

Rectangular Coordination Polymer Nanoplates: Large-Scale, Rapid Synthesis and Their Application as a Fluorescent Sensing Platform for DNA Detection

Yingwei Zhang¹, Yonglan Luo¹, Jingqi Tian^{1,2}, Abdullah M. Asiri^{3,4}, Abdulrahman O. Al-Youbi^{3,4}, Xuping Sun^{1,3,4*}

1 State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Changchun, Jilin, People's Republic of China, **2** Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Beijing, People's Republic of China, **3** Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia, **4** Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

Abstract

In this paper, we report on the large-scale, rapid synthesis of uniform rectangular coordination polymer nanoplates (RCPNs) assembled from Cu(II) and 4,4'-bipyridine for the first time. We further demonstrate that such RCPNs can be used as a very effective fluorescent sensing platform for multiple DNA detection with a detection limit as low as 30 pM and a high selectivity down to single-base mismatch. The DNA detection is accomplished by the following two steps: (1) RCPN binds dye-labeled single-stranded DNA (ssDNA) probe, which brings dye and RCPN into close proximity, leading to fluorescence quenching; (2) Specific hybridization of the probe with its target generates a double-stranded DNA (dsDNA) which detaches from RCPN, leading to fluorescence recovery. It suggests that this sensing system can well discriminate complementary and mismatched DNA sequences. The exact mechanism of fluorescence quenching involved is elucidated experimentally and its use in a human blood serum system is also demonstrated successfully.

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* E-mail: sunxp@ciac.jl.cn

Introduction

Simple, fast, cost-effective, and sensitive detection of specific DNA sequences is crucial to molecular diagnostics for pathogen detection and biomedical research. The past years have witnessed the growing importance in developing specific methods for DNA detection, which has various applications in gene expression profiling, clinical disease diagnostics and treatment, fast detection of biological warfare agents, and forensic applications etc [1]. Detecting genetic mutations at the molecular level opens up the possibility of performing reliable disease diagnostics in clinical practice even before any symptom of a disease appears. Polymerase chain reaction (PCR) as a technique for DNA amplification and sequencing has found extensive application in modern biological and medical sciences; however, it has the disadvantages of high cost, risk of contamination, and false-negative results [2,3]. Gene chip is a widely used high-throughput DNA detection technique, but it requires highly precise and expensive instrumentation for fluorescent signal readout and needs sophisticated numerical algorithms to interpret the data [4]. Thus, new DNA detection methods need to be developed. Many efforts have recently been made to develop homogeneous fluorescence assays based on FRET (fluorescence resonance energy transfer) or quenching mechanism for DNA sequence detection [5]. It is shown that nanostructures can be used as a quencher in this assay with the advantage of eliminating the selection issue of fluorophore-quencher because they can quench

dyes of different emission frequencies [5,6]. Until now, we and other researchers have successfully demonstrated that versatile structures can serve as an effective quencher for fluorescence-enhanced DNA detection, including gold nanoparticles [7–11], single-walled carbon nanotubes (SWCNTs) [12], carbon nanoparticles [13], nano-C₆₀ [14], graphene oxide (GO) [15,16], poly(*p*-phenylenediamine) nanobelts (PNs) [17], poly(*m*-phenylenediamine) (PMPD) nanorods [18], Ag@poly(*m*-phenylenediamine) core-shell nanoparticles [19], polyaniline nanofibres [20], poly(*o*-phenylenediamine) colloids [21], supramolecular microparticles [22], etc. However, all the above systems have their inherent drawbacks which limit their practical use. For example, the SWCNT or GO system suffers from the high cost that both SWCNT and graphite powder used for producing GO are usually purchased from some manufacturers and suppliers, and on the other hand, an organic solvent like N,N-dimethylformamide (DMF) is used to disperse SWCNT by a period of several hours sonication or the GO preparation by the Hummer's method is time-consuming and labor-intensive [12,23]. Our PN system has the disadvantage that the nanobelts are tens of micrometers in length and tend to sink in the aqueous solution due to the gravity, causing the problem of stability in detection [17]. An additional limitation is that its discrimination ability toward complementary and single-base mismatched target sequences is very poor.

Coordination polymers (CPs) are a class of organic-inorganic hybrid materials, in which metal ions are linked together by