Supporting Information for:

Probing Quantum Capacitance of Typical Two-dimensional Lattices Based on Tight-binding Model

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S1. The effect of the band filling factor on the electronic structures and quantum capacitance

The band filling factor (*f*) of the electrodes changes during the charging and discharging process in supercapacitors. Thus, in addition to the half-filling case in the main manuscript, the filling factors away from half-filling with $f = 0.25$ and $f = 0.75$ have also been considered and analyzed as follows.

S1.1 The density of states and quantum capacitance of three lattices with only considering the nearest neighboring hopping parameter of t_1

The spin-polarized density of states (PDOS) and total density of states (TDOS) of three lattices at the band filling factors of 0.25, 0.5 and 0.75 with only considering the nearest neighboring (NN) interaction are presented in Figure S1. Under the rigid band approximation without strongly correlated interactions, the *f* only influences Fermi level (E_F) position. The electronic structure properties of the three lattices are basically kept intact. As shown in Figure S1(k, q), the TDOS of the square and hexagonal lattices relative to the E_F is symmetric for the half-filling factor of $f = 0.5$. In contrast, the downward shift and upward shift of the E_F corresponding to $f = 0.25$ and $f = 0.75$ respectively leads to the asymmetric electron-hole feature in TDOS for square and hexagonal lattices in Figure S1(j, p, l, r). For triangular lattice in Figure S1(m, n, o), the electron-hole asymmetric character in TDOS is all present for $f = 0.25$, $f = 0.5$ and $f =$

0.75 cases.

After introducing the ferromagnetic (FM) spin polarization, the distribution of the TDOS especially around the maximum value is more expanded although the maximum value is reduced. At the same time, the relatively high TDOS range moves with the change of the *f*. When *f* is less than 0.5, the higher TDOS range moves to the high-energy region. Conversely, when *f* is greater than 0.5, the higher TDOS range moves to the low-energy region. In particular, for the hexagonal lattice, the spin-up state moves to the low-energy region and the spin-down state moves to the high-energy region due to the spin splitting. Thus, relative to the non-magnetic state, a certain degree of FM spin polarization significantly improves the TDOS of the system near the energy of E_{Dirac} in Figure S1(p, q, r), which is expected to modulate the quantum capacitance (C_q) properties of the system.

