

Self-regulated Gd atom trapping in open Fe nanocorralsR. X. Cao,¹ Z. Liu,¹ B. F. Miao,¹ L. Sun,¹ D. Wu,¹ B. You,¹ S. C. Li,¹ W. Zhang,¹ A. Hu,¹ S. D. Bader,² and H. F. Ding^{1,*}¹*National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, 22 Hankou Road, Nanjing 210093, People's Republic of China*²*Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA*

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Utilizing open Fe nanocorrals built by atom manipulation, we demonstrate self-regulated Gd atom trapping in open quantum corrals. The number of Gd atoms trapped is exactly determined by the diameter of the corral. The quantization can be understood as a self-regulating process, arising from the long-range interaction between Gd atoms and the open corral. We illustrate with arrays of open corrals that such atom trapping can suppress unwanted statistical fluctuations. Our approach opens a potential pathway for nanomaterial design and fabrication with atomic-level precision.

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I. INTRODUCTION

Statistical fluctuations are fundamental processes in nature. For large-scale materials, this is not a dominant issue, as the number of atoms dwarfs the fluctuations. At the nanoscale, virtually every atom counts, and even a small fluctuation can limit the uniformity of the structure and influence its properties and functionalities. Therefore, it is imperative to explore new strategies to minimize the influence of fluctuations at the nanoscale, where quantum size effects emerge. Quantum confinement could actually be invoked to minimize the influence of fluctuations. Indeed, quantum confinement can have a decisive influence on the growth of thin films and nanostructures, resulting in novel effects, such as a critical thickness for smooth film growth, magic heights of nanoislands, quantum diffusion, and quantum rings and onions [1–10]. Recently, a network of metal-organic quantum boxes were used to self-assemble Fe clusters [11], besides the typical self-assembly approaches [12–22]. These clusters have uniform space separation but broad distributions in size due to fluctuations in the growth. In the present work, utilizing open Fe nanocorrals built via atom manipulation [23] by means of scanning tunneling microscopy (STM) techniques, we demonstrate, in real space, a self-regulated trapping of Gd atoms by open quantum corrals. Depending on the diameters of Fe open corrals (5 to 12 nm), one to seven Gd atoms are trapped. The quantization is a self-regulating process: when an insufficient number of atoms are inside the nanocorral, trapping is automatically triggered; however, when too many atoms are inside a corral, a repulsion process occurs that expels the extra atoms. As illustrated with arrays of open corrals, self-regulated atom trapping can reduce the unwanted influence of statistical fluctuations. Thus, it opens a pathway for nanomaterial design and fabrication with atomic-level precision. In comparison with previous methods, our approach can create nano-objects with a tunable size (e.g., one to seven atoms) and offer the possibility for designing materials with locally different properties via changing the diameter of the open corral. Furthermore, it has a self-repairing capability,

which also provides an alternate way to extend the functional reliability of nanostructures.

Our single-atom fluctuation-free control provides similar reproducibility to atomic manipulation. It also compares favorably with other recent efforts, such as atomtronics [24] or atoms on a chip [25] in the field of cold atoms. Moreover, our structures can provide a complementary way to explore issues in few-body physics.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed in an ultrahigh vacuum chamber (2×10^{-11} mbar) equipped with a low-temperature STM and a sputter gun. The single-crystal substrate Ag(111) was cleaned by repeated cycles of argon ion sputtering at 1.5 keV and annealing at 870 K. Then, the crystal was transferred into the STM stage and cooled to 4.7 K. By pumping liquid He in the cryostat, the sample could be further cooled to 3.0 K. High-purity Fe and Gd were deposited by means of electron beam evaporation onto the Ag(111) substrate in the STM stage at ≈ 6 K from thoroughly outgassed rods. The typical rate of deposition was 0.002 monolayer per minute. Electrochemically etched and *in situ* e-beam cleaned tungsten tips were used for the STM measurements [26]. The bias voltage U refers to the sample voltage with respect to the tip.

