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Communication

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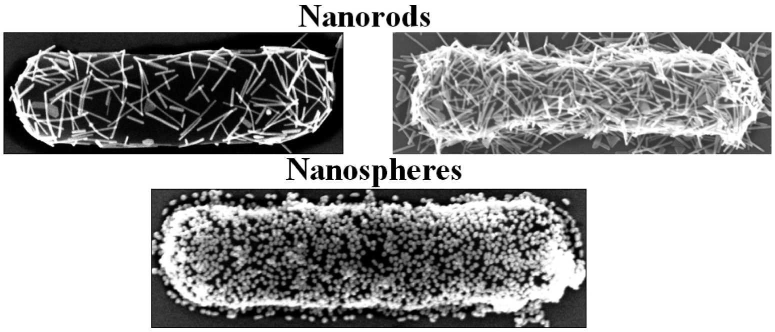

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Deposition of CTAB-Terminated Nanorods on Bacteria to Form Highly Conducting Hybrid Systems

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Interaction of nanoparticles with biological systems ranging from biomolecules to biological cells is of importance for a range of applications, such as high-resolution biomedical imaging,[1] gene sequencing for molecular diagnostics,[2] and sensitive electronic devices.[3] In this report, we demonstrate that positively charged cetyltrimethylammonium bromide (CTAB), which is a stabilizing agent used to synthesize different metal nanoshapes[4−7] (such as rods, spheres, cubes, prisms, stars, and hexagons), is an effective nanoparticle coating for self-assembling an electrically percolating monolayer of different nanoshapes on gram-positive bacterium, such as *Bacillus cereus*. The versatility of CTAB is especially realized for deposition of nanorods, where we observe 4 orders of magnitude larger conductivity compared to that of nanospheres at 3 times smaller area coverage. For the deposition on a "physical surface", the rods do not form electrically percolating channels.[8] Formation of such a percolating−conducting network on bacterium is attributed to high adhesion that overcomes steric interaction (responsible for liquid-crystalline order (see Figure 1a)), leading to random orientation (see Figure 2a). Furthermore, the strong adhesion (evidenced by conformal deposition of a rod causing bending) lowers the contact resistance, leading to 10^4 increase in conductivity at 13.5% area coverage compared to spheres with 41% area coverage (see Figure 3). This high conductivity is achieved well below the percolation threshold for random structure at 45% area coverage in two dimensions.[9] With only $\sim$10% of bacterium surface covered, the microorganism may remain alive for a time longer than that for >40% coverage systems with nanosphere deposition.[10] While CTAB alone is toxic to cells, CTAB-coated nanoparticles are nontoxic.[11] Electronic coupling between nanorod monolayers with microorganisms can open the possibility of novel hybrid devices utilizing the machinery of the biological system.

Bacillus cereus (ATCC 21634), a gram-positive bacteria of size $\sim$3−4 μm, with highly negatively charged teichoic acid brushes on its surface, is deposited on silica substrate by a method explained in the Supporting Information. CTAB-coated Au nanospheres and nanorods are prepared in an aqueous solution at pH 4.5 and 6, respectively, by a seed-mediated growth process also described in the Supporting Information. CTAB forms a bilayer on the nanoparticles, and particles are always positively charged independent of pH (details in Supporting Information). From TEM images, the estimated diameters (D) for rods and spheres are $\sim$25 and 45 nm, respectively. The nominal length, l, of the rods from FESEM is 400 nm. The nanospheres and nanorods (zeta potential +48 to +71 mV) were deposited by exposing the bacterial substrate to the nanoparticle solutions for only 15 min.

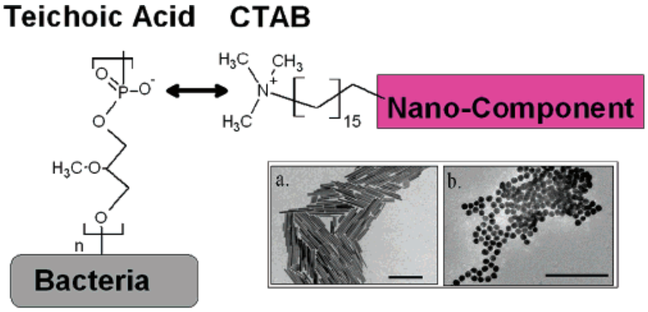

Figure 1. Electrostatic deposition of nanospheres and nanorods is accomplished by capping the nanocomponent with CTAB that electrostatically binds to the teichoic acid brush on the gram-positive bacterial surface. Insets show the TEM images of (a) nanorods and (b) nanospheres. Bar size = 500 nm.