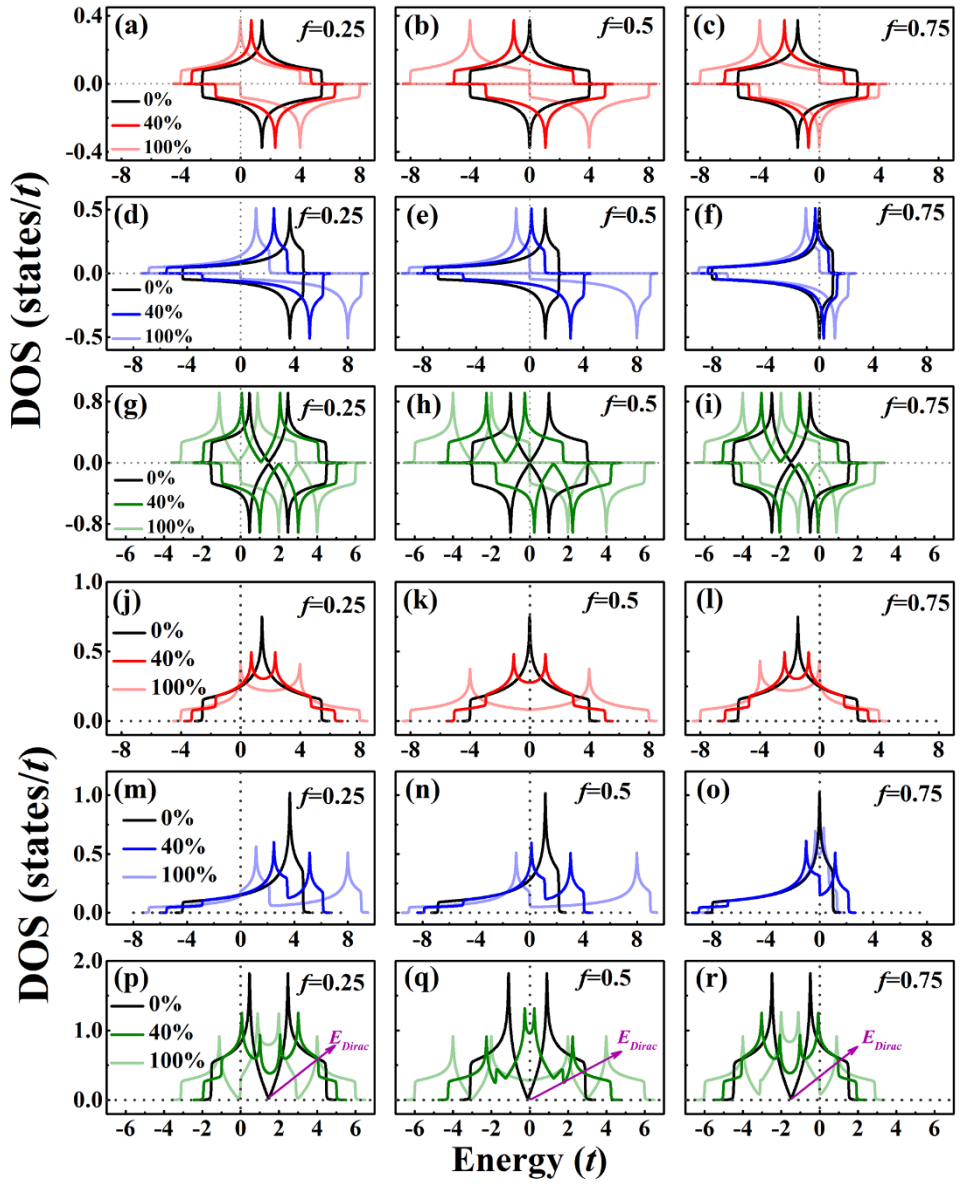

Figure S1. Spin-polarized density of states (PDOS) in (a-i) and total density of states (TDOS) in (j-r) at different spin polarizations for square lattice in (a-c, j-l), triangular lattice in (d-f, m-o), hexagonal lattice in (g-i, p-r) with $t_1 = t$, $t_2/t_1 = 0$. The band filling factors are 0.25 in (a, d, g, j, m, p), 0.5 in (b, e, h, k, n, q) and 0.75 in (c, f, i, l, o, r), respectively. E_{Dirac} in (p, q, r) is the energy corresponding to the Dirac point of graphene. The Fermi level marked by vertical dotted lines is set to zero.

The E_F marked by vertical dotted lines is set to zero. The above electronic structures directly affect the specific C_q of two-dimensional (2D) lattices. As shown in Figure S2(b, h), the specific C_q of the square and hexagonal systems are symmetric relative to zero bias. The triangular

system in Figure S2(e) is asymmetric relative to zero bias. Compared to the non-magnetic state, the voltage range with considerable specific C_q is expanded in the FM spin-polarized state although the maximum value of the specific C_q is reduced. When the system is less than half-filling in Figure S2(a, d, g), the range with high specific C_q moves to the negative bias voltage region. When the system is larger than half-filling in Figure S2(c, f, i), the range of high specific C_q moves to the positive bias voltage region. Especially for the hexagonal lattice, a certain degree of FM spin polarization significantly increases the specific C_q near the voltage of V_{Dirac} in Figure S2(g, h, i).

