Supporting information

How the moiré superstructure determines the formation of highly stable graphene quantum dots on Ru(0001) surface

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1. Fitting $E_{GB-M}(r)$

The unit cell of moiré superstructure of CVD grown graphene on Ru(0001) is generally quite large. According to our DFT calculations, the best commensurate structure consists of 12×12 super cells of graphene matching 11×11 Ru(0001) surface cells, making it difficult to extract atomic position-dependent $E_{GB-M}(r)$. Therefore, we first constructed a (1×1) commensurate model of graphene on a Ru(0001) surface by biaxially stretching/compressing the lattice constants of graphene/Ru(0001) surface by ~4%. We then obtained a map of $\boldsymbol{E_{GB\text{-}M}}$ per primitive cell of graphene for the case of graphene sliding over the Ru(0001) surface, via DFT calculations, which is simply the sum of contributions from the two carbon atoms, labeled as A and B, in a primitive cell. Thus,

$$E_{GB-M}^{cell}(r) = E_{GB-M}(r_A) + E_{GB-M}(r_B). \tag{1}$$

We next fit the $E_{GB-M}(r)$ with the following equation:

$$E_{GB-M}(r) = E_{GB-M}^{0} + \Delta E_{GB-M}(r), \tag{2}$$

where E_{GB-M}^{0} and $\Delta E_{GB-M}(r)$ represent, respectively, the average and position-dependent variance of the VDW energy between graphene and the Ru(0001) surface. Apparently, the $E_{GB-M}(r)$ is a two-dimensional periodic function of the atomic position **r,** and considering the three-fold symmetry of graphene on Ru(0001), can be expanded as

$$E_{GB-M}(r) = E_{GB-M}^{0} + \sum_{k} \alpha_k S_k(r) \tag{3}$$

$$S_k(r) = \sum_{\{\Lambda\}} e^{i\Lambda k \cdot r} \tag{4}$$

where **k** is the reciprocal lattice vector of the Ru(0001) surface, while Λ is the point group rotation operator. The fitting performance and the best fitted $E_{GB-M}(r)$ are shown in Fig. 2i and 2h, respectively. The $E_{GB-M}(r)$ value reaches a minimum when the carbon atoms in graphene exactly locate over the Ru atoms, namely, at the four corner sites in Fig. 2i. The best fitting leads to the following expression for $E_{GB-M}(r)$,

$$\begin{aligned} E_{GB-M}(r) = & -1.300\times10^{-1} - 7.365\times10^{-2}\left[\cos\left(b_1\cdot r + 144.44^{\circ}\right) + \cos\left(-b_2\cdot r + 144.44^{\circ}\right) + \cos\left(\right.\right. \\ & - 8.996\times10^{-2}\left[\cos\left((b_1+b_2)\cdot r\right) + \cos\left((b_1-2b_2)\cdot r\right) + \cos\left((b_2-2b_1)\cdot r\right)\right] \end{aligned}$$

,

(5)

where $\boldsymbol{b_1}$ and $\boldsymbol{b_2}$ are the basis vectors of the reciprocal lattice and $\boldsymbol{r}$ is the atomic position of the carbon atom.

2. Generation of GQDs with zigzag edges.

We mainly focus on GQDs with zigzag edges, since the outermost edge of HSGQDs has been experimentally found to be zigzag. The shapes of GQDs with zigzag edges can be triangle, parallelogram, trapezoid, or hexagon. The structures of zigzag-edged GQDs can be unambiguously defined based on the distance from center to the six outermost zigzag edges, termed **di** (**i** = 1 to 6). The quantity **di** is given in units of the distance between neighboring zigzag chains, so that the indices of (**d1**, **d2**, **d3**, **d4**, **d5**, **d6**) would uniquely determine a structure of GQD. Due to the ambiguity in selecting the central point, only four of the six distances are independent. For example, the structures of (**6**, **6**, **6**, **6**, **6**, **6**) and (**5**, **5**, **6**, **7**, **7**, **6**) are exactly the same. In addition, the number of unique indices can be greatly reduced by taking the rotation and mirror symmetry of the honeycomb lattice into consideration.

