

Photocatalytic properties of graphene-supported titania clusters from density-functional theory

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Abstract

Density-functional theory calculations of $(\text{TiO}_2)_n$ clusters ($n = 1-5$) in the gas phase and adsorbed on pristine graphene as well as graphene quantum dots are presented. The cluster adsorption is found to be dominated by van der Waals forces. The electronic structure and in particular the excitation energies of the bare clusters and the TiO_2 /graphene composites are found to vary largely in dependence on the size of the respective constituents. This holds in particular for the energy and the spatial localization of the highest occupied and lowest unoccupied molecular orbitals. In addition to a substantial gap narrowing, a pronounced separation of photoexcited electrons and holes is predicted in some instances. This is expected to prolong the lifetime of photoexcited carriers. Altogether, TiO_2 /graphene composites are predicted to be promising photocatalysts with improved electronic and photocatalytic properties compared to bulk TiO_2 .

KEYWORDS

constrained DFT, density functional theory, graphene, photocatalytic properties, titania clusters, van der Waals

1 | INTRODUCTION

Photocatalysis is a promising technology to surmount environmental problems and also provide a renewable and sustainable energy resource.^[1-5] Among the different types of photocatalytic materials, namely TiO_2 ,^[5] ZnO ,^[6] CdS ,^[7] CdSe ,^[8] MgO ,^[9] $\alpha\text{-Fe}_2\text{O}_3$,^[10] and WO_3 ,^[11] titanium dioxide (TiO_2 ; titania) draws considerable interest because of its excellent photoactivity, high oxidation potential, non-toxicity, earth abundance, and long-standing physical and chemical stability.^[12,13] In general, TiO_2 based photocatalysts were intensely used in wastewater treatment of dyes,^[14,15] industrial wastewater,^[16] microbial disinfection,^[17,18] pharmaceuticals,^[18,19] and hormones.^[20] Nevertheless, two undesired characteristics of the TiO_2 , namely its lack of response to visible light and fast recombination rate of electron-hole pairs, hinder its wider application.^[21,22]

In principle, several strategies, including surface dye sensitization,^[23,24] particle doping,^[25,26] precious metal deposition,^[27,28]

particle size modification,^[29,30] and surface modification^[30-32] have been employed to overcome these drawbacks for the utilization of high-efficiency solar energy in photocatalytic applications. Even though all of these strategies extend the wavelength of photoactivation of TiO_2 into the visible region of the spectrum, surface modification is more promising to avoid several adverse effects such as thermal instability, charge recombination defects, and higher costs for practical applications.^[33-37] Accordingly, in recent years an accessible pathway for enhancing the photocatalytic activities of TiO_2 type materials is to combine it with several allotropes of carbon materials, because they are more likely to behave as an effective electron donor^[38-43] or acceptor^[44] to boost the photoinduced charge transfer and to mitigate the recombination of the photogenerated electron-holes.

Graphene (GR), a two-dimensional allotrope of carbon, has a particular set of unique features, including superior electron mobility, high thermal conductivity, high transparency, flexible structure, large specific surface area, outstanding optical properties, and quantum hall

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effects at room temperature.^[45–48] Owing to the high adsorption capacity of GR for organic pollutants, it has been utilized as an electrocatalyst and promotor in photocatalysis.^[49,50] Besides, because of the enhanced electrical and electronic properties and the synergistic effect between graphene and metal(oxide) nanoparticles, graphene-metal(oxide) composites also offer great potential for various applications including photocatalysis, batteries, photovoltaic devices, bioimaging, supercapacitors and sensors.^[51–55] Indeed, GR appears as a suitable candidate to be combined with TiO₂, in order to mitigate electron–hole recombination by exploiting the higher mobility of charge transferred into the GR sheet.^[49,50] The presence of GR may also act as a sensitizer by extending photoabsorption into the visible region.^[49,50] Furthermore, new reaction sites can also increase the overall reactivity. Zhang et al.^[56] suggested that the π -d electron coupling is instrumental for the fast transport of the photoinduced electron between GR and TiO₂, which efficiently suppresses the recombination of the photogenerated electron–hole pairs in TiO₂.