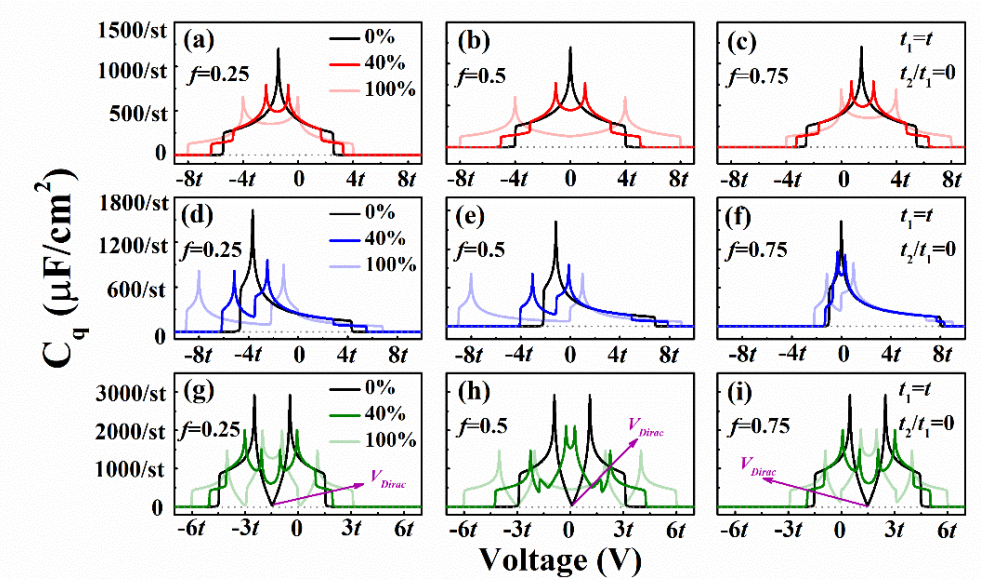

Figure S2. The specific quantum capacitance (C_q) at different spin polarization for square lattice in (a-c), triangular lattice in (d-f), hexagonal lattice in (g-i) with $t_1 = t$, $t_2/t_1 = 0$. The band filling factors are 0.25 in (a, d, g), 0.5 in (b, e, h) and 0.75 in (c, f, i), respectively. V_{Dirac} in (p, q, r) is the voltage corresponding to the Dirac point of graphene.

S1.2 The density of states and quantum capacitance of three lattices with both considering the nearest and the next nearest neighboring

hopping parameters of t_1 and t_2

After including the next-nearest neighboring (NNN) interaction in Figure S3, the electron-hole symmetric feature in TDOS is absent for three lattices. Since the occupied state is more extended than the empty state, the TDOS gets higher in the high-energy region. When the systems deviate from half-filling, e.g. f = 0.25 in Figure S3(j, m, p) and f = 0.75 in Figure S3(l, o, r), the shift direction of the E_F is similar to the t_2 = 0 case in Figure S1. Nevertheless, the shift of E_F for f = 0.25 in Figure S3(j, m, p) is larger than that of f = 0.75 case in Figure S3(l, o, r) due to the lower TDOS in occupied states. Because of the above electron-hole asymmetry of the TDOS, the specific C_q of the half-filled system in Figure S4(b, h) is no longer symmetric with respect to zero bias. When the system is less than half-filled, the voltage range with relatively high specific C_q shifts to the negative bias direction as shown in Figure S4(a, d, g). In contrast, when the system is higher than half-filled, the voltage range with high specific C_q shifts to the positive bias direction as shown in Figure S4(c, f, i). The shift of f = 0.25 is greater than that f = 0.75. The role of the FM polarization on the specific C_q is similar to t_2/t_1 = 0.0 case. Although the maximum value of TDOS decreases in FM spin-polarized state relative to that of the non-magnetic state, the range of the systems with high TDOS increases.