III. METHOD OF CALCULATION

Kinetic Monte Carlo (KMC) calculations were used to simulate the Gd atom trapping in open Fe corrals on Ag(111). The method has been used previously for the simulation of quantum onion formation [8], quantum diffusion of Gd atoms in nanosize Fe corrals [9], and the superlattice formation of Fe on Cu(111) [13,27] and Gd on Ag(111) [12]. In the simulations, the hopping rate of an adatom from site i to site j on the Ag(111) surface is calculated using the Arrhenius law $v_{i \rightarrow j} = \nu_0 \exp(-E_{i \rightarrow j}/k_B T)$, where T is the temperature of the substrate, ν_0 is the attempt frequency, k_B is the Boltzmann constant, and $E_{i \rightarrow j}$ is the hopping barrier. The influence of the long-range interactions through the surface-state electrons is included in the hopping barrier, i.e., $E_{i \rightarrow j} = E_d + 0.5(E_j - E_i)$ [28,29], where E_d is the diffusion barrier for an isolated atom on a clean surface and $E_i(E_j)$ is the

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total energy caused by the long-range interactions. The values of E_d and the Gd-Gd and Fe-Gd long-range interactions were experimentally determined previously [9,12].

IV. RESULTS AND DISCUSSION

Fe adatoms were chosen to build the nanocorrals because of the favorable diffusion barrier of ≈ 43 meV on Ag(111) [13]. With a barrier of this magnitude, atomic manipulation can be achieved, while the adatoms can then be immobilized at 4.7 K after positioning [9]. Single adatoms of Fe were first deposited for building the open corrals. Gd was also chosen due to its compatible diffusion characteristics, as will become clear below. Single adatoms of Gd were deposited either before or after the construction of the Fe corrals. In the following, we describe the case in which Gd adatoms are deposited first, if it is not explicitly mentioned; however, the results are essentially the same for both cases. The scanning conditions utilized for atomic manipulation are $U = -0.5$ V and tunneling current $I_t = 1$ nA. With these conditions, Gd adatoms are driven out of the scanning area, which may be due to their stronger interaction with the tip and/or their lower diffusion barrier of ≈ 7.6 meV [12]. Open nanocorrals of different diameters were made under the same conditions reported previously [9]. The nearest-neighbor atomic separation was kept between 2.0 and 2.5 nm. In contrast to the full corrals built previously [9,30], we construct herein open corrals with one atom missing. The separation between the two atoms at the opening is fixed to be ≈ 4.5 nm. As will be discussed below, the opening forms a gate to regulate the flow of Gd atoms traveling in and out, resulting in quantized atom trapping.

After building the open corrals, the scanning conditions were changed to $U = 0.5$ V and $I_t = 2$ pA to minimize the interaction between the tip and Gd adatoms [31]. In such a case, Gd adatoms can diffuse back into the scanning area, where the open corrals reside. After a few minutes, we found that Gd adatoms are trapped in the open Fe corrals. However, the Gd adatoms display a fuzzy image due to their finite mobility at 4.7 K. To improve the image quality, we cooled the sample to 3.0 K to reduce the mobility of Gd adatoms. Figure 1 presents the Gd atom trapping in six open Fe corrals with different diameters. The Gd adatoms (center red dots) appear larger and brighter than the Fe adatoms (in light yellow color) due to their different atomic radii and electronic properties. Interestingly, we find that the atom trapping is quantized, i.e., one to seven Gd adatoms are trapped, depending on the diameter of the open corrals. Gd adatoms in the corrals prefer to form equilateral polygons, which are confocal with the Fe

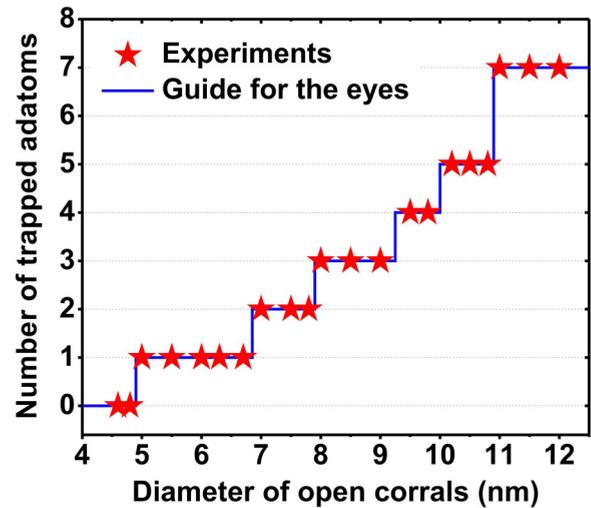


FIG. 2. (Color online) Plateaus of stability for the number of trapped Gd adatoms versus the open corral diameter at fixed gate width.

