Multipass Resistive-Pulse Observations of the Rotational Tumbling of Individual Nanorods

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ABSTRACT: Rotational tumbling of nanorods as they translocate through a glass nanopipet modulates the flux of charge carrying ions, generating a resistive pulse with multiple peaks. The measured times between maxima and minima in the resistive pulse correspond to an average rotation of approximately 90° and can be used to compute the rotational diffusion coefficient, $D_r$. Analytical expressions for the rotational diffusion coefficient ($D_r$) in terms of the nanorod length ($L$) allow the calculation of the rod length. We report experiments in which an individual Au nanorod (nominal length of 77–122 nm) is driven repeatedly through the nanopipet orifice by voltage switching at up to 30 Hz, allowing rapid measurement of $D_r$ and $L$ of individual nanorods with ~15% error. Measured values of $D_r$ between 2000 and 4000 rad2 s−1 for Au nanorods of 77–122 nm length are in good agreement with theoretical predictions.

INTRODUCTION

Anisotropic particles suspended in a fluid will undergo Brownian motion as a combination of translational and rotational motion. It has been previously detailed that single-particle microscopy can monitor the orientations of surface-bound rotating nanorods.1,2 Optical coherence tomography has been implemented to measure a rotational diffusion coefficient from an ensemble of gold nanorods in the bulk of highly viscous solutions.3 Resonance light scattering correlation spectroscopy has been used to measure rapid translational and rotational diffusion of gold nanorods in solution.4 However, these techniques are only applicable to plasmonic nanoparticles.

Resistive-pulse sensing is a real-time and label-free method that has been widely used in characterizing individual entities at the nanoscale.5,6 Based on the Coulter principle,7 a resistive-pulse signal is a momentary drop in current between two electrodes placed either side of an orifice when a particle translocates through the orifice. The magnitude of the pulse is used to determine the particle size, while the duration of translocation is related to charge of the particle.8−10 Recent resistive-pulse studies of rod-shaped nanoparticles have focused upon surface charge,11 distinguishing nanorods from spheres,12 and dynamics of stiff viruses translocating through nanopores under rotational restrictions.13,14 Resistive-pulse amplitude-modulating rotations of larger disk-shaped particles during translocations have been reported in micrometer-sized channels5,16 but these approaches did not relate the tumbling rate with the rotational diffusion coefficient.

In this manuscript, we present resistive-pulse observations of individual Au nanorods tumbling as they translocate through a glass nanopipet giving rise to multiple peaks within a single resistive pulse, illustrated schematically in Figure 1. Multiple measurements are performed on each nanorod, enabled by an automated multipass Coulter counter,17 allowing statistical averaging. We infer that the average time between maxima and minima in the resistive pulse corresponds to a rotation of the nanorod on its long axis of about 90° (Figure 1c), and this time is used to compute the rotational diffusion coefficient ($D_r$) using rotational random walk theory. Analytical expressions for $D_r$ in terms of the nanorod length ($L$) allow estimation of the length of the individual nanorod.15 Resistive-pulse analyses of three different Au nanorods ($L = 77$, 106, 122 nm) are presented to demonstrate the utility of this method and are contrasted with results obtained using spherical Au nanoparticles (67 nm diameter) to further support the hypothesis that the nanorods are tumbling during translocation. The methodology presented here may lead to a better understanding of the rotational motion of rod-like nanostructures in resistive-pulse sensing.

EXPERIMENTAL SECTION

Chemicals and Materials. Nanorod tumbling measurements were performed in a solution of 100 mM NaCl (Fisher) with 10 mM of K$_2$HPO$_4$/KH$_2$PO$_4$ (Macron) and 0.1 vol % Triton X-100 (Sigma-Aldrich) in ultrapure water (Barnstead...
case was connected to a 1 mL air-containing syringe and a pressure gauge (Traceable Pressure Meter, Fisher Scientific). The external solution was left open to atmospheric pressure.

**Cell Configuration and Data Acquisition.** A Daqan Cornerstone Chem-Clamp amplifier connected to a computer through a field programmable gate array data acquisition card (FPGA card, PCIe-7852R, National Instruments) was used to apply potentials and measure currents between two Ag/AgCl electrodes (one within the pipet, as described above, and the second in the external solution, containing the Ag nanoparticles and nanorods). The program running on the FPGA card, which we described in detail previously, acquired both the data and implemented the voltage-switching protocol described herein. All particle/rod trapping experiments were performed inside a Faraday cage at room temperature.

