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Direct Imaging of the Percolation Network in a Three-Dimensional Disordered Conductor-Insulator Composite

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We have directly imaged the percolation network at the surface of a three-dimensional carbon-black–polymer composite using an electric force microscope. At intermediate length scales the conductive area exposed at the surface increases with surface area according to a power law corresponding to a three-dimensional infinite cluster of fractal dimension $D = 2.6 \pm 0.1$. This value is in good agreement with the scaling theory prediction, $D = 2.53$. At large length scales the behavior is homogenous with the classical exponent $D = 3$.

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Disordered conductor-insulator composites have interesting and incompletely understood structural and transport properties [1]. Some of these properties have important practical applications [2]. Until now, the microscopic structure of the percolation network in these systems has been experimentally inaccessible. This Letter reports the direct observation of the percolation network in a three-dimensional disordered conductor-insulator composite. This is accomplished using a novel scanning probe microscopy technique aimed at mapping conductive pathways in materials. Quantitative analysis of the images gives estimates of the fractal dimension D and the correlation length ξ of the infinite cluster. Previously, scanning probe potentiometries [3,4] were used to examine electrostatic forces on surfaces, though this work was limited to metallic and semiconductor systems and done at lower resolution.

Scanning probe microscopies have attracted much attention recently due to their ability to image atoms and molecules directly through detection of short-range repulsive forces [5,6]. By moving the tip several nanometers away from the sample, long range attractive forces, such as electrostatic forces, can also be detected [3,4,7,8]. Electric force microscopy (EFM) is a type of scanning probe microscopy that measures electric field gradients near the surface of a sample using a sharp conductive tip. The grounded tip measures these gradients by being oscillated near its resonant frequency. The effective spring constant of the tip is altered as it encounters a force gradient from the electric field, changing the cantilever's resonant frequency. This change is monitored, producing a map of the strength of the electric field gradients. The EFM mode produces two images, one of topography and the other of electric field gradients, through the "lift-mode" technique. In this technique, a line is scanned to give topography; a second pass is made over the same line a prescribed distance above the topography to image the electric force gradients. This ensures that topography will not affect the electric force image. The surface features were imaged in the "tapping mode," where a tip intermittently contacts the sample surface and oscillates with sufficient amplitude to prevent the tip from being trapped by adhesive or frictional forces.

The samples are composed of commercial carbon-black and polymer. The carbon-black resistivity is of order 10^{-2} Ω cm and the polymer resistivity is of order 10^{18} Ω cm. The carbon-black consists of 200 nm mean diameter aggregates composed of smaller fused semispherical particles of 80 nm mean diameter [9]. The polymer is high density polyethylene. The sample fabrication and characterization procedures have been described elsewhere [10].

A commercial Digital Instruments Nanoscope Multimode AFM with Phase Extender Box (for EFM imaging) was used for imaging the composites. Tips were metal coated and made of single-crystal silicon with a 5 nm radius of curvature. The composite samples were attached onto metal substrates using conductive silver paint. Measurements with a voltmeter verified good electrical contact between the top of the composite samples and the metal substrate. The samples were held at 3 V relative to the conductive tip and imaged at ambient conditions.

Figure 1 shows (a) a tapping mode atomic force microscope (TMAFM) and (b) an electric force microscope (EFM) image of a 20 μm × 20 μm region of a composite sample with a carbon-black concentration (volume fraction) of 0.1978. The TMAFM image is relatively featureless, showing only surface roughness and impressions from the mold used to form the composite sample. The EFM image is dramatically different and clearly shows contrast arising from conductive and insulating regions of the surface. These images are representative of the images obtained on different trials using different tips. Conductive regions appear as darker areas while insulating regions appear as lighter areas. The conductive regions are the fraction of carbon-black aggregates at the surface which are part of the infinite cluster. The insulating regions are the polymer and the fraction of carbon-black

