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# Hydrothermal synthesis of CdS nanoparticle/functionalized graphene sheet nanocomposites for visible-light photocatalytic degradation of methyl orange

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## ABSTRACT

CdS nanoparticle/functionalized graphene sheet (CdS NP/FGS) nanocomposites were successfully prepared in a one-step hydrothermal synthesis route. The samples were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, photoluminescence spectroscopy, and Raman spectroscopy. In addition, the photocatalytic performance of CdS NP/FGS composites and pure CdS in the degradation of methyl orange (MO) was examined using visible light. Results show that the addition of FGS can enhance the photocatalytic performance of CdS NP/FGS composites with a maximum degradation efficiency of 98.1% under visible light irradiation as compared with pure CdS (60.1%). This finding can be attributed to three reasons. First is the strong redox ability of CdS in the nanocomposite with smaller crystal size. Second is the increase in specific surface area for more adsorbed MO. Third is the reduction in electron–hole pair recombination with the introduction of FGS. Based on their high photocatalytic activity, the CdS NP/FGS composites can be expected to be a practical visible light photocatalyst.

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## 1. Introduction

Semiconductor quantum dots are quasi-zero-dimensional materials that have gained considerable research interest in the past decade because of their unique size- and shape-dependent properties. Among these materials, CdS is an important II–VI semiconductor because it can be potentially applied in many fields, such as in light-emitting diodes, thin-film transistors, solar cells, photocatalysts, etc. [1–5]. The narrower band gap of CdS (2.42 eV) than that of TiO<sub>2</sub> (3.2 eV) facilitates the utilization of visible light, making CdS a competitive photocatalyst candidate [6,7]. When CdS is irradiated by visible light, electrons located in the valence band can be excited to the conduction band, forming electron–hole pairs that are responsible for photocatalytic activity. However, the rapid recombination of the excited electron–hole pairs is an obstacle limiting the photocatalytic activity of catalysts. One way to delay the recombination of these electron–hole pairs is the hybridization of CdS with other materials, such as conductive polymer films [8],

carbon nanotubes [9], and graphene [10–12], which have promising catalyst applications.

Graphene, as a new two-dimensional carbon nanomaterial, has received increasing attention in recent years because of its outstanding physical and chemical properties and excellent electrocatalytic ability [13–19]. When semiconductor nanoparticles are incorporated into matrices, graphene can remarkably improve the properties of these host materials [20–25]. When graphene is added into CdS, photogenerated electrons of CdS can transfer from the conduction band to graphene by a percolation mechanism, where graphene serves as an electron acceptor and effectively suppresses the electron–hole pair recombination. Moreover, the excellent electron conductivity of graphene can carry out the rapid transport of charge carriers and subsequent effective charge separation. Therefore, the photocatalytic performance of CdS nanoparticle/functionalized graphene sheet (NP/FGS) has attained effective enhancement. Graphene-based nanocomposites clearly exhibit superior performance to pure host materials in practical fabrication. As a new type of nanocomposite material, these nanocomposites have been widely used in some optoelectronic and photodegradation applications.

In this study, we report a novel, facile, one-step synthetic route for CdS NP/FGS nanocomposites with promising photodegradation properties. The synthetic route is illustrated in Scheme 1. The novel route for the fabrication of CdS NP/FGS nanocomposites was

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## Reliable solvothermal growth of diverse heterostructures based on CdS nanowires

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**Keywords:** Heterostructure, Growth Mechanism, Cadmium Sulfide, Semiconductor

**Abstract:** In the present study, the heterostructures of ZnO Nanoparticle (NP)/CdS nanowire (NW), SnO<sub>2</sub>NP/CdS NW, NiS NP/CdS NW, FeS NP/CdS NW, Ag<sub>2</sub>S NP/CdS NW, and Au NP/CdS NW have been successfully fabricated via the two-stage solvothermal process. Field-emission scan electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were adopted to characterize the as-prepared products. The optical properties of the as-obtained heterostructures were separately investigated. New insights into understanding and controlling the synthesis of different NW heterostructures are demonstrated in the reliable solvothermal route. We demonstrate that CdS NWs synthesized for 2h are the bifunctional mediator acting as catalyst or active spot for the growth of NW heterostructures. Furthermore, understanding and controlling this phenomenon is a great asset for the realization of the formation mechanism of the NW heterostructures and opens up new ways toward for construction of other semiconductor heterostructures with novel properties.