As schematically shown in Figure 1, the nanoparticle deposition is driven by attractive electrostatic interaction between the negatively charged teichoic acid on the bacteria[10] and the positively charged CTAB molecules on the Au nanoparticle surface. The figure also shows the TEM images of nanorods and nanospheres. Figure 2 shows the resultant morphology indicating three features. Figure 2a indicates that nanorods in full contact *bend* under the electrostatic attraction to conform to the bacteria surface. Second, primarily at the edges, the rods are partially attached and tend to stick out of the surface. As seen in the inset of Figure 2a-1, this nonconformal deposition becomes more prevalent at high coverage because the available contiguous space for deposition is limited and becomes less than the length of the rod, making conformal deposition difficult. Third, the deposition of rods on the bacteria is percolating, while on the physical surface (see Figure 2a-2) it is not. For the conformal deposition, where the Au nanorods with modulus 70 GPa[12] bend around the bacteria of a nominal diameter of $\sim$1 μm, the adhesion force due to electrostatic interaction is at least 0.038 N/m or a total force of $\sim$15 nN. The force is comparable to the electrostatic force between positively charged poly-L-lysine monolayers and negatively charged silica microspheres.[13] If the subtended angle of contact is 2α along the curvature, the ratio of rod to microsphere contact area is $\sim 10^{-4}$ for $\alpha \sim 0.05$ rads. Therefore, the force per unit area between nanorods and bacteria is over 1000-fold higher than that between poly-L-lysine monolayers and microsphere.[13]

The current (I) versus applied voltage (V) measurements were made on both nanorod and nanosphere monolayers on bacterial bridges spanning between gold electrodes 7 μm apart. About three bacteria make a bridge, and a typical device has 10−15 bridges. The measurements showed ohmic behavior, as shown in Figure 3. In contrast to poly-L-lysine-coated Au nanoparticles (pH $\sim$ 7) that took 4−8 h deposition to form a percolating network, CTAB-terminated nanoparticles form a percolating monolayer in only 15 min. This is perhaps due to charge compensation of amine groups on poly-L-lysine when they are coated on negatively charged nanoparticles. Table in the inset of Figure 3 shows the coverage

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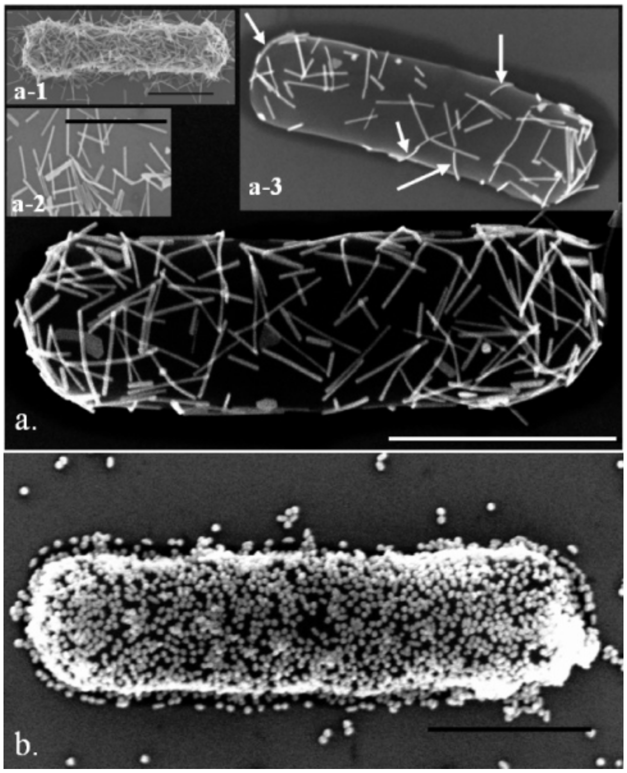
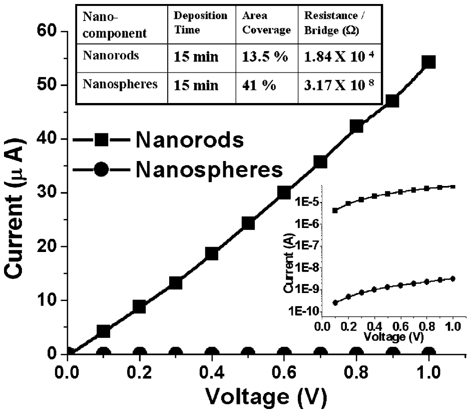