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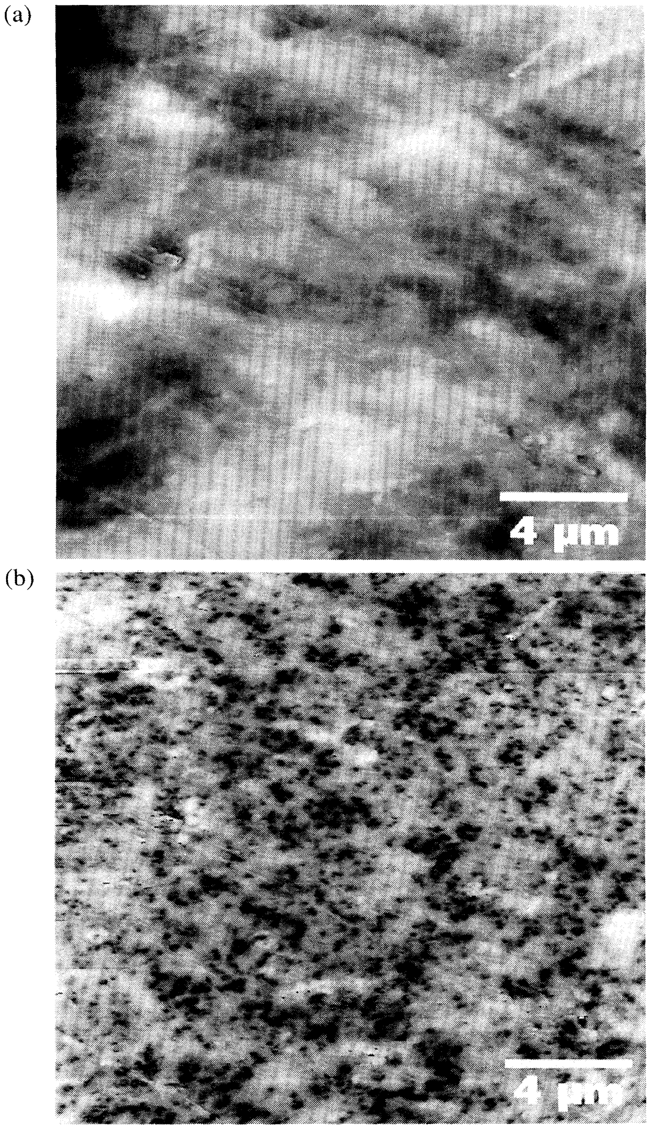

FIG. 1. (a) Tapping mode atomic force microscopic image of a 20 μm × 20 μm area of a carbon-black–polymer composite with a carbon-black concentration (volume fraction) of 0.1978. The image is fairly flat and featureless, with some grooves from the mold visible. (b) Electric force microscope image of the same area, taken simultaneously. Note the large degree of contrast between conductive regions (darker areas) and insulating regions (lighter areas). The feature size and shape of the conductive regions resemble those of carbon-black aggregates.

aggregates at the surface which are not part of the infinite cluster. We increased the bias voltage above the nominally set 3 V and observed increased contrast between the conductive and nonconductive areas. This confirms that the observed conductive areas are part of a conductive carbon-black network that extends through the 250 μm thickness of the composite sample.

Earlier experimental work [10] showed that the percolation threshold for this particular carbon-black–polymer composite occurs at a carbon-black concentration of 0.170 ± 0.001. We checked the validity of our direct imaging technique by repeating the experiment on samples slightly below and slightly above the percolation threshold. A composite sample containing 0.168 carbon-black concentration was imaged, resulting in a featureless EFM image even after ramping up the bias voltage. This indicates that an infinite cluster had not been formed. A composite sample containing 0.179 carbon-black concentration was imaged and did show conductive areas similar to Fig. 1(b), with a lower average density of conductive areas. This indicates that an infinite cluster had been formed, with a correlation length larger than that observed at 0.1978 carbon-black concentration.

To further quantify the network, we binarized the original EFM image to highlight the conductive features. A threshold grayscale value was selected for binarization based on a qualitative determination of how well the binarized image resembled the original image. The binarized image, shown in Fig. 2, was then analyzed in terms of the scaling theory of percolation [11]. A point that is part of the conductive backbone is chosen as the origin. The conductive area or "mass" $M(L)$ in squares centered on this origin is counted as a function of the square size L. The density of the conductive area is then calculated as $\rho(L) \equiv M(L)/L^2$, a dimensionless quantity. This procedure is repeated for 25 largely nonoverlapping areas on the binarized image, and the resulting data are averaged together.

Figure 3 shows a plot of the average $\rho(L)$ as a function of L for the binarized image in Fig. 2. There are three distinct regions. Below 0.6 μm the density obeys a power law corresponding to $M(L) \propto L^{D'}$, where D' is the effective dimensionality or fractal dimension of the conductive areas. The slope of the fitted line below 0.6 μm corresponds to a fractal dimension of 0.9 ± 0.1. Since the fractal dimension D' of a fractal object embedded in a d-dimensional space and cut by a surface of dimensionality d_s is $D' = D - (d - d_s)$, we can estimate the fractal dimension of the carbon-black aggregates to be $D = 1.9 \pm 0.1$. This value is in good agreement with measurements of the fractal dimension of similar carbon blacks using electron microscopy image analysis [12]. However, note that the edges of the carbon-black aggregates are not well resolved at small length scales in Fig. 2. Therefore this value for the fractal dimension of the carbon-black aggregates should be considered only a rough estimate.