**RESULTS AND DISCUSSION**

Ortega and García de la Torre used bead shell modeling to assess rotational and translational diffusion coefficients of cylindrical rods. Combining the equations in their work, we derive (see Supporting Information, section S-X, for full derivation) that the rotational diffusion coefficient (major axis), $D_\theta$, of a cylindrical rod, can be related to its length, $L$, by:

$$D_\theta = \frac{2k_BT\beta^2}{3\pi\eta_0 f(\beta)L^2}$$  \hspace{1cm} (1)

where $d$ is the rod diameter, $\beta = L/d$ is the aspect ratio of the rod, $\eta_0$ is the viscosity of the solution, $T$ is the absolute temperature, $k_B$ is the Boltzmann constant, and $f(\beta)$ is the following function of the aspect ratio of the rod:

$$f(\beta) = 1.18 + 1.16(\ln \beta + 0.2877)^2 - 0.9729(\ln \beta + 0.2877)^3 + 0.4954(\ln \beta + 0.2877)^4$$  \hspace{1cm} (2)

For a cylindrical nanorod, the rotational diffusion coefficient in the major axis, $D_\theta$, (rad\(^2\)/s), is related to the mean squared angular displacement (radians), also in this axis (see Figure 1b), by:

$$\langle \theta^2 \rangle = 4D_\theta t$$  \hspace{1cm} (3)

By setting $\theta$ equal to $\pi/2$ and rearranging to make $t$ the subject, we arrive at the tumbling duration, $\tau_{90}$ which corresponds to the average time that the nanorod takes to rotate 90° about its major axis.

Figure 2 shows the average time expected for a nanorod to tumble rotate 90° on its long axis, $\tau_{90}$ as a function of $L$, for different aspect ratios, $\beta = L/d$, calculated using eqs 1 and 3. The range shown encompasses the Au nanorod sizes used in the experiments described herein. Translocations of individual nanoparticles in our experimental system typically take 0.5 to 5 ms (full width measured at the base of the peak), while $\tau_{90}$ is in the range of 0.1 to 0.5 ms; thus, we expect a small number of 90° rotations to occur during a single translocation. The above relations suggest that we may be able to infer the rod length from accurate measurements of the average tumbling duration for a single nanorod. However, as we expect only a small number of tumbles during a single translocation, precisely determining $\tau_{90}$ by monitoring tumbling during a single translocation of a nanorod is not possible. In order to improve the precision of the measurement, we have employed a multispas resistive-pulse method in which an individual nanorod is driven back and forth through the nanopipet orifice multiple times.
Figure 3 schematically illustrates the predominant forces acting on a nanorod in a nanopipet under the application of negative (a) and positive (b) potentials (all potentials reported herein are measured vs ground outside the nanopipet) and a negative differential pressure (external pressure > internal pressure). The individual forces sum to give the total force shown by the red arrow, which in this diagram, and the experiments presented herein, drives the nanorod into the pipet while applying a negative potential and conversely drives the nanorod out of the pipet for a positive applied potential. The electroosmotic force (EOF) drives flows outward at a positive applied potential, due to the negative charge on the quartz surface, and is the dominant force on the nanorod, overcoming both the flow induced by applying a negative differential pressure and the electrophoretic force (EPF). Both EPF and EOF are a function of the electric field and are modulated by the applied potential.

In order to improve resolution of resistive-pulse measurements, we recently developed an automated multipass Coulter counter, which is illustrated in Figure 4 for the measurement of nanorods. The direction of the force driving the particle through the nanopipet orifice is reversed upon detection of a translocation, in this case by switching the applied potential between +1 V and −1 V. This protocol, when repeated, causes the particle to change direction and pass back through the orifice, where each translocation through the orifice represents another measurement of the nanorod.

Figure 4b shows a short portion of the current–time trace from a resistive-pulse measurement of a single nanorod. Initially, upon application of −1 V, the nanorod was driven...
into the nanopipet, which generated the resistive pulse labeled (i). The programmable data acquisition card detected this resistive pulse, and after waiting for ∼2 ms to allow the complete entry of the rod into the pipet, automatically switched the applied voltage to +1 V. Upon application of +1 V, the nanorod was then pushed out through the orifice which led to pulse (ii) and the subsequent switching to −1 V, from whence this cycle was repeated. One further cycle resulting in pulses (iii) and (iv) is shown; however, in this work, nanorods were typically measured for several tens of translocations before they were "lost," presumably after randomly diffusing beyond the sphere of influence of the forces. All resistive pulses, shown on an expanded scale in Figure 4a, show a drop in current magnitude; their differing directions are merely a function of the changing polarity of the applied potential (baseline currents ∼−35 nA (i) and (iii) and ∼+35 nA (ii) and (iv)). Notably, in the outward translocations (resistive pulses (ii) and (iv)), we observe multiple peaks, which we will demonstrate arise from tumbling of the nanorod. The four translocations in Figure 4b occur in a period of ∼70 ms, which equates to an average duration of 35 ms per complete cycle (∼30 Hz).