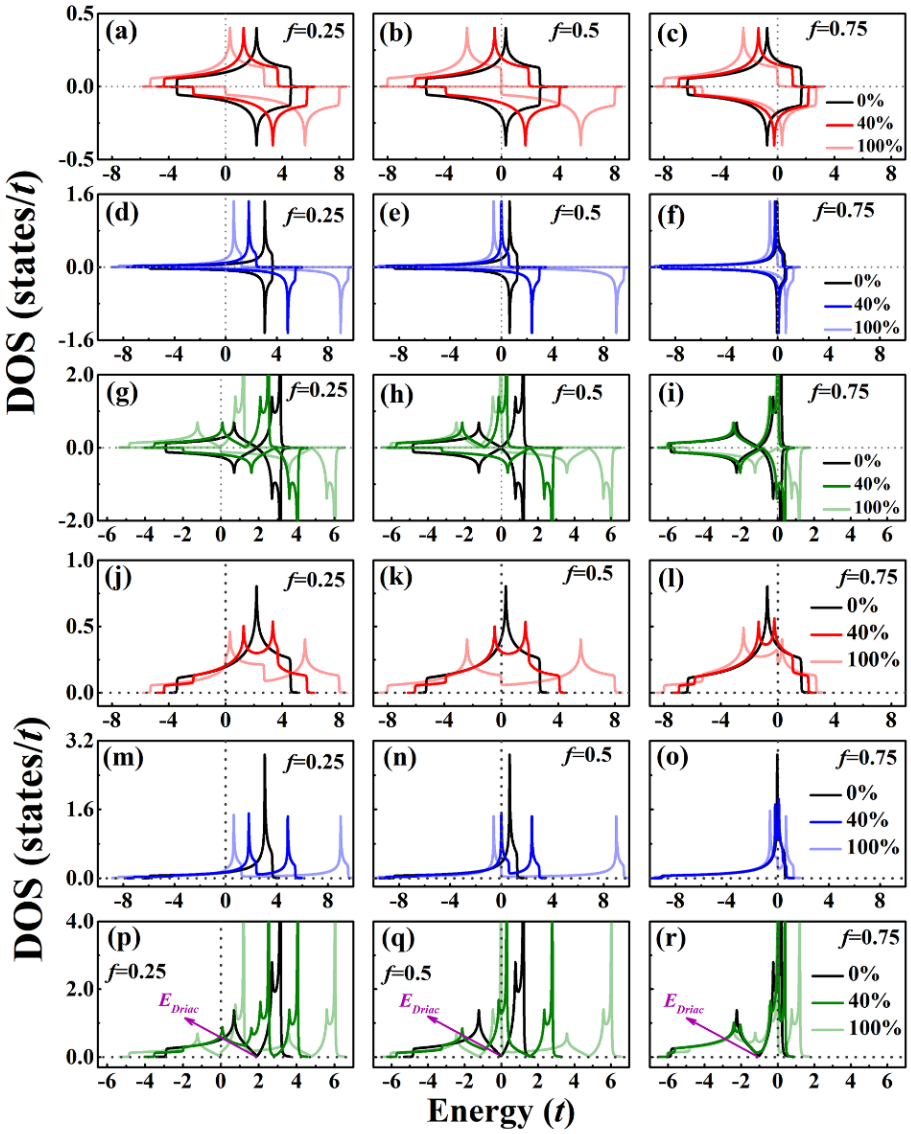

Figure S3. Spin-polarized density of states (PDOS) in (a-i) and total density of states (TDOS) in (j-r) at different spin polarizations for square lattice in (a-c, j-l), triangular lattice in (d-f, m-o), hexagonal lattice in (g-i, p-r) with $t_1 = t$, $t_2/t_1 = 0.2$. The band filling factors are 0.25 in (a, d, g, j, m, p), 0.5 in (b, e, h, k, n, q) and 0.75 in (c, f, i, l, o, r), respectively. E_{Dirac} in (p, q, r) is the energy corresponding to the Dirac point of graphene. The Fermi level marked by vertical dotted lines is set to zero.

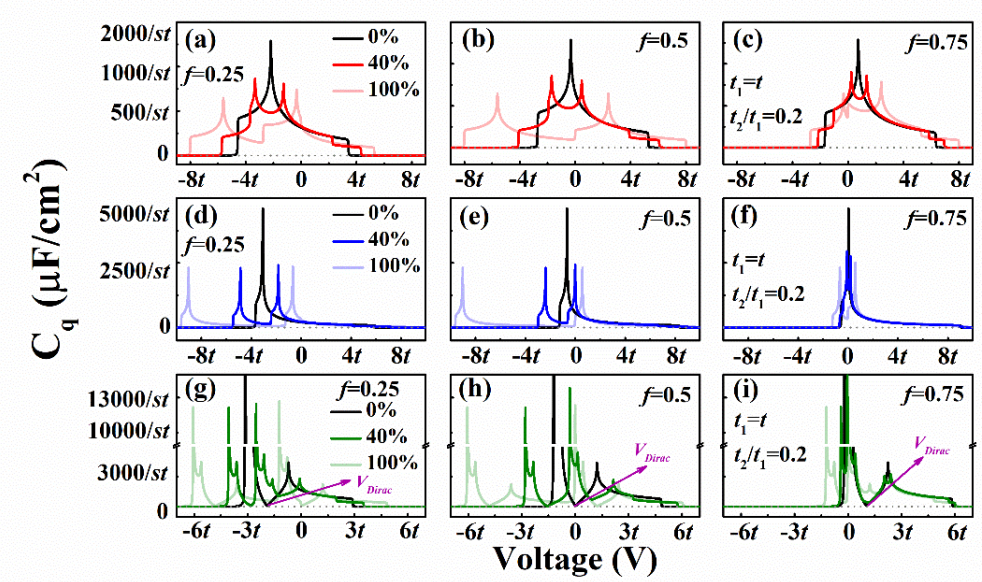

Figure S4. The specific quantum capacitance (C_q) at different spin polarizations for square lattice in (a-c), triangular lattice in (d-f), hexagonal lattice in (g-i) with $t_1 = t$, $t_2/t_1 = 0.2$. The band filling factors are 0.25 in (a, d, g,), 0.5 in (b, e, h) and 0.75 in (c, f, i), respectively. V_{Dirac} in (p, q, r) is the voltage corresponding to the Dirac point of graphene.