Between about 0.8 and 2 μm the density follows a similar power law corresponding to $M(L) \propto L^{D'}$ with a fractal dimension $D = 2.6 \pm 0.1$. Above 3 μm the density is roughly constant with $D = 3$ within the experimental error, corresponding to homogeneous behavior. The crossover from power law behavior gives approximately

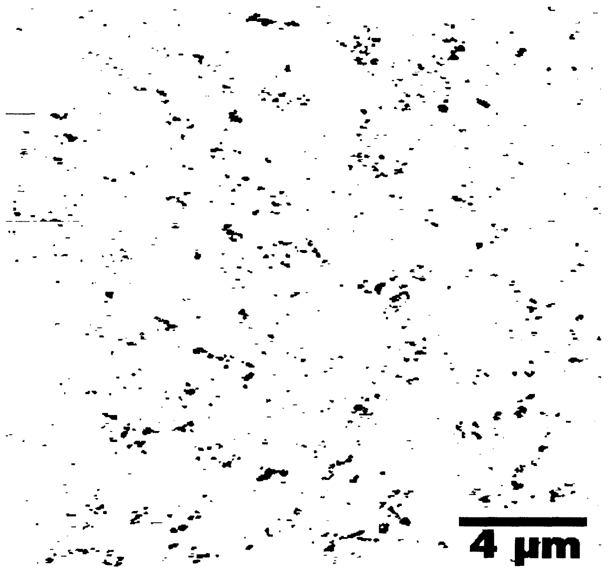

FIG. 2. Binarized image of Fig. 1(b)—the conductive and insulating regions are separated into "on" (black) or "off" (white) pixels. This image can now be quantitatively analyzed.

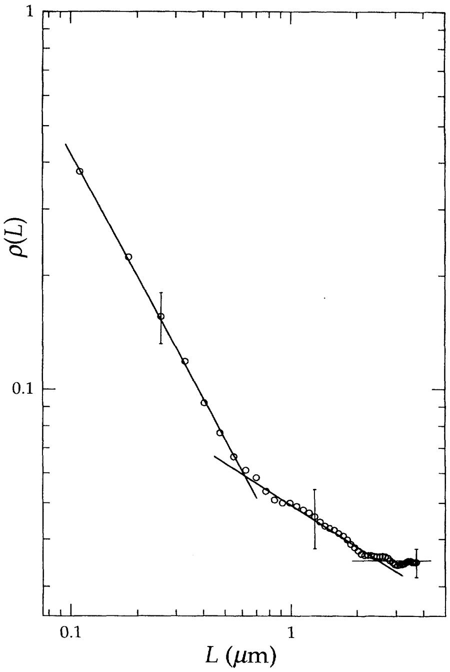

FIG. 3. Log-log plot of the average density of conductive regions $\rho(L)$ versus the length scale L for Fig. 2. The error bars represent the standard deviations of the 25 areas used to obtain the averages. Note that the minimum conductive unit is a square of side $L = 0.037\ \mu$m.

the correlation length ξ of the conductive network, which in this case is about 3 μm.

The fits at small and intermediate length scales were done with a weighted least-squares algorithm. Significant changes in the threshold grayscale value used for binarization [increasing the large L limit of $\rho(L)$ by a factor of 3] resulted in no significant changes in the fitted value of the slope in the intermediate length scale regime. Reducing the intermediate fitting range by up to a factor of 2 resulted in no significant changes in the fitted value of the slope in the intermediate length scale regime.

Theory [13] predicts $D = d - \beta/\nu$, where d is the system dimensionality, β is the density critical exponent, and ν is the correlation-length critical exponent. Using the currently accepted values $\beta = 0.41$ and $\nu = 0.88$ for three-dimensional systems [14] gives a theoretical fractal dimension of $D = 2.53$, in good agreement with our experimental result.