### Introduction

Semiconducting nanowire (NW) heterostructures with modulated compositions and/or doping are at the forefront of the current scientific revolution of nanoscience, which is increasingly important in the assembly of electronic and photonic devices. Compared with notable progress in the NW preparation for the homogeneous systems, the desired one-dimensional (1D) heterostructure formation with well-defined interfaces has been lagging far behind in the past few decades.<sup>1</sup> Furthermore, the control over the selective location of metallic/semiconductor domains on the surface of semiconductor nanocrystals (NCs) and the quality of the interface between them are very important issues when considering the possible use of such types of heterostructures in electronic devices. It is well known that there are two types of solution routes in the literature for creating nano-objects with heterostructures. One is the seeded growth.<sup>2-5</sup> Another is the catalyst-assisted growth.<sup>6-10</sup> In the seeded growth, the second materials epitaxially grow on the suitable crystallographic facet offered by seeds, which lead to heterostructure nanomaterials. Therefore, a proper lattice mismatch between the growing crystallographic facets of two different types of nanomaterials and accurately controlling the surface states of seed are required in the seeded growth, which are difficult and limit the wide use of the method.

In catalyst-assisted growth, a metal or alloy with a low melting point is mainly used as a catalyst for growing NWs. Compared with the catalytic growth of semiconductor NWs, the catalytic growth of 1D semiconductor-semiconductor nanoheterostructure is quite rare. Recently, the catalytic fabrication of Cu<sub>2</sub>S-In<sub>2</sub>S<sub>3</sub> heterostructure by using Cu<sub>1.94</sub>S NCs as a catalyst has been reported by the Han *et al.*<sup>11</sup> Xu *et al* demonstrate that Ag<sub>2</sub>S NCs are the catalyst for the preparation of semiconductor-semiconductor heterostructures such as construction of Ag<sub>2</sub>S-ZnS, Ag<sub>2</sub>S-CdS, Ag<sub>2</sub>S-CdS-ZnS.<sup>10</sup> They think that Ag<sub>2</sub>S is a kind of fast ion conductor and Ag cations in Ag<sub>2</sub>S behave like a “fluid”; therefore, although Ag<sub>2</sub>S is a stoichiometric compound, there are a lot of cation vacancies in Ag<sub>2</sub>S NCs.<sup>10,13</sup> This unique feature would enable Ag<sub>2</sub>S NCs potentially to be an excellent

## $\lambda$ -DNA在锥形纳米孔中易位的研究

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**摘要:**纳米孔是目前单分子测序的一项重要技术,文中利用聚焦离子束在氮化硅薄膜上制备了30/60 nm的锥形孔,并通过膜片钳装置对 $\lambda$ -DNA易位的电学信号进行了统计和分析。发现在一定的电场( $>200$  mV)驱动下,DNA分子随着离子电流进入纳米孔,由于体积阻塞效应引起电流的下降。随着偏置电压的增大,阻塞电流也增大,同时易位的速度加快,DNA易位的弛豫时间减少。还可以根据阻塞信号的特点区分不同形貌的易位分子。

**关键词:**纳米孔;DNA;偏置电压;阻塞电流;易位时间

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## Translocation of $\lambda$ -DNA Through Solid-state Nanopore

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**Abstract:** Nanopores have become an important tool for molecule detection at single molecular level. Here, the conical nanopores were fabricated in silicon nitride (SiN) membrane by focused ion beam (FIB) technology. And the translocation of  $\lambda$ -DNA molecules through the prepared nanopores was characterized based on the ionic current obtained by patch clamp amplifier. Under the applied electric field ( $>200$  mV), these macromolecules were driven into the nanopore with the ionic current. A transient current decrease was observed due to the excluded volume of transition DNA in the background electrolyte. With the enhanced of driven voltages, the corresponding blockage current increased while the dwell time was decreased with the increase of the transition speed. Meanwhile, discrete folded types of DNA molecules passing through the pores were detected based on the multiple levels of blockade current signals.