open corrals. In particular, the square and pentagon patterns shown in Fig. 1 are clearly different from the hexagonal lattice on a flat surface [12,17], providing evidence of the controlling effect of quantum confinement by the corrals. The trapping of six Gd adatoms was attempted several times utilizing open corrals, with diameters between 10.5 and 11.0 nm, but was not realized. Nevertheless, the observation of one to seven atom structures without six-atom trapping demonstrates that atoms can be captured with single-atom accuracy by tuning the size of open quantum corrals.

To further illustrate the stability of the quantized atom trapping, we explored the number of trapped Gd adatoms as a function of the open corral diameter at a fixed gate width. For this, we built a series of open Fe corrals of various diameters and observed the Gd atom trapping inside. The results are shown in Fig. 2. The red stars are the experimental data, while the blue line serves as a guide to the eye. We find a staircaselike curve for trapping one to seven (excluding six) Gd adatoms, once again demonstrating the quantization of the trapping process. The wide plateaus give large tolerance for nanomaterial design and fabrication via this method.

The rigorously controlled atom trapping suggests that the opening of the corrals forms a gate to control the trapping: if insufficient atoms are located inside the nanocorral, trapping is automatically triggered; while if too many atoms are placed inside the corral, a repelling process occurs to remove the

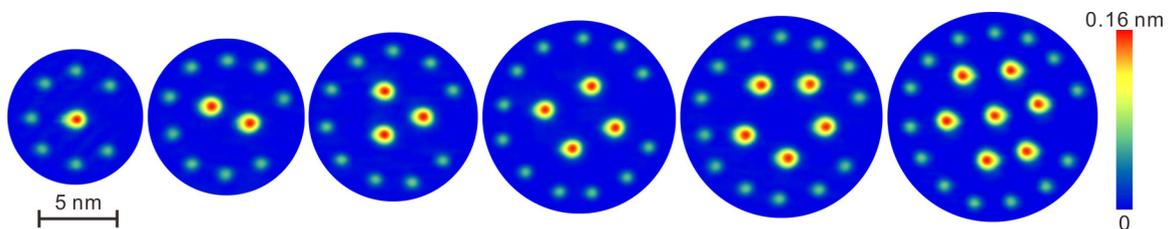


FIG. 1. (Color online) STM images of one, two, three, four, five, and seven Gd adatoms trapped in Fe open corrals with diameters of 6.0, 7.5, 8.5, 9.8, 10.5, and 11.0 nm on Ag(111), respectively. All images are of the same scale and obtained at 3.0 K, with the scanning conditions of $U = 0.5$ V and $I_t = 2$ pA.