Figure 2. Nanoparticle deposition on bacteria. (a) Percolating monolayer of nanorods (25 nm in diameter and 400 nm long) is formed in a deposition time of 15 min. Nanorods sticking out at the edge of bacteria and conformally deposited on the bacteria can be seen. Inset (a-1) shows deposition on bacteria for 10 h. Deposition chemistry is identical to the 15 min deposition. The inset (a-2) shows deposition of nanorods on a flat silica surface for 10 h after sequential monolayer deposition of poly(allylamine hydrochloride) (PAH) and poly(sulfonate styrene) (PSS). Inset (a-3) shows low-density nanorod deposition. The arrows indicate bent rods. (b) Nanospheres (45 nm diameter) on bacteria after 15 min deposition. All the bars are 1 μm.



Nano-component	Deposition Time	Area Coverage	Resistance / Bridge (Ω)
Nanorods	15 min	13.5 %	1.84×10^{4}
Nanospheres	15 min	41 %	3.17×10^{8}

Figure 3. Current (I) versus voltage (V) measurements of nanorod and nanosphere monolayer on bacteria. The currents are normalized to a single bacteria bridge. The table in the inset shows the corresponding resistance and area coverage of the two nanocomponents. The process and deposition time is identical to conditions in Figure 2. The second inset shows the log-scale plot of the same $I-V$ characteristics.

and conductivity data for the two monolayers. Analogous to surfactant-stabilized conducting polymer in insulating polymer matrix,[14,15] the significantly high conductivity in the nanorod monolayer well below the percolation threshold of 45% area coverage for two-dimensional "random" structure[9] is attributed to the high radius of gyration of the nanorod cluster due to their random orientation. The high conductivity in nanorods compared to that in nanospheres, as seen in the Figure 3 table, could be partly attributed to the fewer number of tunnel junctions in the nanorod network. Assuming random orientation of the rods, the orientation order parameter is $2\langle\cos(\theta)\rangle^2 - 1 = 0$, where θ is the angle between the long axes of the rod and the bacteria.[16] Thus, the average projected length along the bacteria axis is $\sim 400/\sqrt{2}$, leading to $\sim$7-fold fewer tunnel junctions in the shortest percolating cluster for rods compared to spheres. However, this is not sufficient to explain the 4 orders of magnitude larger conductance. We attribute the high conductivity to low contact resistance that could occur due to high rod/bacteria adhesion that presses the rods against each other as they randomly overlay to form the monolayer structure. Furthermore, the contact resistance of the nanorods to the interconnection pads is also lower compared to that of nanospheres for similar reasons.

In this report, we have shown that CTAB, which is an effective surfactant for synthesizing a variety of shapes of nanoparticles, is also an effective capping agent for deposition of nanoscale components on gram-positive bacteria. The strong electrostatic interaction between teichoic acid and CTAB coating on nanorods results in bending of the nanorods and a 4-order enhancement in conductivity compared to nanospheres. This high conductivity at only $\sim$10% coverage (which is well below the percolation threshold of 45%) opens the possibility of fabricating electronic circuitry on bacteria without suffocating the microorganism.

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Supporting Information Available: Nanorod and nanosphere solution preparation; nanoparticle deposition on bacteria. This material is available free of charge via the Internet at http://pubs.acs.org.

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