**Key words:** nanopore; DNA; applied voltages; block currents; dwell time

## 0 引言

纳米孔作为一种新型的纳米探测器,是单分子检测的一项重要技术,其低成本高通量的特性成为DNA超快速测序技术实现的关键<sup>[1-3]</sup>。1996年Kasianowicz等人首次报道了 $\alpha$ -溶血素( $\alpha$ -HL)<sup>[4]</sup>蛋白质纳米孔,在电场的作用下驱动单链DNA和RNA穿过了纳米孔,并检测出分子穿过孔产生的阻

塞电流,根据阻塞电流阻塞的时间长度推算出核酸的长度。此方法一经提出就引起了广泛的关注,也是生物膜上各种通道转变为纳米孔的开端。不过,由于生物纳米孔具有化学不稳定性、使用寿命短、大小尺寸不可控等缺点,使得其使用受到限制。随着材料学的发展,固态纳米孔应运而生。2001年, Li等人首次采用了绝缘的 $\text{Si}_3\text{N}_4$ 制备纳米孔<sup>[5]</sup>。相对于生物纳米孔,固态纳米孔就是在固态膜上制备的

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# Recognition Of MicroRNA-binding Sites In Proteins From Sequences Using Laplacian Support Vector Machines With A Hybrid Feature

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**Abstract**—The recognition of microRNA (miRNA)-binding residues in proteins would further enhance our understanding of how miRNAs silence their target genes and some relevant biological processes. Due to the insufficient labeled examples, traditional methods such as SVMs could not work well on such problems. Thus, we propose a semi-supervised learning method, i.e., Laplacian Support Vector Machine (LapSVM) for recognizing miRNA-binding residues in proteins from sequences by making use of both labeled and unlabeled data in this article. A hybrid feature is put forward for coding instances which incorporates evolutionary information of the amino acid sequence and mutual interaction propensities in protein-miRNA complex structures. The results indicate that the LapSVM model receives good performance with a F1 score of  $22.06\pm 0.28\%$  and an AUC (area under the ROC curve) value of  $0.760\pm 0.043$ . A web server called MBindR is built and freely available at <http://cbi.njupt.edu.cn/MBindR/MBindR.htm> for academic usage.

**Keywords**—Laplacian Support Vector Machine; miRNA-binding residues; evolutionary information; mutual interaction propensities

## I. INTRODUCTION

A microRNA (miRNA) is a small non-coding RNA molecule found in plants and animals, which functions in transcriptional and post-transcriptional regulation of gene expression[1]. A microRNA usually results in gene silencing via translational repression or target degradation by pairing to messenger RNA transcripts (mRNAs) of protein-coding genes [2]. MicroRNAs are playing an important role in a range of diseases such as cancer, inherited diseases, heart disease, the nervous system, obesity[3]. Their involvement in many physiological pathways, makes them an excellent target for pharmaceutical drug development and their use as biomarkers or for profiling and screening turns them into a valuable tool for diagnostics[4]. The process of miRNAs for silencing target mRNAs is performed by RISCs (RNA-induced silencing complexes) in which the main catalytic subunit is one of the Argonaute proteins (AGO), and miRNA serves as a template for recognizing specific mRNA sequences[5]. Consequently, the recognition of miRNA-binding residues in RISCs can significantly improve our understanding of how miRNAs silence target genes and many related biological processes, and also can provide further insights into protein

functions and mechanisms of protein - miRNA specific interaction.

Recently, various computational methods have been developed to recognize RNA-binding residues in proteins directly from amino acid sequences [6-10]. As we know, there are many types of RNA molecules with diverse structures and the mechanism of different RNA molecules recognizing their protein partners is not exactly the same. Thus, it is not easy to identify the ground-truth miRNA-binding residues in proteins by the RNA-binding residue prediction methods. Is it possible to develop a computational method specifically for recognizing miRNA-binding residues in proteins?

Currently, there are few available structures of protein-miRNA complexes in the Protein Data Bank (PDB) database[11]. Thus, it is difficult to build an ideal computational model for predicting miRNA-binding residues in proteins due to insufficient labeled examples. So far, there is not a computational method specifically for predicting miRNA-binding residues in proteins from sequences. Meanwhile, we observe that numerous miRNA-binding protein sequences can be obtained from the UniProt database (<http://www.uniprot.org/>)[12]. Such sequences prepare sufficient unlabeled data for constructing classifiers to predict miRNA-binding residues in proteins. Therefore, it is a good choice to use semi-supervised learning methods for building miRNA-binding residues prediction models by making use of both labeled and unlabeled data.