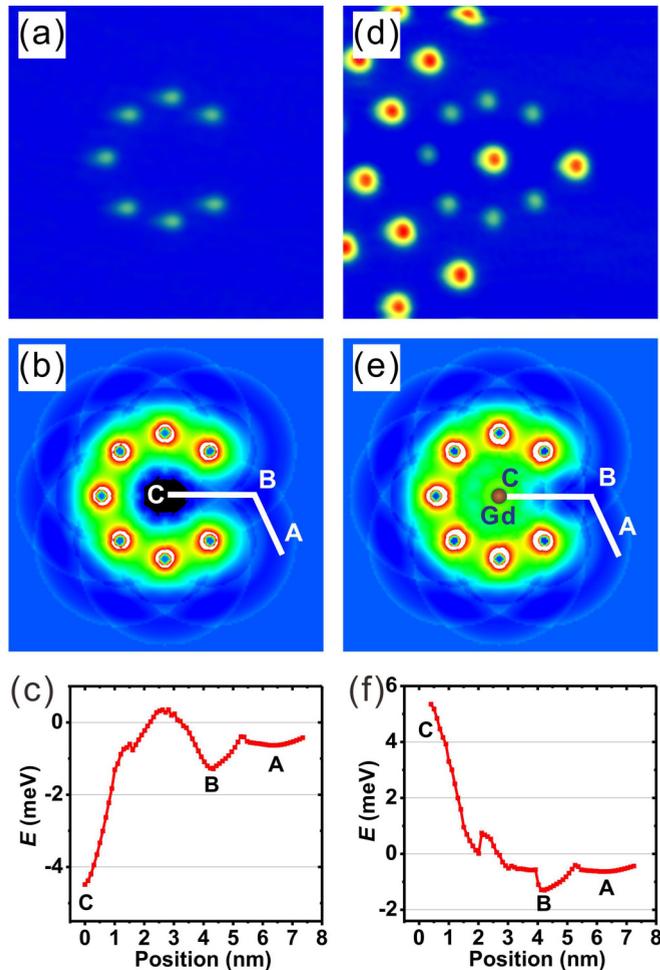


FIG. 3. (Color online) STM image of an open Fe corral with a diameter of 6.0 nm before (a) and after (d) trapping one Gd adatom. (b) The calculated distribution of the interaction between one Gd adatom and the 6.0-nm corral. (c) The line profile of the interaction distribution from position A to C marked in (b). (e) The distribution of the interaction between one Gd adatom and the 6.0-nm corral with one Gd atom trapped at the center. (f) The line profile of the interaction distribution from position A to C marked in (e). The image sizes of (a), (b), (d), and (e) are $15 \times 15 \text{ nm}^2$.

extra atoms. To gain further insight, we focus on the one-atom trapping process for the open corral with a diameter of 6.0 nm shown in Fig. 3(a). Consecutive scans of the corral area at a rate of 50 s per frame were taken at 4.2 K (see Supplemental Material Movie S1 [32]). We find that the Gd adatoms prefer to diffuse near the corral. Sometimes a Gd adatom diffuses into the region near the gate of the corral and diffuses away. After several attempts, the Gd adatom is trapped by the 6.0-nm corral; the final result at 3.0 K is shown in Fig. 3(d). This demonstrates that trapping is automatically triggered when insufficient atoms are located inside the corral at the favorable temperature. To understand the mechanism, we calculated the distribution of the interaction between a Gd adatom and an open Fe corral within a first-order approximation by simply summing up the long-range interaction energies between Gd and all Fe adatoms [9,31]. The result is shown in Fig. 3(b). We find that attractive potential wells exist both at the center

and the surrounding area of the open Fe corral, which agrees with the diffusion study near the corral mentioned above. To be quantitative, we show in Fig. 3(c) the line profile of the interaction distribution from position A to C, which is marked in Fig. 3(b). When Gd adatoms diffuse outside the open Fe corral, they prefer to occupy position B whose potential is lower than that of other positions outside the corral, such as position A. In such a case, the occupation probability at position B is high for adatom diffusion outside the quantum corral. On the other hand, the attractive potential well at position C is $\approx -4.5 \text{ meV}$, with a barrier of 4.8 meV for adatom hopping from C to B. This barrier is much larger than the barrier of 1.6 meV for adatom hopping in the reverse direction. At 4.2 K, this barrier difference yields a hopping probability that is ≈ 6500 times higher for atoms hopping from B to C compared to the reverse direction. Therefore, the Gd is automatically trapped at position C at this favorable temperature. We note that the real potential from position A to C should be the superposition of the interaction and the diffusion barrier of Gd adatoms on Ag(111) [12,13,33]. In addition, we used a cutoff distance of 4.1 nm to describe the interaction between adatoms. The long-range, oscillatory, and decaying nature of the surface-state-mediated interactions between adatoms and the open corrals make the corrals attractive centers for the surrounding Gd adatoms [31,34,35].