S2. The effect of the hopping parameters on the electronic structures and quantum capacitance

For different 2D electrode materials, their different bandwidths imply the different carrier hopping parameters. With the assumption of the NN hopping parameter $t_1 = t$, the ratio of the NNN carrier hopping parameter t_2 to t_1 is different, resulting in the change of the electronic structures and the C_q. Thus, besides $t_2/t_1 = 0.0$ and $t_2/t_1 = 0.2$, two sets of different hopping parameter ratios of $t_2/t_1 = 0.1$ and $t_2/t_1 = 0.5$ have been added to simulate the specific C_q of different materials as follows.

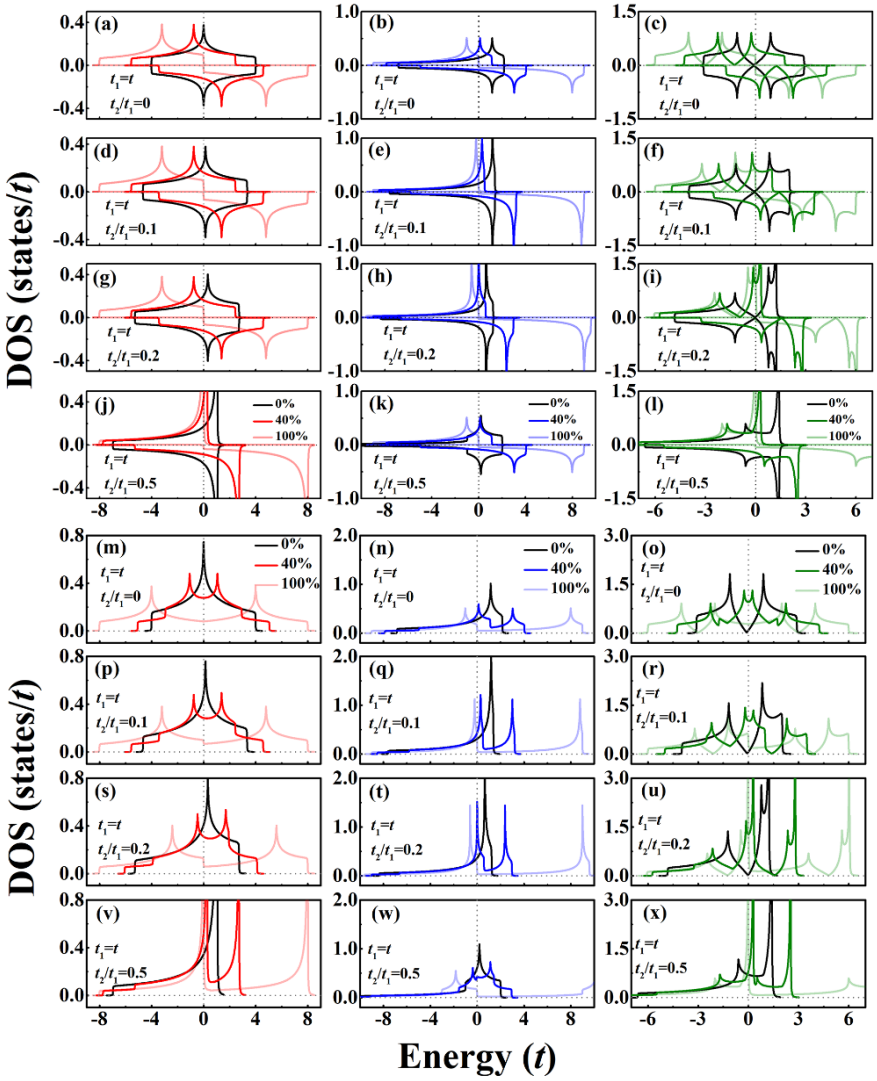

Figure S5. Spin-polarized density of states (PDOS) in (a-l) and total density of states (TDOS) in (m-x) at different spin polarization for square lattice in (a, d, g, j, m, p, s, v), triangular lattice in (b, e, h, k, n, q, t, w), hexagonal lattice in (c, f, i, l, o, r, u, x) with band filling factor of 0.5. The hopping parameters are $t_1 = t$, $t_2/t_1 = 0$ in (a-c, m-o), $t_2/t_1 = 0.1$ in (d-f, p-r), $t_2/t_1 = 0.2$ in (g-i, s-u) and $t_2/t_1 = 0.5$ in (j-l, v-x), respectively.