To assess whether tumbling of the nanorod could reasonably explain the observed current fluctuations as it translocated through the nanopipet, we developed a rudimentary finite element model that described the potential distribution and resulting ionic current in the pipet as the nanorod translocated and rotated (see Supporting Information, section S-VII, for full description). From this model the current was calculated as a function of the nanopipet geometry and nanorod shape, position, and orientation. As assessment of the current modulation arising from nanorod rotation was the goal of this modeling, we kept the model as simple as possible. Rather than calculating the forces on the nanorod or attempting to take into account stochastic fluctuations giving rise to Brownian motion, we chose a particle trajectory, which, by design, would not show any randomness. Figure 5a shows a simulated resistive pulse, calculated using the same parameters as the experiment shown in Figure 5b. The simulated response displays multiple peaks of comparable magnitude to those of the experimental data. As we used a simple steady-state model that did not include surface charges, the exact simulated current values are only semiquantitative. Moreover, the particle was translated and rotated at a constant rate, in lieu of a more complicated model that evaluates the forces on nanoparticle to update its position; thus, precise interpretation of the temporal nature of this response, such as the sharpness of the main peak, or the regularity of the local maxima/minima should not be inferred. However, the simulations indicate that the current fluctuations we experimentally observe are semi-quantitatively consistent with nanorod tumbling.

The simulated nanorod rotates through exactly 90° between the local maxima and minima. In the experiments the angular orientation of the rod, which evolves as a random walk caused by microscopic fluctuations, need not have local extremum at precisely 0/90°. We can infer the nanorod orientation from the experimentally measured current. The large current fluctuations between local maxima and minima indicate orientations of approximately 0 and 90° (see Supporting Information, section S-VIII, for detailed simulation results); however, these angular differences could lie anywhere in the region ∼70–110°. The attribution of 90° rotation to the peaks is thus only an approximation, the consequences of which are discussed below.

Figure 5. (a) Simulated and (b) experimental i–t responses corresponding to the outward translocation of a (nominally) 50 × 122 nm (d × L nm) nanorod through a ∼130 nm diameter nanopipet. Details of simulation parameters are available in Supporting Information, section S-VII.

Figure 6 shows (i) scanning electron micrographs (SEM) and (ii) multipass resistive-pulse measurements made with the same nanopipet of (a) nominally 67 nm spherical Au nanoparticles and (b) nominally 50 × 122 nm Au nanorods. All resistive-pulse measurements were made using the same nanopipet (∼130 nm diameter). The 10 current–time pulses correspond to consecutive inward and outward translocations of a single sphere/rod that was trapped using voltage switching. Image analysis of the SEM is presented in section S-II of the Supporting Information. Baseline currents are ∼±35 nA.
respectively, the spherical nanoparticles having a volume that is ∼67% that of the nanorods. Note, SEM measurements reflect the size of the Au core of the nanorods, excluding the thickness of the proprietary methylated polymer shell. Communication with the nanorod manufacturer has established that this film is ∼1 nm thick. Hence, we are introducing minimal error when throughout this work we make the assumption that the dimension of the Au core is interchangeable with the hydrodynamic dimensions, measured by the resistive pulse measurements presented herein.

Figure 6a(ii) shows 10 consecutive resistive pulses that result from a single spherical nanoparticle being driven back and forth through the nanopipet using the voltage-controlled multipass Coulter counter. The pulse durations for inward translocations (∼0.4 ms) are much shorter than outward translocations (∼2.3 ms), which is the result of the negative differential pressure (typically ∼0.05 PSI) we apply during the experiment to increase the likelihood that a particle is recaptured after it leaves the nanopipet. The measured amplitudes of the resistive pulses of inward translocations are smaller than outward translocations, which can be explained, at least in part, due to the filtering effect of the amplifier (filter frequency 10 kHz). The resistive pulses of spherical nanoparticle are asymmetric with a single maximum/minimum, which is consistent with previous reports of spherical particle translocation through a conical nanopore.22,23