After one Gd adatom was trapped at position C, the potential distribution is altered; see Fig. 3(e). From the line profile shown in Fig. 3(f), one can find that the potential well at the center position disappears, and an energy maximum of $\approx 5.4 \text{ meV}$ forms. In such a case, the gate is self-closed after one-atom trapping—no more trapping will occur. Even when more adatoms are accidentally deposited inside the corral, the extra adatoms will be expelled from the corral.

To demonstrate this in a more general manner, we chose an open corral with a different size (8.5 nm) in our study. The calculated trapping and repelling mechanism of the 8.5-nm open corral is similar to that mentioned in the 6.0-nm corral. The STM image in Fig. 4(a) shows that three Gd adatoms are automatically trapped via the process mentioned above. To intentionally add an additional Gd adatom into the open corral, we used atomic manipulation to drive a Gd adatom that was originally located outside the corral into it (via scanning conditions of $U = -0.5 \text{ V}$ and $I_t = 0.8 \text{ nA}$). After that, we found that the four Gd adatoms form a distorted structure in the corral, as shown in Fig. 4(b). With a diffusion barrier of $\approx 7.6 \text{ meV}$, the Gd adatoms are immobile at 3.0 K. Therefore, this structure can be formed even though it has high potential energy. To overcome the diffusion barrier, we heated the sample to $\sim 4.0 \text{ K}$. Due to the increased thermal energy, Gd adatoms started to diffuse, and the extra one was expelled from the corral [see Fig. 4(c) and the Supplemental Material with the consecutively obtained images in Movie S2 [32]. The remaining three Gd adatoms are trapped stably in the open corral, as shown in Fig. 4(d). This demonstrates that the open corral has the ability to eject extra adatoms. This, together with the mechanism mentioned above, ensures the quantized atom trapping. We note that the above experiments also demonstrate that the structures built with this method also have a self-repairing capability, which is important in stabilizing their functionalities.

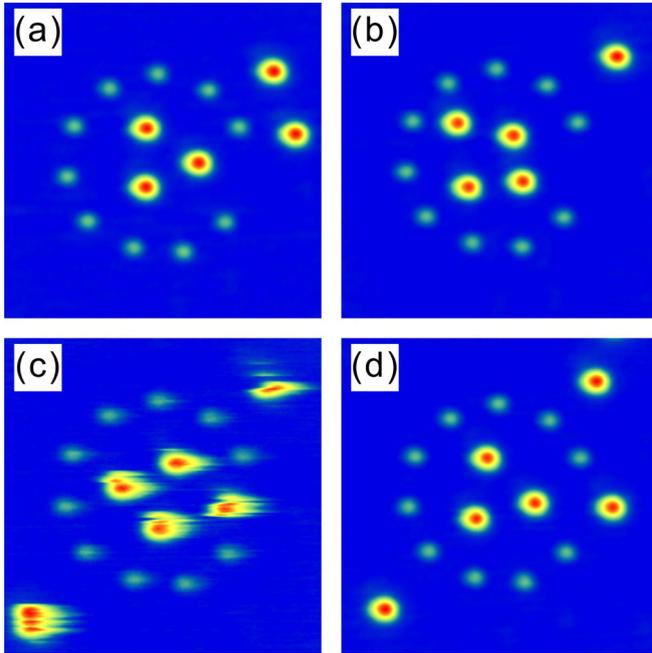


FIG. 4. (Color online) (a) STM image of three Gd adatoms trapped in an 8.5-nm open corral. (b) Four Gd adatoms trapped in the corral after artificially moving an extra Gd adatom into the corral. (c) STM image at 4.0 K of expelling the extra adatom from the corral. (d) STM image of the remaining three Gd adatoms trapped in the corral after the fourth was expelled. All the image sizes are $15 \times 15 \text{ nm}^2$.

