Supporting Information

Electrostatic Barriers to Nanoparticle Accessibility of a Porous Matrix

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Calibration of the axial position

We imaged ~ 4 µm diameter red fluorescent beads embedded within a polymer matrix (Thermo Fisher Scientific TetraSpeck kit T14792, NO.4), to calibrate the axial position using the relative azimuthal angle between the lobes. The piezo stage was used to scan the objective lens axially through the sample in 0.15 µm steps over a range of 3 µm, recording 5 images at each step with an acquisition time of 0.05 s. The z position was extracted by interpolating the relative azimuthal angle between two lobes from a cubic polynomial fit $\theta = a_1h^3 + a_2h^2 + a_3h + a_4$, where $\theta$ is the relative angle, $h$ is the axial position, and $a_1$, $a_2$, $a_3$ and $a_4$ are fitting parameters. A representative calibration curve is shown in Figure S4. For this example, the fitting function was $\theta = -7.8126h^3 - 4.9858h^2 + 77.732h + 97.467$.

**Figure S1.** Calibration curve of relative azimuthal angles between two lobes as a function of the axial position
Criteria to measure the size of interconnecting circular holes

The structures of inverse opal films on a microscope glass slide were imaged using a JEOL JSM-7401F scanning electron microscope.

**Cavity size measurement**: The size of the template particles was measured before use, these polystyrene particles had an extremely uniform size distribution according to SEM measurement (Figure S2a), with a mean diameter of 495 nm (Figure S2b). This value from SEM measurement was slightly smaller than the value provided by manufacturer, due to the different measurement technique. Specifically, the manufacturer used photon correlation spectroscopy (Coulter Nanosizer N4 Plus) to measure the hydrodynamic radius, which is expected to be slightly larger than geometrical measurements using SEM. The cavity size of the inverse opal structure also measured using SEM, had a mean diameter 494 nm (Figure S2c), very similar to the size of templating particles. These measurements confirm the consistent accuracy of SEM measurement.

![Template nanoparticle size measurement](image)

![Cavity size measurement](image)

**Figure S2.** (a) A representative SEM picture of templating nanoparticle. (b) Templating particle size distribution. (c) Silica inverse opal cavity size distribution.

**Hole size measurement**: Due to the angle of the SEM image relative to the interconnected cavity network, the planar projection of the circular holes connecting the spherical cavities appears as
elliptical areas whose major axis is the actual diameter of the hole. Therefore, the black areas (Figure 1b in main content) were modeled as ellipses to determine the major axis length. SEM images were first converted into 8-bit gray images, and a threshold was defined to distinguish the black areas from the background. The black areas thus identified were fit to elliptical shapes to determine the outer contour lines. The major axis was then obtained by measuring the fitted ellipse. The distribution of the identified major axis length in a SEM image is shown in Figure S3. For each inverse opal sample, at least three SEM images at different location of the sample were used to perform the hole size analysis. Maximum likelihood estimation was used to determine the mean value of the measurement, and this was denoted as the diameter of the interconnecting circular hole for this inverse opal sample.

Figure S3. (a) Hole size measurement with a mean hole size of 127 nm, and a standard deviation of 8 nm. (b) Hole size measurement with a mean hole size of 149 nm, and a standard deviation of 7 nm.

Criteria to identify escape events
Nanoparticle trajectories reflected the inner shape of the inverse opal structure (Figure 1b); therefore by analyzing the spatial positions of nanoparticles, we were able to differentiate confinement in the cavity from hopping between adjacent cavities in order to measure sojourn times. Specifically, we used a maximum allowed displacement method to separate the trajectories into different states, which corresponded to confinement in different cavities. Escape events occurred at transitions between states. Specifically, the amplitude of the time-dependent position fluctuations for a nanoparticle confined in a given cavity was related to the cavity diameter. The center of the first cavity was defined by averaging the particle position in x, y and z dimensions. An escape event was identified when the position of the particle relative to the center of the cavity exceeded a maximum allowed displacement, i.e., a threshold that was associated with the cavity diameter. For an inverse opal with a cavity diameter of 500 nm, a threshold of 500 nm was used. After an escape event, a new center was set by averaging the following particle positions in three dimensions, and the process was repeated until the end of the trajectory was reached. This method was robust with respect to variations in the data analysis parameters. For example, changing the threshold by +/- 20 nm, still resulted in the correct identification of escape events.