Our measured value for the fractal dimension of the infinite network is in good agreement with the theoretical value when the three-dimensional values for the critical exponents β and ν are used. Earlier measurements [10] of the conductivity critical exponent t from bulk transport data gave a result in good agreement with mean-field behavior (the six-dimensional value $t = 3$). In the mean-field limit, theory [15] predicts $D = 4$, in clear disagreement with our measured value $D = 2.6 \pm 0.1$. One possible interpretation is that macroscopic transport obeys mean-field percolation behavior while microscopic geometry obeys three-dimensional percolation behavior. A second possible interpretation is that transport behavior in these materials is nonuniversal [16]. This is an unresolved issue.

In earlier studies of geometric scaling behavior in two-dimensional discontinuous metal films [11], the conducting channels and the insulating channels all had approximately the same width. In such physical systems, rescaling to this width results in a system which approximates a two-dimensional lattice. In the three-dimensional physical system we have studied, the minimum conductive units are carbon-black aggregates which have a wide range of sizes and also have fractal structure. The insulating regions also have a wide range of sizes. It is not obvious that the carbon-black–polymer system should be explainable in terms of standard percolation theory, or that it should be in the same universality class as three-dimensional lattice percolation problems. The intermediate scaling regime where we observe the fractal dimension $D = 2.6 \pm 0.1$ is not very wide. For these reasons, the interpretation of our experimental results in terms of standard percolation theory should be considered tentative at this stage.

In conclusion, we have directly imaged the percolation network at the surface of a carbon-black–polymer composite using an electric force microscope. Quantitative analysis of the image yields estimates of the fractal dimension of the three-dimensional infinite cluster in good agreement with the scaling theory of percolation for the three-dimensional case. Quantitative analysis also yields an estimate of the correlation length ξ in this system. This demonstrates the direct imaging and quantitative characterization of these three-dimensional percolative systems. This work demonstrates the extent of conductive mapping information that can be obtained on these composite systems. By repeating these experiments on composites with different carbon-black concentrations, it may be possible to directly measure the correlation-length critical exponent and other microscopic critical properties.

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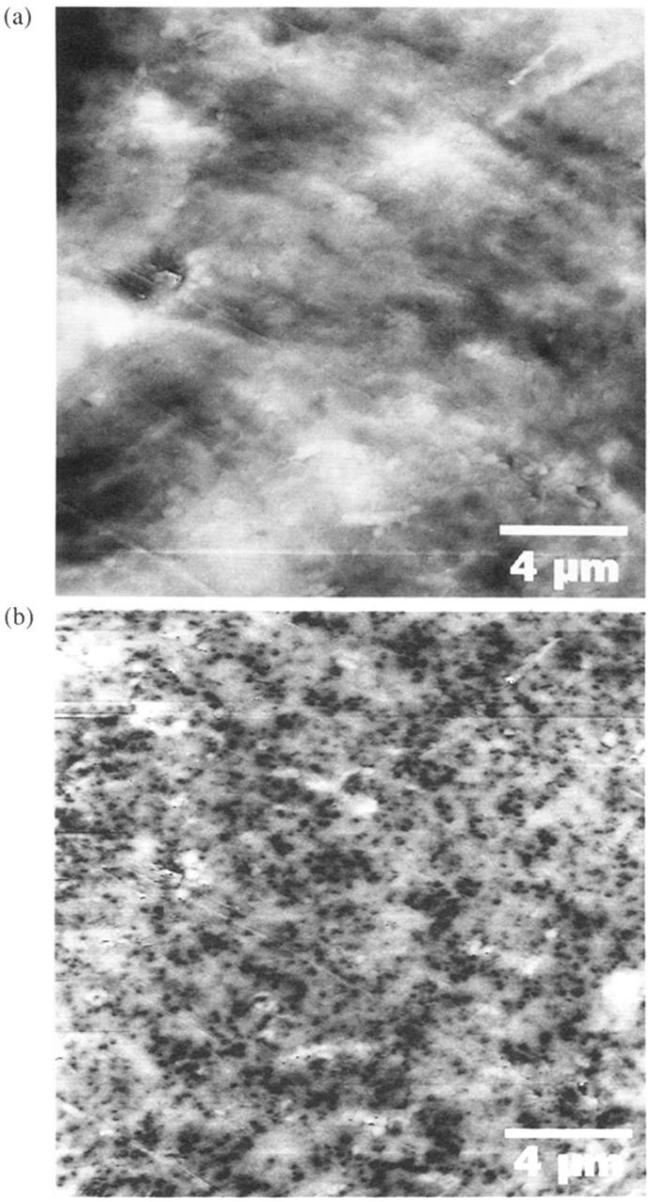

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