To further verify the trapping mechanism, we performed KMC simulations to obtain the trapping behavior in the open corrals. The total energy is calculated by summing up all two-body interactions from each adatom in the quantum corral, as in Fig. 3. The simulated probability as a function of the open corral diameter is shown in Fig. 5. We find that it agrees with the experimental findings (unfilled stars)

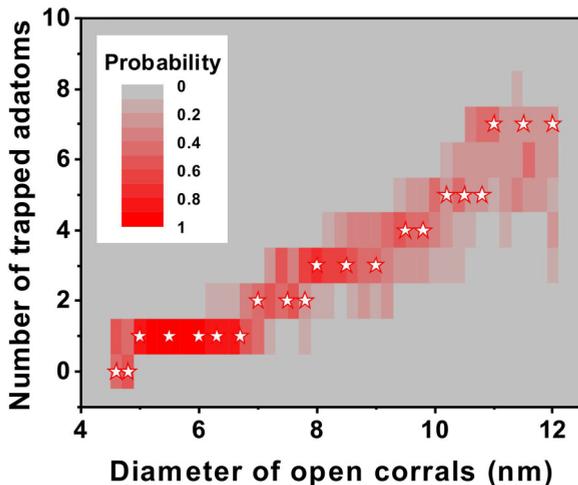


FIG. 5. (Color online) Comparison between the experimental finding (unfilled stars) and the simulated trapping probability as a function of the open corral diameter. The simulation is performed by summing up the two-body interactions from each adatom.

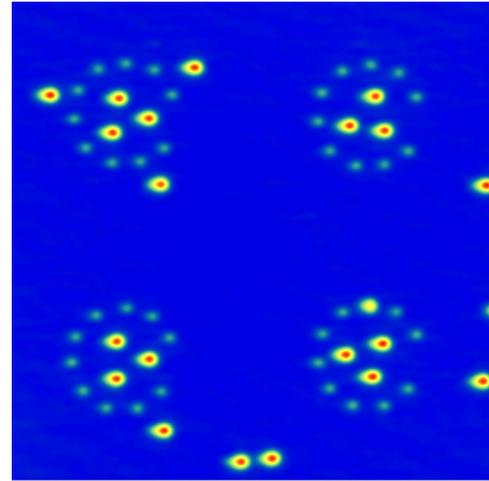


FIG. 6. (Color online) STM image ($40 \times 40 \text{ nm}^2$) of three Gd trapping in the 2×2 array of open Fe corrals of diameter $\sim 8.5 \text{ nm}$.

qualitatively. To describe the observed effects quantitatively, many-body interactions and more rigorous theory, such as *ab initio* calculations, are needed. Nevertheless, the agreement verifies that the quantized atom trapping can be understood as a self-regulating process, arising from the long-range interaction between Gd atoms and the open corral.

Such atom trapping can minimize the influence of statistical fluctuations since the trapping is quantized. This could improve the uniformity of the designed materials and device structures. To demonstrate this, we built arrays of open Fe corrals with a diameter of 8.5 nm. After that, we deposited Gd adatoms and cooled the system to 3.0 K. The end state of the 2×2 array in Fig. 6 shows that all four open corrals have three Gd adatoms trapped, which illustrates the uniformity. We note that the brighter yellow spot in the lower right corral in Fig. 6 is due to the Fe dimer accidentally formed during the atomic manipulation, which appeared to have no influence on the quantized trapping.

As a comparison, we also built arrays of the closed Fe corrals and repeated the same measurements. Figure 7(a) shows a typical 2×2 array of closed corrals with a diameter of 8.5 nm, in contrast to the open corrals discussed above. Figures 7(b)–7(d) present the results with the deposition of $\sim 3.6 \times 10^{-3}$ monolayer Gd. The coverage is chosen to attempt trapping three Gd atoms in each corral, as shown in Fig. 6. The pink and larger spots in the STM image are dimers accidentally formed during deposition. The result, however, shows that the numbers of Gd adatoms in each of the four closed corrals are different due to fluctuations, even with many attempts. This is in agreement with Ref. [11] and can be explained by the natural randomness of the growth. It is generally believed and has been demonstrated that the growth of atoms at a small scale follows a random distribution [13]. With this, we can roughly estimate the probability of trapping three Gd atoms in each corral by assuming 12 Gd atoms are deposited into the four closed corrals. It is only $\sim 3\%$. This demonstrates a more than one order of magnitude suppression of fluctuations with open corrals, since we always obtain three Gd atoms in each open corral, as shown in Fig. 6.