**Theoretical calculation of the energy barrier at the hole entrance**

The potential energy between the nanoparticle and the hole of inverse opal was evaluated using the approach described by Bowen et al. based on Derjaguin’s approximation, yielding

\[
U(h_0) = U_e(h_0) + U_m(h_0)
\]

\[
= \frac{\pi \epsilon_0 \epsilon_r g}{6 \delta h_0} \left( (\psi_p + \psi_m)^2 \ln \left( 1 + \exp \left( -\kappa h_0 \right) \right) + (\psi_p - \psi_m)^2 \ln \left( 1 - \exp \left( -\kappa h_0 \right) \right) \right) - \frac{A}{6 \delta h_0}
\]

where \( \kappa \) is the inverse Debye length, \( \epsilon_0 \) is the permittivity of the vacuum and \( \epsilon_r \) is the relative dielectric constant of the medium. \( \psi_p \) is nanoparticle surface potential, \( \psi_m \) is the inverse opal
surface potential, $A$ is the Hamaker constant. $h_0$ is the closest distance between wall and nanoparticle, $g$ is the steric factor determined by the geometrical characteristics of the system.

Here, we set $\epsilon_r = 46.98$, which is the permittivity of 90wt% glycerol/water mixture, $\psi_p$ and $\psi_m$ as -25.7 mV. The Hamaker constant $A$ was $2.36 \times 10^{-21}$ J and $\kappa^{-1}$ equals to 0.96 nm for 0.1 M salt concentration solvent, 3.04 nm for 0.01 M salt concentration solvent, and 9.6 nm for 0.001 M salt concentration solvent.

As described in the main text, this model divides the hole area into three regions (Figure 4 in the main text). In region I, the particle interacts with a flat plate adjacent to the hole; in region II, the particle interacts with the curved entrance of the pore, and in region III, the particle interacts with the cylindrical inner surface of the hole. Here, we focus only on the area of the hole entrance, which is the buffer zone between region II and region III. The interaction energy in this buffer zone was assumed to be proportional to the fractions of the particle surface projected on the appropriate part of the inverse opal surfaces.

For different region, we used different steric factors, $g$.

In region I, $g_1 = \frac{1}{a}$.

In region II, $g_2 = \sqrt{\frac{1}{a} + \frac{1}{b} \left(\frac{1}{a} - \frac{1}{r_0 + b}\right)}$.

In region III, $g_3 = \sqrt{\frac{1}{a} - \frac{1}{r_0}}$.

Here, $a$ is the radius of nanoparticle, equal to 23 nm, $r_0$ is the hole radius, $b$ is the radius of curvature of the rounded edge of the hole entrance. We used the standard deviation of hole size from SEM measurements as the $b$ value, which was about 5% of the hole size.
The calculations were relatively insensitive to the specific choice of b. For example, when we changed the value from 2% of the hole size to 8% of the hole size, the effective hole size only changed from 100 nm to 99 nm (Figure S6b).

Using the above parameters and equations, the potential energy near the hole was calculated, then divided $k_B T$ to obtain the dimensionless potential energy. Figure S4 shows a representative potential energy plot of 46 nm nanoparticle near a 149 nm hole entrance with three different salt concentrations. From this calculation, we can also obtain the potential energy plot for a nanoparticle at the hole entrance (Figure S6a). In this case, the width of the apparent well 53 nm; adding the nanoparticle size of 46 nm, gave an effective hole size for this case of 99 nm.

**Figure S4.** Three-dimensional plots of the potential energy in the hole area. (a) 0.1M salt concentration with 149 nm hole size. (b) 0.01M salt concentration with 149 nm hole size. (c) 0.001M salt concentration with 149 nm hole size.
**Figure S5.** Contour plot of dimensionless potential energy of 46 nm nanoparticle near the hole entrance for 149 nm hole size. The immersion solution is contained 0.001 M salt.

**Figure S6.** (a) Plot of dimensionless potential energy for a 46 nm nanoparticle at the entrance of a 149 nm hole, the immersion solution is contained 0.001 M salt. (b) Plot shows the lack of sensitivity of the potential energy calculation to the specific choice of the b value.
Random walk simulation procedure

Here we describe the random walk simulation in a spherical cavity with twelve holes on the surface. The generalized random walk simulations were performed on a three-dimensional Cartesian coordinate system. The walker was initially placed at the origin at the initial time $t = 0$. The simulation time step was $dt = 0.05$ s. The total simulation time of each walk was $180$ s. Each step was drawn from a Gaussian distribution where $P$ is the probability, $r$ represents displacement in a time interval $\Delta t$, and $D$ is the diffusion coefficient of a tracer particles in inverse opals as determined by experimental results at short lag time regimes, shown in Figure 1a in the main text. The center of the spherical cavity is located at the origin with a radius of $R = 250$ nm.