Figure 6b(ii), shows 10 consecutive resistive pulses corresponding to consecutive inward and outward translocations of a single 122 nm long Au nanorod. The pulses for the outward translocations of nanorods shown in Figure 6b(ii) are strikingly different to those of spherical nanoparticles, displaying multiple local maxima and minima. Local maxima and minima have been reported using irregularly shaped pores, where the particle essentially “images” the pore.24 In our case, because the spherical nanoparticles show no fluctuations, we can rule out this possibility, and can unambiguously assign the fluctuations to an attribute of the rods. Based on this finding, in addition to the simulation results, we attribute the multiple peaks observed on these resistive pulses to the rotational tumbling of the nanorod and the measured times between maxima and minima in the resistive pulse correspond to an average rotation of 90°. The magnitude of the current blockade for the 122 nm long Au nanorod is slightly larger than that observed for the spherical particles, which is in line with the nanorods having, on average, a larger volume, as noted above.

Nanorod tumbling is stochastic. This is reflected in the position and number of the local maxima and minima changing from one resistive pulse to the next. Only a single peak is visible in some translocations, such as the third outward translocation in Figure 6b(ii). The benefit of measuring the same nanorod multiple times is apparent.

As with the spherical particles, the durations of the inward translocations of the Au nanorod (∼0.6 ms) are also much shorter than the outward translocations (∼4.5 ms), which we again attribute to the application of a negative differential pressure. The short durations of the inward translocations are such that we have been unable to resolve multiple peaks. Thus, the discussion in the following sections focuses solely on the i−t pulses for the outward translocations (in all cases, the corresponding inward translocations are reported in sections S-IV and S-V of the Supporting Information).

Figure 7 presents measurements of Au nanorods with three combinations of different lengths and aspect ratios. The three Au nanorod samples used here are 39 ± 4 nm in diameter and 77 ± 10 nm in length, 50 ± 8 nm in diameter and 122 ± 12 nm in length, 60 ± 8 nm in diameter and 106 ± 10 nm in length, as determined by analysis of SEM images (see Supporting Information, section S-II). Note that, in each case, a wide range of aspect ratios were observed in the SEM images (Figure 7) and, in some cases, for example, particles highlighted by red circles, particles with an aspect ratio around 1 were observed. In Figure 7, each set of resistive pulses show the consecutive outward translocations of a single nanorod, while the corresponding intervening inward translocations are shown in Supporting Information, section S-IV. Since resistive-pulse sensing is based on the exclusion of conductive electrolyte solution by the translocating object, while the corresponding pulse amplitude is approximately proportional to the volume of the translocating object, although its shape and orientation also have an effect. This is reflected in the translocation of the largest nanorod generating the highest pulse amplitudes, and the smallest the lowest. Multiple examples of these data and all others from the main text are presented in section S-IV of the Supporting Information. Control experiments using nominally 67 nm spherical nanoparticles showed only single peaks (see Supporting Information, section S-V).

For each of the series of three different aspect ratio nanorods, we observe multiple peaks during single translocations. While this was typically the case, we occasionally (∼10%) measured a rod that displayed only a single peak over multiple translocations, which we attribute to particles having an aspect ratio close to unity, as noted in the above description of the SEM images; these nearly spherical rods were excluded from further analysis. The tumbling duration for each nanorod, was measured by manually assigning local maxima and minima and calculating the average elapsed time (details showing this are reported in section S-III of the Supporting Information). For the single nominally 39 × 77 nm nanorod measured in Figure 7a, the time between maxima and minima (tR0) is 0.13 ± 0.04 ms (±1σ; average from 18 tumbles in 12 trapping cycles, in which 10 pulses display multiple peaks, while 2 pulses display...
only a single peak). For the data corresponding to the nominally 50 × 122 nm nanorod shown in Figure 7b, the time of \( t_\text{avg} \) is 0.32 ± 0.11 ms (±1σ; average from 6 tumbles in 7 trapping cycles, in which 4 pulses display multiple peaks, while 3 pulses display only a single peak). And for the nominally 60 × 106 nm nanorod data shown in Figure 7c, \( t_\text{avg} \) is 0.40 ± 0.15 ms (±1σ; average from 8 tumbles in 7 trapping cycles, in which 6 pulses display multiple peaks, while 1 pulse displays only a single peak). We use eq 3 to estimate the rotational diffusion coefficients \( D_r \) of these Au nanorods as (a) 4.7±(±2.1) × 10^3 rad^2 s\(^{-1}\), (b) 1.9±(±1.0) × 10^3 rad^2 s\(^{-1}\), and (c) 1.5±(±0.9) × 10^3 rad^2 s\(^{-1}\), from which the lengths of these Au nanorods can be further calculated by eq 1 as (a) 77 ± 9, (b) 113 ± 15, and (c) 106 ± 15 nm (±1σ).