The introduction of t_2 makes the electron-hole asymmetry in TDOS, which is more evident especially in square and hexagonal lattices. As t_2/t_1 increases in Figure S5, the energy range of the occupied state is more expanded and the empty state is more localized. Thus, the maximum of the TDOS gradually increases and moves to the direction of higher energy region in Figure S5(m, p, s, v) of square lattice and in Figure S5(o, r, u, x)

of hexagonal lattice, leading to the increase of the specific C_q peak and the shift of the specific C_q to the direction of negative bias in Figure S6(a, d, g, j) of square lattice and in Figure S6 (c, f, i, l). When a certain degree of FM spin polarization occurs, the energy range with relatively considerable TDOS increases in the square and hexagonal systems. The voltage range with higher specific C_q of the 2D electrodes in Figure S6(a, d, g, j, c, f, i, l) is thus increased, indicating that electrolyte materials with wider operating voltage window could be matched and the energy density of supercapacitors would be increased.[1] For the triangular lattices, the FM spin polarization and smaller t_2 demonstrate similar effects on the TDOS and the specific C_q. However, as shown in Figure S5(w) for $t_2/t_1 = 0.5$, the unoccupied state is relatively expanded, leading to that the maximum of the specific C_q decreases and the voltage distribution around zero bias is extended with moderate specific C_q in Figure S6(k). Generally, t_2 is much weaker than t_1 since only t_1 is considered in some systems and $t_1/t_2 = 0.2$ in graphene.[2] Thus, the value of t_2/t_1 might not be that large and the effect of t_2 on the electronic structures and the specific C_q of 2D metallic electrodes is similar to the case of $t_2/t_1 = 0.1$ or $t_2/t_1 = 0.2$.

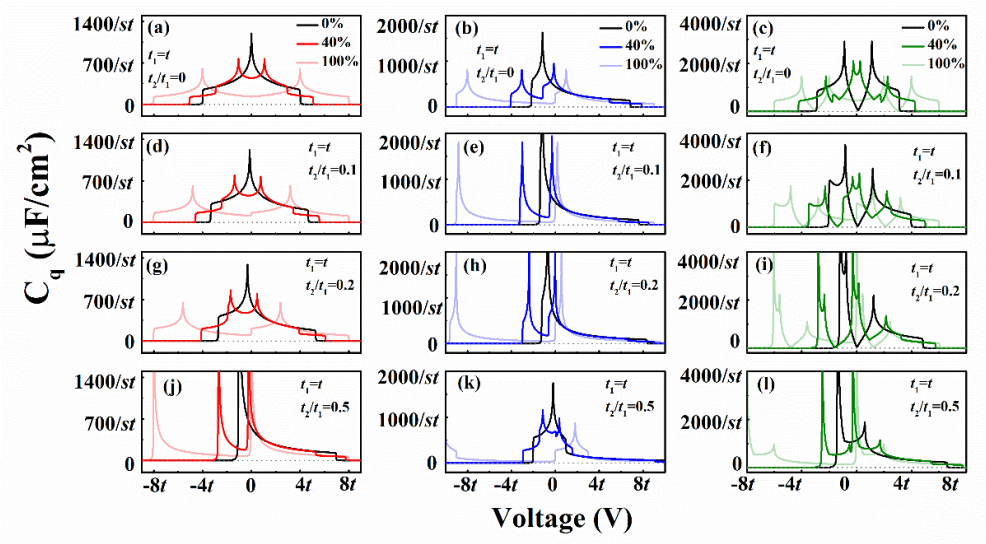

Figure S6. The specific quantum capacitance (C_q) at different spin polarization for square lattice in (a, d, g, j), triangular lattice in (b, e, h, k), hexagonal lattice in (c, f, i, l) with the band filling factor of 0.5. The hopping parameters are $t_1 = t$, $t_2/t_1 = 0$ in (a-c), $t_2/t_1 = 0.1$ in (d-f), $t_2/t_1 = 0.2$ in (g-i) and $t_2/t_1 = 0.5$ in (j-l), respectively.

REFERENCES

1. Yang, G.; Zhang, H.; Fan, X.; Zheng, W. Density Functional Theory Calculations for the Quantum Capacitance Performance of Graphene-Based Electrode Material. *J. Phys. Chem. C* **2015**, *119*, 6464-6470.

2. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109-162.