In the present study, we will attempt to build an optimal model for predicting miRNA-binding residues in proteins from sequences. In order to train a perfect prediction model, the following points will be taken into consideration. (1) There are multiple semi-supervised learning algorithms [2, 13-15], and it is important to find a fast and efficient semi-supervised learning algorithm for our task. (2) Nucleic acid molecules can recognize specific structural motifs in proteins. Such motifs are more conserved in evolution, and usually have preferences in physico-chemical properties. Therefore, it is beneficial for predicting miRNA-binding residues in proteins to obtain novel feature descriptors by analyzing preferences of physico-chemical properties in miRNA-binding regions and mining correlations among different properties. (3) The number of miRNA-binding residues in proteins is greatly less than that of non-binding ones. In situations where the minority class is more important, the F1 score is a more appropriate measure,

Corresponding author. E-mail address: [jansen@njupt.edu.cn](mailto:jansen@njupt.edu.cn) (J. Wu). We would like to acknowledge the support by the National Natural Science Foundation of China (No.61203289, No. 61205057, 61305072), Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (No.12KJB520010), the Open Research Fund of State Key Laboratory of Bioelectronics, Southeast University (No.BK212001), China Postdoctoral Science Foundation (No.20110490129, No.2013T60523) and Postdoctoral Science Foundation of Jiangsu Province (No.1102013C).

# Chapter 201

## Research on Construction of Bilingual-Teaching Model Course for Bioinformatics

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**Abstract** Bioinformatics is an important professional basic course in Biomedical Engineering, which tells about the important theoretical basis of using information technology in modern medicine and biology. In order to build a bilingual model curriculum and bring up the comprehensive talents who can make active learning and have creativity and teamwork spirits, we should actively explore the teaching system that suits the bioinformatics bilingual curriculum and train a high-quality teaching team. In addition, we also need to accumulate teaching resources for students' independent learning, create an independent learning environment, expand the opportunities for communicating the results of course reform.

**Keywords** Bilingual teaching · Model curriculum · Curriculum system · Bioinformatics CLC number: Q811

### 201.1 Preface

Twenty-first century is the era of life science, the information age. The bioinformatics has developed rapidly since it was born internationally in 1987. Broadly speaking, bio-informatics is a discipline that uses theories, techniques, methods of mathematical and information science to study the phenomenon of life, organize and analyze the biological data that presents exponential growth [1]. It reveals the biological significance behind the data by acquiring, processing,

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# Fabrication and Characterization of Silicon Nitride Nanopore

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**Abstract**—Nanopores have become an important tool for molecule detection at single molecular level. In our work, the solid nanopore in silicon nitride membranes are fabricated and characterized by experiments. Firstly, the free-standing silicon nitride membranes are designed and etched by delicate techniques. Then, the free-standing membranes are drilled by focus ion beam. A set of nanopores with varied diameters and shapes are fabricated by different acting time of focused ion beam. These nanopores display the high quality of morphologies and electric signals. In addition of DNA, a series of evident block currents appear corresponding to the translocation of single DNA molecule through the pore. The results will shed light on the engineering of nanopore devices for single-molecule sensing.

**Keywords**- nanopore; silicon nitride; focused ion beam; block currents

## I. INTRODUCTION

Over the last decades, nanopores have evolved into powerful and indispensable devices for the investigation of unlabeled molecules at the single-molecule level, which is of obvious interest for the low-cost and high-throughput DNA sequencing applications. It was firstly reported in 1996 by Kasianowicz and co-workers on the biological pore  $\alpha$ -haemolysin that can distinguish single-stranded DNA and double-strand DNA [1]. However, the fixed small size (diameter  $\sim 1.3$  nm) and instability of the  $\alpha$ -haemolysin nanopore limits its application. More recently, artificially fabricated (solid state) nanopores have increasingly gained attention. A variety of techniques have been used to fabricate the pores, including direct drilling with a tightly focused high-energy electron or ion beam [2-4], shrinking of pre-patterned larger openings with a defocused electron or ion beam (“sculpting”) [5-7], and ion-track etching techniques [8-10]. The solid nanopores are good candidates for such biological molecule sensors with the advantage of long-term stability and controllable pore size and shape. The nanopores have been exploited as inexpensive and ultrafast sensors for the detection and discrimination of different biomolecules, including DNA, RNA and proteins.