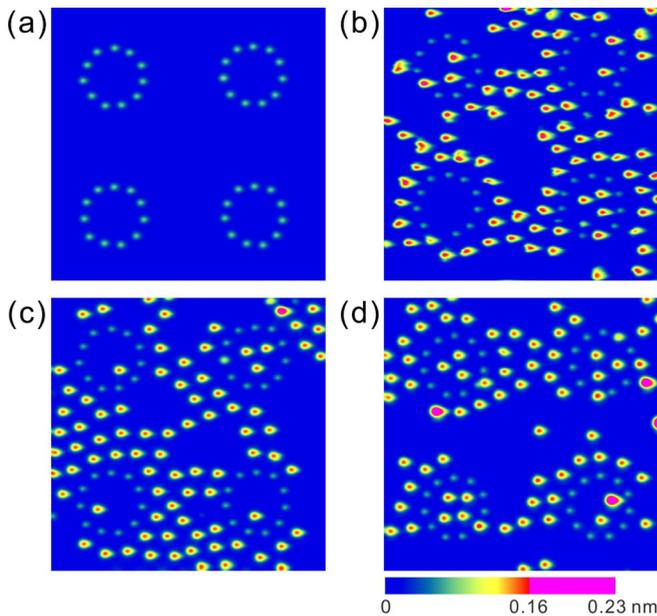


FIG. 7. (Color online) STM image ($40 \times 40 \text{ nm}^2$) before (a) and after (b)–(d) Gd deposition in the 2×2 array of closed Fe corrals of diameter $\sim 8.5 \text{ nm}$.

We also plot the experimentally obtained histogram of the number of trapped adatoms for the 8.5-nm open and closed corrals in Fig. 8. In the closed corral in Fig. 8(a), it shows a broad distribution. We find that the probability of having three Gd adatoms trapped in a closed corral is $\sim 33\%$. This yields $\sim 1\%$ success rate for having three Gd adatoms in each closed corral of a 2×2 array, in good agreement with the previously mentioned rough analysis. On the contrary, in Fig. 8(b), the histogram shows a single value for nine open corrals. The sharp contrast clearly demonstrates the fluctuation-suppression effect with the open corral.

Moreover, we also prepared open corrals with various diameters within one experiment and found that the structures shown in Fig. 1 can be stabilized within a single-shot experiment despite their different Gd area densities. This indicates that our approach also offers the capability of designing materials with locally different properties via locally changing the diameters of the open corrals.

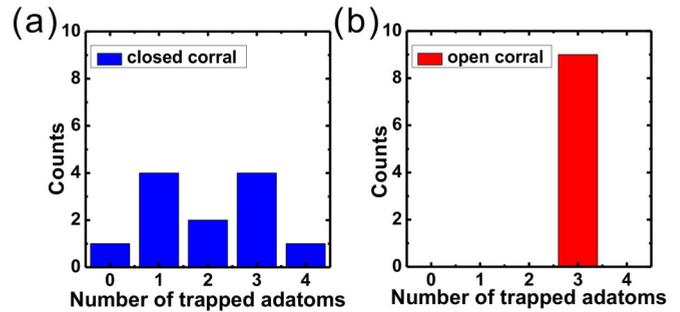


FIG. 8. (Color online) Comparison of the histogram for the number of trapped Gd adatoms in closed (a) and open (b) 8.5-nm corrals.

V. SUMMARY

In summary, we experimentally demonstrated self-regulated Gd atom trapping in open Fe nanocorrals. Depending on the diameters of the Fe open corrals (5 to 12 nm), one to seven Gd atoms are trapped. The quantization can be understood by means of a surface-state-mediated long-range interaction between the Gd atoms and the open Fe quantum corrals. As illustrated with arrays of open corrals, such atom trapping can remove the unwanted influence of statistical fluctuations. The atom trapping is demonstrated in our work specifically utilizing Gd atoms and Fe corrals, but the results should not be limited to this system and can be generalized. The trapping only requires a rigid, open corral and mobile atoms on a surface with a surface state at a given temperature. Thus, our observations open a pathway for nanomaterial design and fabrication with atomic-level precision. The nano-objects created by our method can have a tunable size (e.g., one to seven atoms) and self-repairing capability.

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