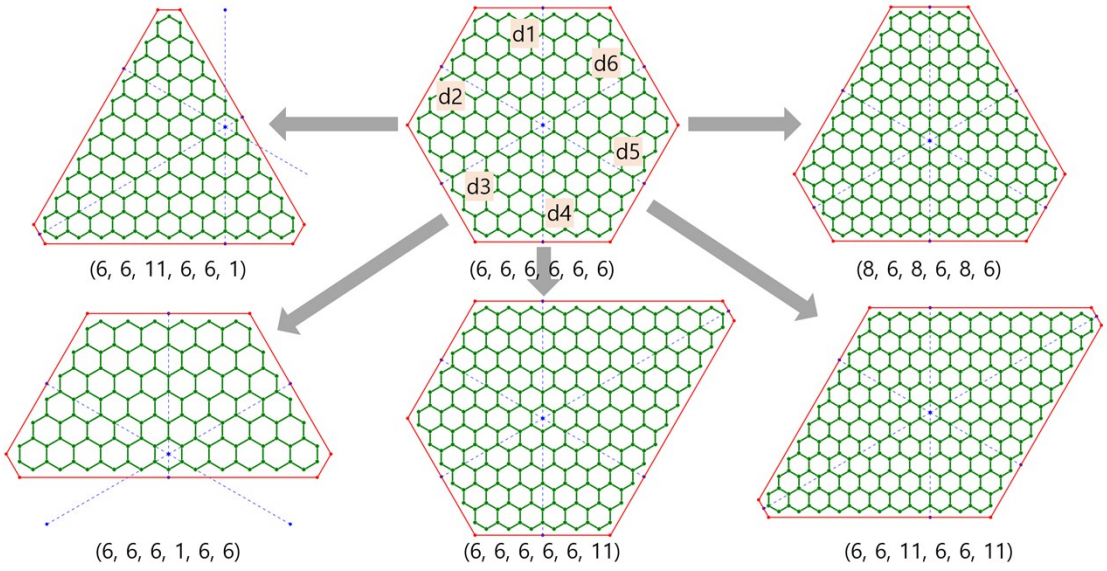

Figure S1. Structures of zigzag-edged GQDs determined based on the distances from the central point to the six outermost zigzag edges.

3. Fitting $E_{GE-M}(r)$

In order to estimate the oscillation in the interaction between a graphene edge and the Ru(0001) surface, we use a fragment of a carbon cluster with a small segment of zigzag edges to represent the edge of GQD; the other edges are terminated by hydrogen atoms. We then move the carbon cluster along the in-plane directions to calculate the two-dimensional map of the formation energy of a zigzag edge, based on DFT method. Next, the $E_{GE-M}(r)$ is fitted in the same

manner as $E_{GE-M}(r)$, namely,

$$E_{GE-M}(r) = E_{GE-M}^{0} + \Delta E_{GE-M}(r), \quad (6)$$

Where E_{GE-M}^{0} and $\Delta E_{GE-M}(r)$ represent the minimum and oscillation of the formation energy of a graphene edge on the Ru(0001) surface. Fig. 4j and 4d illustrate the fitting performance and the best fitted two-dimensional map of $E_{GE-M}(r)$. Note that $E_{GE-M}(r)$ has a lower symmetry than $E_{GE-M}(r)$, since zigzag graphene edges have only a mirror symmetry. The best fitting leads to the following expression for $E_{GE-M}(r)$,

$$E_{GE-M}(r) = -1.283 + 0.202\cos\left(-b_2 \cdot r - 0.825^{\circ}\right) - 0.290\left[\cos\left(b_1 \cdot r + 64.838^{\circ}\right) + \cos\left((b_2 - \right.\right. \quad (7)$$

where $\boldsymbol{b_1}$ and $\boldsymbol{b_2}$ are basis vectors of the reciprocal lattice, and $\boldsymbol{r}$ is the atomic position of a carbon atom.

4. Effect of GE-M oscillation on shapes of magic-sized GQDs.

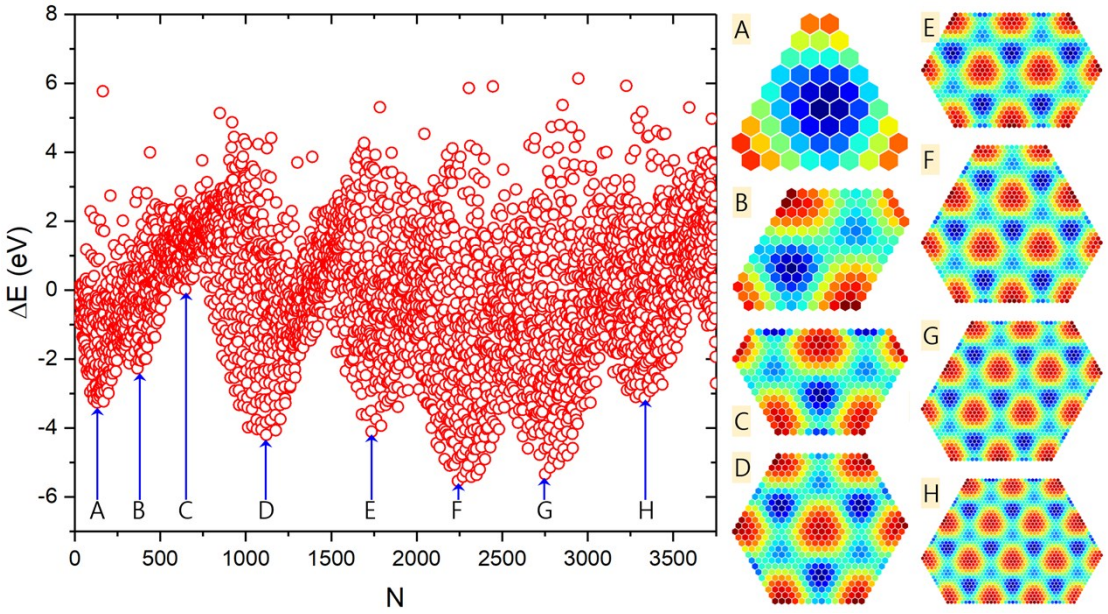

Figure S2. Highly stable graphene quantum dots on Ru(0001) surface predicted assuming modulated graphene edge-metal interaction. (Left) Difference in formation energy between numerical values and that estimated by eq. 2. in which, the oscillation of $\boldsymbol{E_{GB\text{-}M}}$ energies is set to be 0. (Right) Structures of GQDs corresponding to each of the local minima in left panel.