As nanopore used for analytical tools grows, it is desirable to have simple fabrication methods available that employ machinery and techniques widely accessible. In this

paper, we employed focus ion beam to fabricate nanopore with controllable diameters in a silicon nitride membrane, which is supported by a thick silicon substrate. A set of nanopores with different diameters and shapes are fabricated by focused ion beam. Subsequently, the designed nanopore devices are characterized by scanning electron microscope and patch-clamp technique. The geometry of nanopore can be controlled by the action time of ion beams at the fixed accelerated potential. The larger nanopore are prepared by longer drilling time. Ionic currents through the open nanopore are steady with low noise by the applied voltages. The well-defined nanopore is employed to monitor the transition of nucleic acids. Upon addition of  $\lambda$ -DNA, typical current drops are observed corresponding to the translocation of single DNA molecule across the pore. Translocation events are characterized by current blockage and translocation time. The statistic histograms of current blockage signals have been studied in our work.

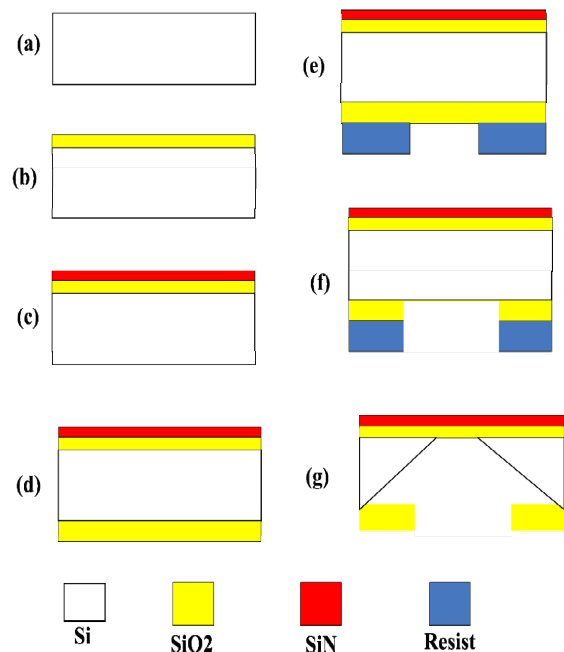


Figure. 1 The fabrication of the free-standing silicon nitride membrane (a) Wash with piranha solution and ultrasonography, (b) Deposition with 300 nm silicon dioxide (SiO<sub>2</sub>), (c) Deposition with 100 nm SiN, (d) Deposition with 500 nm SiN, (e) Lithography, (f) Etching with SiN, (g) Etching with Si.

# 蛋白质在固态纳米孔中的易位行为

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**摘要:** 纳米孔是目前单分子检测的一项重要技术。除了 DNA, 蛋白质也成为纳米孔研究的重点对象。作者以血清蛋白为例, 研究了蛋白质在氮化硅纳米孔中的易位行为, 并对蛋白质的易位事件进行了分析。和 DNA 相比, 蛋白质本身的荷电和结构特性, 使其进入纳米孔的通量较低, 同时, 蛋白质和纳米孔表面存在吸附现象, 减慢了蛋白质在纳米孔中的易位速度。当电压增大时, 蛋白质的易位事件增加, 过孔速度加快, 吸附现象减弱。不过, 在高电压下, 蛋白质在电场力的拉扯下构象发生变化, 出现部分或者全部解折叠。这些结果表明纳米孔提供了一个独特的获得蛋白质结构和功能信息的检测平台, 可为蛋白质相关疾病的诊断和治疗提供技术支持。