It is apparent from the \( i-t \) traces in Figure 7 that the nominally 50 × 122 nm (b) rods give proportionally the greatest current difference between maxima and minima. These rods have the greatest aspect ratio of any of the rods measured (\( \beta = 122/50 = 2.44 \)). However, the next largest fluctuations are observed in the nominally 60 × 106 nm nanorods (c), which display the lowest aspect ratio (\( \beta = 106/60 = 1.77 \)). This complex relation between the magnitude of current fluctuations due to tumbling and the particle geometry mirrors that which was found through finite element simulations (reported in detail in section S-VIII of the Supporting Information).

From the values of \( t_\text{avg} \) measured for these particles, we used eq 1 to evaluate the length of the nanorod. Note, for this conversion we have used the value of the aspect ratio, \( \beta \), that was measured from SEM; thus, we are implicitly assuming that the shapes within a single batch are all geometrically similar, in the formal sense.

The resistive-pulse data presented in Figure 7 were from individual nanorods coming from each of the polydisperse samples. From the average tumbling time of each rod we were able to estimate its length. The data presented in Figure 8 extend this result to multiple particles from each sample. It presents the mean size (points) and distribution (error bars represent ±1 std dev) of each sample calculated by two different methods. The abscissa represents the length as calculated by SEM, \( L_\text{SEM} \) (~50 particles per sample). The ordinate was derived by applying the resistive-pulse based method, described in the preceding section, to estimate the nanorod length (10 nanorods per sample). The lengths from resistive-pulse sensing, \( L_\text{RPS} \), of 81 ± 9, 96 ± 13, and 110 ± 12 nm (\( D_r = 3.9(\pm1.7) \times 10^3 \) rad^2 s\(^{-1}\), 2.0(±1.2) × 10^3 rad^2 s\(^{-1}\), and 2.0(±0.9) × 10^3 rad^2 s\(^{-1}\)), respectively) (±1σ) compare favorably with the lengths assessed by SEM of 77 ± 10 nm, 106 ± 10 nm, 122 ± 12 nm (±1σ), suggesting that we may use resistive-pulse assessment of tumbling times as a method to infer the length of nanorods.

Perfect agreement between the two methods of assessing the nanorod length would see all points lying on the line \( L_\text{RPS} = L_\text{SEM} \) (red dashed line). The discrepancy between the two methods may come from a number of sources. First, our technique has some inherent biases. Short tumbles (~0.1 ms) will be elongated by the filtering (10 kHz). Longer tumbles have the potential to be ignored, either through not completing a full 90° rotation during the translocation or through tumbling so slowly that it is impossible to reliably discriminate the current modulations due to particle rotation superimposed upon the canonical resistive pulse. Second, while we can unambiguously attribute the local extrema to nanorod rotation, we cannot be sure that every local extremum represents the particle rotating between exactly 0 and 90°. Instead they reflect a particle rotationally diffusing to an angle close to one of these values before random fluctuations cause it to move away. The proportionality of eqs 2 and 3 mean that small inaccuracies in the angle do not cause drastic changes in the calculated rod length. For example, if the angle was only 70°, then it would predict that the rod was (70/90)^2 × 1.18 longer. Furthermore, the conversion from tumbling time to rod length using eq 1 makes the geometric assumption of rods being flattened cylinders, to which we added the assumption that all particles within a sample have the same aspect ratio. While the electron microscopy in Figure 7 suggests that the 39 × 77 nm rod have relatively flat ends, the other samples appear to have faceted ends. A faceted rod would be expected to tumble more quickly than a nonfaceted rod that has the same dimensions,28 which could lead to an underestimation of its length. The variability in the aspect ratios will also lead to some broadening of the derived distribution.

