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6. AUTHORS
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14. ABSTRACT
We have been investigating an electrochemical single-molecule counting experiment called nanopore resistive-pulse sensing. The sensor element is a conically shaped gold nanotube embedded in a thin polymeric membrane. We have been especially interested in counting protein molecules using theses nanotube sensors. This is accomplished by placing the nanotube membrane between two electrolyte solutions, applying a transmembrane potential difference, and measureing the resulting ionic current flowing through the nanopore. In simplest terms,

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Report Title

Final Report for contract Number W911NF-06-1-0515

ABSTRACT

We have been investigating an electrochemical single-molecule counting experiment called nanopore resistive-pulse sensing. The sensor element is a conically shaped gold nanotube embedded in a thin polymeric membrane. We have been especially interested in counting protein molecules using theses nanotube sensors. This is accomplished by placing the nanotube membrane between two electrolyte solutions, applying a transmembrane potential difference, and measureing the resulting ionic current flowing through the nanopore. In simplest terms, when a protein molecule enters and translocates the nanopore, it transiently blocks the ion current, resulting in a downward current pulse. In this way, single-molecule pore-translocation events are counted as individual current pulses. The frequesndy of theses current-pulse events is proportional to the concentration of the analyte, and the identity of the analyte is encoded in the current-pulse signature, as defined by the average magnitude and the duration of the current pulses. See attachment.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Mukaibo, H.; Horne, L.P.; Park, D.; Martin, C.R. "Controlling the Length of Conical Pores Etched in Ion-Tracked Polyethylene Terephthalate (PET) Membranes" Small, 2009,5(21),2474-2479

Kececi,K.; Sexton, L.T.; Buyukserin, F.; Martin, C.R. "Resistive-Pulse Detection of Short Double-Standed DNAs Using a Chemically functionalized conical nanopore Sensor" Nanomedicine, 2008,3,787-796

Sexton, L.T.; Horne, L.P.; Sherrill, S.A.' Bishop, G.W.; Baker, L.A.; Martin, C.R. "Resistive-Pulse Studies of Proteins and Protein/Antibody Complexes Using a Conical Nanotube Sensor" J.Am. Chem. Soc., 2007,129,13144-13152

Xu, F.; Wharton, J.E.; Martin, C.R. "Template Synthesis of Carbon nanotubes with Diamond-Shaped Cross-Sections," Small, 2007,3,1718-1722

Number of Papers published in peer-reviewed journals: 4.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

NAME	PERCENT_SUPPORTED
Lindsay Sexton	0.30
Kaan Kececi	0.30
Lloyd Horne	0.30
FTE Equivalent:	**0.90**
Total Number:	**3**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Lane Baker	0.50
Hitomi Mukaibo	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Charles Martin	0.10	No
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Stephanie Sherrill	0.10
FTE Equivalent:	**0.10**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Dooho Park

Total Number: 1

Names of personnel receiving PHDs

NAME
Lindsay Sexton
Pu Jin

Total Number: 2

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

We have been investigating an electrochemical single-molecule counting experiment called nanopore resistive-pulse sensing. The sensor element is a conically shaped gold nanotube embedded in a thin polymeric membrane. We have been especially interested in counting protein molecules using these nanotube sensors. This is accomplished by placing the nanotube membrane between two electrolyte solutions, applying a transmembrane potential difference, and measuring the resulting ionic current flowing through the nanopore. In simplest terms, when a protein molecule enters and translocates the nanopore, it transiently blocks the ion current, resulting in a downward current pulse. In this way, single-molecule pore-translocation events are counted as individual current pulses. The frequency of these current-pulse events is proportional to the concentration of the analyte, and the identity of the analyte is encoded in the current-pulse signature, as defined by the average magnitude and the duration of the current pulses.

While deceptively simple, there is much we currently do not understand about this experiment. For example, while current pulse durations in the 10s of millisecond range or shorter are most often observed, there are examples of current pulses that last in excess of a second. Such very long-duration pulses cannot be explained in terms of a transport time associated with diffusional or electrophoretic transport of the protein through the nanotube sensing element. Some other factor is determining the magnitude of the pulse duration in this experiment, and in order to probe what this factor might be, we have conducted resistive-pulse experiments on a number of different proteins of differing size and charge. The two key experimental parameters obtained from the resistive-pulse method are the pulse duration, τ, and the pulse amplitude, Δi. Our data show that pulse duration is a more useful metric for exploring the effect of protein size on current-pulse signature. This is because pulse duration varies more dramatically with protein size than does pulse amplitude. Indeed, within experimental error, the pulse amplitudes for the different proteins studied here are indistinguishable.

We observed current pulses with average durations in excess of one second and with standard deviations that increase with the size of the protein. We have proposed a simple model that accounts for these key observations. This model assumes that the protein molecule engages in repeated adsorption/desorption events to/from the nanotube wall as it translocates through the detection zone in the tip of the nanotube sensor.

This model not only accounts for the long pulse duration but also for the triangular shape of the current pulse and the increase in the standard deviation of the pulse duration with increasing protein size. Furthermore, the results of our analyses are in general agreement with results obtained from other investigations of protein adsorption to surfaces. This includes the observations that smaller proteins stick more readily to the surface, but remain adsorbed for shorter times, than larger proteins. In addition, the sticking probabilities calculated from our data, are in general agreement with results obtained from other methods.