![Figure S7. Representative example of random walk simulation of confined nanoparticle diffusion in an inverse opal structure](image.png)

The origin of the coordinate system was defined as the center of the cavity. Twelve holes were created on the cavity surface to mimic the inverse opal structure. The position of the centers of the twelve holes were:
respectively. The walkers were sterically confined by the boundary of the cavity. The walker could escape from the cavity only through a hole. The sojourn time was then defined as the average time that walkers spent in a cavity prior to escape. More than ten thousand trajectories were simulated in a cavity with varying L to yield statistically meaningful results of the cumulative sojourn time distribution.

Table and figures mentioned in the main text

**Table S1.** Experiment and simulation data of sojourn time for different hole size and salt concentration.

<table>
<thead>
<tr>
<th>Mean hole diameter L (nm)</th>
<th>Standard deviation of hole diameter (nm)</th>
<th>Salt concentration (M)</th>
<th>Debye length (nm)</th>
<th>Mean sojourn time, $T_{soj}$ (s)</th>
<th>Effective hole size from simulation, $L_s$ (nm)</th>
<th>Hole size difference, $L-L_s$ (nm)</th>
<th>Effective hole size from calculation using DLVO theory, $L_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>127</td>
<td>8</td>
<td>0.001</td>
<td>9.60</td>
<td>19.5 +/- 0.47</td>
<td>86</td>
<td>31</td>
<td>76</td>
</tr>
<tr>
<td>127</td>
<td>8</td>
<td>0.01</td>
<td>3.04</td>
<td>7.4 +/- 0.92</td>
<td>107</td>
<td>20</td>
<td>112</td>
</tr>
<tr>
<td>127</td>
<td>8</td>
<td>0.1</td>
<td>0.96</td>
<td>4.0 +/- 0.20</td>
<td>123</td>
<td>4</td>
<td>123</td>
</tr>
<tr>
<td>149</td>
<td>7</td>
<td>0.001</td>
<td>9.60</td>
<td>9.5 +/- 0.33</td>
<td>101</td>
<td>48</td>
<td>99</td>
</tr>
<tr>
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<td>7</td>
<td>0.01</td>
<td>3.04</td>
<td>4.2 +/- 0.09</td>
<td>125</td>
<td>24</td>
<td>135</td>
</tr>
<tr>
<td>149</td>
<td>7</td>
<td>0.1</td>
<td>0.96</td>
<td>2.6 +/- 0.15</td>
<td>149</td>
<td>0</td>
<td>146</td>
</tr>
</tbody>
</table>
Figure S8. Complementary cumulative distribution of sojourn times for different hole sizes and salt concentrations. The lines represent a double exponential fitting function $P(t)=A\exp(-t/T_1)+(1-A)\exp(-t/T_2)$, permitting the calculation of the mean sojourn time, $T_{soj} = A\cdot T_1 + (1-A)\cdot T_2$.

Figure S9. Long-time diffusion coefficient vs. $R_0/6T_{soj}$ for different hole sizes and salt concentrations.
Figure S10. Distribution of the nanoparticle position when confined in the cavity at different salt concentrations. The standard deviations of are 103 nm, 110 nm, 114 nm, for 0.001 M, 0.01 M, and 0.1 M salt, respectively.

Figure S11. Dimensionless potential energy when the nanoparticle is located in the entrance plane of a hole. The horizontal axis represents the lateral position of the center of the nanoparticle. The black dashed line indicates the value (potential energy) / k_B T=1.

Three values of nanoparticle surface potential used to calculate the potential energy for
the nanoparticle when located in the entrance plane of the hole, for holes 149 nm in diameter connecting cavities 500 nm in diameter, at 0.001 M, 0.01 M and 0.1 M salt concentrations. This figure indicates that the potential energy calculation is relatively insensitive to the nanoparticle surface potential over a reasonable range.

**Figure S12.** Mean sojourn time vs. effective pore size calculated based on an electrostatic energy barrier model at the hole entrance. Three energy values, 0.8\(k_B T\), 1\(k_B T\), 1.2\(k_B T\) were used as criteria to determine the effective pore size here. This figure indicates that chose 1\(k_B T\) as the criterion is reasonable, and the results are relatively insensitive to the specific choice of the criterion.