Nanosized TiO₂ has a higher surface-to-volume ratio than bulk titania, that is, TiO₂ clusters have a high density of active surface sites for adsorption and catalysis. Furthermore, TiO₂ clusters allow the photogenerated charges to reach the catalyst surface, so it reduces the undesired recombination rate of electron–hole pairs. Several theoretical and experimental studies have been conducted on neutral TiO₂ clusters.^[57–65] Also, the combination of TiO₂ clusters with GR-based materials has been theoretically studied.^[66–69] Geng et al. reported that the charge separation of valence band maximum (VBM) and conduction band minimum (CBM) by location at the cluster and GR sheet decreases the probability of electron–hole recombination, and the excitation energy decrease in the visible light region for the VBM contributed from C-2p is far lower than for Ti-3d.^[67] C vacancies in graphene or epoxide groups are suggested as preferred anchor points for TiO₂ on an otherwise rather shallow potential energy surface.^[68] As reported by Fischer et al.,^[69] the carbon support to TiO₂ clusters affects the binding energy of CO₂ significantly. Zhue et al. reported five times higher photocatalytic performance of the graphene quantum dot/TiO₂ complex compared to the highly efficient CaIn₂O₄ photocatalyst.^[70] More recently, Guidetti et al.^[71] found that GR flake-TiO₂ nanoparticle composites degrade as much as 70% more atmospheric NO_x than the titania photocatalyst. Following Georgakilas^[72], graphene monolayer flakes with dimensions of a few nanometers (2–20 nm) are termed graphene quantum dots (GQDs).

The present article aims at rationalizing the photocatalytic properties of TiO₂/GR composite materials. To this end, we use van der Waals-corrected density-functional theory (DFT) to determine the ground-state atomic structures of bare as well as GR and GQD adsorbed (TiO₂)_n clusters ($n = 1–5$). The electronic excitation properties of the respective systems are studied using local, hybrid, and constrained DFT. Subsequent to the description of the methodology in Section 2, the structural and energetic properties of bare and GR/GQD supported TiO₂ clusters are presented in Section 3. Section 4 concludes the manuscript.

2 | COMPUTATIONAL METHODOLOGY

The DFT calculations were performed using the Vienna ab-initio Simulation Package (VASP).^[73] The electron exchange and correlation energies were described within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.^[74] The accurate modeling of weakly bonded adsorbates is a significant challenge for DFT, because semi-local XC functionals do not adequately describe the long-range van der Waals (vdW) interactions.^[75–78] In order to account approximately for dispersion interaction, we utilized a semi-empirical dispersion correction scheme based on the London dispersion formula,^[79] the called DFT-D scheme.^[80–83] Specifically, we selected the DFT-D2 method proposed by Grimme.^[82] Test calculations using DFT-D3^[83] and DFT-D3BJ^[83,84] revealed only negligible deviations. The Bader technique^[85] was used to determine the charge transfer between TiO₂ clusters and GR/GDQ, and to analyze the chemical bonding.

The kinetic energy cut-off for plane-wave expansion was 500 eV, and the energy and force convergence criteria were 10^{−5} eV and 10^{−4} eV/Å, respectively. $4 \times 4 \times 1$ Γ -centred k -point sampling was used for TiO₂ clusters in a $6 \times 6 \times 1$ supercell of GR for geometry optimizations and electronic band structure calculation. Gaussian smearing^[86] of 0.05 eV was used for all geometry and band structure calculation. The partial density of states was calculated with the above computational parameters, except that the tetrahedral smearing with Blöchl corrections^[87] and a denser $9 \times 9 \times 1$ k -point grid were used. All (TiO₂)_n clusters ($n = 1–5$) and their interaction with GR were calculated in a hexagonal supercell with a lattice parameter of 14.81 Å. A cubic supercell with a lattice parameter of 32 Å was used to model TiO₂ clusters interacting with hexagonal armchair GQD. To minimize the interaction between adjacent clusters or material slabs, a minimum vacuum space of 10 Å was used for separation.

The cohesive energy per atom E_{Coh} was calculated as:

$$E_{\text{Coh}} = \frac{1}{n_{\text{Tot}}} \left[\sum_{i=1} n_i E_i - E_{\text{st}} \right], \quad (1)$$

where the E_i represents the energies of a single isolated atom, and the i index denotes the type of atom. E_{st} represents the total ground state energy of the complete system, n_{Tot} and n_i are the total numbers of atoms and the number of isolated i type atoms within the computational unit cell, respectively. The binding energy of adsorbed clusters was calculated as:

$$E_b = -E_{\text{ads}} = E_{\text{GR/GQD}} + E_{\text{cl}} - E_{\text{GR/GQD+cl}}, \quad (2)$$

where the $E_{\text{GR/GQD}}$ denotes the energy of the GR or GQD, E_{cl} is the energy of an isolated adcluster, $E_{\text{GR/GQD+cl}}$ denotes the total energy when the adcluster is adsorbed on GR or GQD.

