to the others produced by

polymer complexation-vapour growth process. The formation of the layered structure ZnO nanorods was explained by crystal growth theory.

4. The optical properties of the 1D ZnO nanostructures were studied by photoluminescence spectroscopy and UV absorption spectroscopy at room temperature. The room temperature PL spectra of the ZnO nanomaterials prepared by polymer complexation process, excited with a wavelength of 325 nm, exhibit a strong UV emission of about 383 nm related to the band to band transition, and a weak blue emission of around 445 nm or a weak green emission of around 506 nm. The near band-edge UV emission might be attributed to a well-known recombination of free excitons, and the blue/green emission might result from the oxygen vacancies and zinc interstitial defects in the ZnO nanomaterials. The bands recombination is dominant in our samples, which indicates the integrity of the ZnO nanocrystal. The optical properties of our samples are consistent with the better results reported in the literatures.

The UV-visible absorption spectra at room temperature show a well-defined exciton band at approximately 360 nm, which are blue-shifted about 13 nm than the absorption band at 373 nm for bulk ZnO. And with decreasing the nanowires diameter, a blue shift of absorbtion peak appears because of the quantum size effect of nano materials.

And these nanomaterials have a photocatalyzed degradation of an organic dye, methyl red, under sunlight

irradiation. The obtained results demonstrated that after about 120 min of irradiation, there is a nearly complete degradation of methyl red at the presence of ZnO, and the degradation percentage is about 100%. It suggested that by using 1D ZnO nanomaterials as photocatalyst, the environment can be purified with the degradation of the poisonous organic waste under sunlight or common light irradiation.

5. The kinetics of the crystallization of ZnO nanowires obtained by using polymer complexation approach and the thermaldecomposition of the complex PAM - Zn^{2+} were investigated by means of differential scanning calorimetry (DSC) and thermogravimetry (TG), and the kinetics equations were $1 - X_t = \exp(-7.475 \times 10^{-2} t^{1.9})$ and $\frac{d\alpha}{dT} = \frac{3.76 \times 10^{23}}{\phi} e^{-21\,340.8/T}(1-\alpha)^{2.8}$, respectively. The relationship between the reaction rate and time, concentration and temperature has been realized. The calculated results are in accordance with the experiments.

6. The application in photoelectric nanodevices of these 1D nanomaterials was investigated experimentally. The field emission of the ZnO nanomaterials obtained by using polymer complexation process has been investigated. It was found that the ZnO nanowires have a good electron field emission property. The turn-on field of the ZnO nanowires is around 2.2 $V \cdot \mu m^{-1}$, which is consistent with the better results