Table 1 summarizes values of \( L_\text{RPS} \) and \( D_r \) for the three Au nanorods measured by resistive-pulse analyses and compares these values to \( L_\text{SEM} \) and theoretical predictions of \( D_r \) computed from eqs 1 and 2 (using SEM measured values of the particle dimensions). Inspection of these values indicates that the resistive-pulse method provides an accurate and precise means of measuring rotational dynamics and lengths of nanoscale particles.
CONCLUSIONS

In this work we have demonstrated that, in contrast to spherical particles, nanorods translocating through a conical pore display multiple extrema in their current blockade. Using finite element modeling, we showed that one may attribute these modulations to the rotational tumbling of the nanorod. By forcing a single nanorod to translocate back and forth through a nanopipet we could assess the average duration of tumbling of an individual nanorod. Furthermore, we showed that lengths derived from these tumbling durations correlate well with lengths calculated ex situ by electron microscopy. In contrast with most resistive-pulse measurements, which are based on the amplitude of the current, the measurements of rod length that we have presented do not involve a calibration. While the amplitude of the current modulations will vary between pipet sizes, the tumbling times should remain constant as long as the pipet walls do not influence the rod’s motion.

The results presented here suggest that measurement of tumbling frequency during translocation might have applications in characterizing the length and possibly the aspect ratio of rod-shaped nanoparticles. Rod-shaped organic nanostructures are important biologically and synthetically as viruses, micelles, microemulsions, and polymers. Rod-shaped metallic and semiconductor nanoparticles exhibit unique optical, electronic and catalytic properties. Their anisotropic shape allows unique tunability of these properties, making optical, electronic and catalytic properties. Their anisotropic metallic and semiconductor nanoparticles exhibit unique et al. Alternatively, if the cone angle of the pore can be conceivably be achieved in two ways. One might push the potential should generate a slightly more potent potential well increasing the number of translocations or the number of resolution is a function of how many tumbles we observe, which should be a function of the applied field; a higher electric potential should generate a slightly more potent potential well to pull the rod back into the particle. The latter could conceivably be achieved in two ways. One might push the particle out of the pipet with a lower force, prolonging the duration of its exit, as we previously demonstrated in German advances in synthetic control over absolute dimensions and aspect ratio and postsynthesis purification, the monodispersity of plasmonic nanorods is far from ideal. This highlights the need for nonensemble averaged characterization methods.

We anticipate that, in the future, the resolution of this technique might be improved in a number of ways. As resolution is a function of how many tumbles we observe, increasing the number of translocations or the number of tumbles per translocation would both be beneficial. The former should be attainable by increasing the probability of recapture, which should be a function of the applied field; a higher electric potential should generate a slightly more potent potential well to pull the rod back into the particle. Alternatively, if the cone angle of the pore can be decreased then the sensing zone (the region where some current blockade is observed) should extend further down the pipet, which would encompass a longer observation window per translocation. This would have the additional benefit that the canonical response of the pipet would vary more slowly, which would allow one to resolve lower current modulations. A pathological example of minimizing the angle is reported by Golibersuch et al., who studied the tumbling of a human erythrocyte (typically 6–8 μm diameter) in a cylindrical pore. For example, assuming measurements are performed at a similar frequency and with a similar variance as those reported in this work, one could resolve the nanorod length to 5% (99.7% confidence interval) by measuring ~90 tumbles; this would take ~3 s per nanorod (see Supporting Information, section S-XI), for details of this calculation.

While this work studied Au nanorod tumbling, the method is not limited by the composition of the particle, as the electroosmotic flow, which drives the nanorod in and out of the pipet, is a consequence of the negative charge of pipet surface and is independent of the charge/conductivity of the particle. For example, we previously demonstrated multipass measurements on polystyrene nanospheres. We anticipate some restrictions on the aspect ratios of the rod-like particles that one might assess with this technique. Nanorods with an aspect ratio approaching unity show smaller modulations in current with their rotation, which would represent a challenge in resolving the extrema above the noise. Note, while small fluctuations are also observed for rods that are small relative to the size of the pore, this should by easy to ameliorate by tailoring the pore size. The size of the pipet has to be larger than the rod length to allow a 90° rotation. For high aspect ratio rods the percentage blockade will be small and the signal-to-noise ratio will be low, which will eventually preclude their measurement. A pore with a diameter smaller than the rod length could be used to measure these rods; however, the interpretation of the resultant data would necessarily be rather different.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b02018.

A scanning electron micrograph of a typical nanopipet and image analysis of nanoparticles and nanorods using scanning electron micrographs to determine their size distributions are provided. A detailed description and examples of measuring tumbling duration are included. Additional current–time traces of additional rods and particles, analysis of the distribution of tumbling durations and computed lengths for individual nanorods are shown. A detailed description of simulation model is provided and simulation results for tumbling nanorods are discussed as well. A full derivation of eq 1 is provided (PDF).

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Notes

The authors declare the following competing financial interest: S.R.G. is an employee of Revalesio Corporation.

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