**关键词:** 纳米孔; 蛋白质; 蛋白质吸附; 蛋白质解折叠

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## 引言

生物体中广泛存在着纳米尺度的孔道, 蛋白质、离子的跨膜运动是生物体内重要的生命活动, 对于整个生命体的物质交换、能量代谢及信号传导具有重要意义<sup>[1]</sup>。1996 年, Kasianowicz 等人<sup>[2]</sup>首次报道了  $\alpha$ -溶血素( $\alpha$ -HL)蛋白质纳米孔, 并成功检测出 DNA 和 RNA 分子, 开启了纳米孔研究的热潮。在此基础上, 随着微加工技术的进步, 人工纳米孔也成为现实。2001 年, Li 等人<sup>[3]</sup>利用高能离子束在氮化硅薄膜上制备得到纳米级的孔洞。固态纳米孔的稳定性高、尺寸大小可控、重复性好等优势, 大大扩展了纳米孔技术的研究范围。除了 DNA, 蛋白质等生物分子也成为纳米孔单分子检测的重要研究对象。通过有效利用电导脉冲传感的简单原理, 纳米孔在蛋白质检测及结构与功能分析方面具有巨大的潜力。当蛋白质分子进入纳米孔, 阻塞电流变化的强度、频率和周期能够提供蛋白质在溶液中的体积和浓度, 以及构象、表面荷电、结合配体或者酶活性等特性<sup>[4-7]</sup>, 这对于研究蛋白质的结构和功能关系具有重要的意义, 同时, 可更加真实地模拟蛋白质分子在生物体内的跨膜运输, 为人们认识生物体内的物质运输和信号传导提供了有力工具。

不过, 和 DNA 相比, 蛋白质具有非常独特的物理化学特性, 使得纳米孔在蛋白质单分



# 硅烷化修饰的固态纳米孔

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**摘要:** 作为一种重要的单分子检测技术, 纳米孔的表面特性至关重要。作者利用聚焦离子束刻蚀方法制备得到了一系列形貌可控的氮化硅纳米孔, 并对纳米孔进行了表面改性修饰。结果发现, 经过化学处理的氮化硅表面具有大量的硅羟基, 非常利于和硅烷发生反应, 从而在纳米孔表面引入活性基团, 如氨基、正辛基和巯基等。通过对修饰有不同硅烷的纳米孔的表面特性和电导特性的研究发现, 当硅烷分子将氮化硅表面的硅羟基变为其它功能基团时, 材料表面电荷会发生变化, 亲、疏水性也发生变化, 从而导致电渗流的改变, 影响纳米孔的电导。同时, 修饰硅烷分子后, 材料表面的电荷特性发生了改变, 也会导致纳米孔器件的膜电容减小, 介电噪声降低。

**关键词:** 纳米孔; 氮化硅; 硅烷化修饰; 电导

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## 引言

纳米孔作为一种新型的纳米探测器, 是单分子检测的一项重要技术, 以其低成本高通量的特性成为 DNA 超快速测序实现的关键技术之一<sup>[1]</sup>。1996 年, Kasianowicz 等人<sup>[2]</sup>首次报道了  $\alpha$ -溶血素 ( $\alpha$ -HL) 蛋白质纳米孔, 并检测出 DNA 和 RNA 分子过孔产生的阻塞电流。此方法一经提出就引起了广泛的关注, 也是生物膜上各种通道转变为纳米孔的开端。不过, 由于生物纳米孔脆弱, 不稳定, 孔径无法随意控制, 限制了它的广泛应用。在生物纳米孔的基础上, 人们利用微电子加工技术, 将硅/氮化硅基底材料作为衬底, 使用高能离子束或电子束刻蚀出纳米级的孔道, 用于生物分子的检测<sup>[3]</sup>。固态纳米孔具有稳定的物理性质, 能够适用于多变的检测环境, 可以长期、稳定地进行多种生物分子的检测和分析; 其次, 固态纳米孔的尺寸在几纳米到几百纳米的范围内可以控制, 对单/双链 DNA 分子均可以实现检测, 还可用于蛋白质、病毒、纳米颗粒等分子的检测, 大大扩展了纳米孔的研究范围<sup>[4,5]</sup>。

由于固态纳米孔材料表面的特性对于器件的影响很大。在分子检测等应用中, 检测分子往往需要检测界面具有很好的相容性, 同时, 为了提高对于特定分子的检测灵敏度, 控