The DFT-GGA electronic structure is known to suffer from an underestimation of electronic excitation energies, as it does not account accurately for electronic self-energy effects.^[88,89] Moreover,

optical excitation energies cannot be directly concluded from ground-state DFT calculations, as they neglect the electron-hole attraction. In order to account for these shortcomings, we complemented the DFT-GGA electronic structure calculations by hybrid DFT, using the Heyd-Scuseria-Ernzerhof (HSE06) functional.^[90] DFT-GGA and hybrid DFT eigenvalues of the HOMO and LUMO states were aligned with respect to vacuum level obtained from the calculated local electrostatic potential in the vacuum region of the supercell. Furthermore, the delta self-consistent field (Δ SCF)^[91–94] method, also termed constrained DFT, was utilized. Within the Δ SCF method, the electron affinity, ionization energy, and the quasiparticle energy gap between the highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO gap) were calculated as:

$$EA_v = E(N) - E(N+1) \approx -E_{\text{LUMO}}, \quad (3)$$

$$EA_{\text{ad}} = E(N) - E^*(N+1), \quad (4)$$

$$IE_v = E(N-1) - E(N) \approx -E_{\text{HOMO}}, \quad (5)$$

$$IE_{\text{ad}} = E^*(N-1) - E(N), \quad (6)$$

$$E_{\text{HL}}^{\Delta\text{SCF}} = IE_v - EA_v, \quad (7)$$

where $E(N)$, $E(N+1)$, and $E(N-1)$ are the energies of the systems with N , $N+1$, and $N-1$ electrons with the geometry of the neutral system, respectively. However, $E^*(N+1)$ and $E^*(N-1)$ are the energies of the systems with $N+1$ electrons $N-1$ electrons in their optimized geometries. According to Koopman's theorem, EA_v and IE_v calculated above can be approximately related to E_{LUMO} and E_{HOMO} , respectively. The explicit calculations suffer from the limitations of the periodic boundary conditions. Therefore, monopole and dipole corrections^[95,96] were applied to the anion and cation systems to compensate for the errors in the total-energy and forces induced by spurious long-range electrostatic interactions between neighboring supercells. The optical gap or electron-hole pair excitation, which includes the attractive Coulomb interaction of the excited electron and hole screened by the remaining electrons, was calculated as:

$$E_{\text{Op}}^{\Delta\text{SCF}} = E(N, e+h) - E(N), \quad (8)$$

where $E(N, e+h)$ is obtained by self-consistent optimization of the electronic degrees of freedom in the presence of an electron-hole pair. This calculation was done by applying the occupation constraint that the HOMO of the ground-state system contains a hole, and the excited electron resides in the LUMO of the ground-state system. The lowest emission energy, measured in luminescence experiments, is calculated as:

$$E_{\text{Op}^*}^{\Delta\text{SCF}} = E^*(N, e+h) - E^*(N), \quad (9)$$

where $E^*(N, e+h)$ is the total energy obtained after structurally and electronically optimizing the system in the presence of the electron-

hole pair. $E^*(N)$ is the self-consistent total energy of the system in its ground state electronic configuration evaluated at the optimized geometry of the pair-excited structure. For clarity, see also the Scheme S1. The Stokes shift between the absorption and emission edges of the system was calculated as:

$$\Delta_{\text{ST}} = E_{\text{Op}}^{\Delta\text{SCF}} - E_{\text{Op}^*}^{\Delta\text{SCF}}, \quad (10)$$

Finally, the exciton binding energy E_b^{ex} of the system is calculated as the difference between the quasiparticle HOMO-LUMO energy gap $E_{\text{HL}}^{\Delta\text{SCF}}$ and optical gaps $E_{\text{Op}}^{\Delta\text{SCF}}$, that is,

$$E_b^{\text{ex}} = E_{\text{HL}}^{\Delta\text{SCF}} - E_{\text{Op}}^{\Delta\text{SCF}}. \quad (11)$$

3 | RESULTS AND DISCUSSION

3.1 | TiO₂ clusters

The calculation started by a systematic search for the neutral titanium dioxide clusters with one, two, three, four, and five units of TiO₂. The optimized (TiO₂)_n structures with $n = 1-5$ (see Figure 1) are in good agreement with those obtained previously by experiment and theory.^[64,65] The minimum energy structures of (TiO₂)₁, (TiO₂)₂, (TiO₂)₃, (TiO₂)₄, and (TiO₂)₅ clusters have C_{2v}, C_{2h}, C_s, C_{2v}, and C_s point group symmetry, respectively. The cohesive energy per atom increases by increasing the unit size of TiO₂, see Table 1 and Figure 1. Hence, bigger size TiO₂ clusters are energetically more stable than smaller ones. The Bader charge analysis reveals that the Ti atom donates 0.7–1.0 e[−] to each bonding O atom, that is, the TiO₂ clusters have ionic bonds.

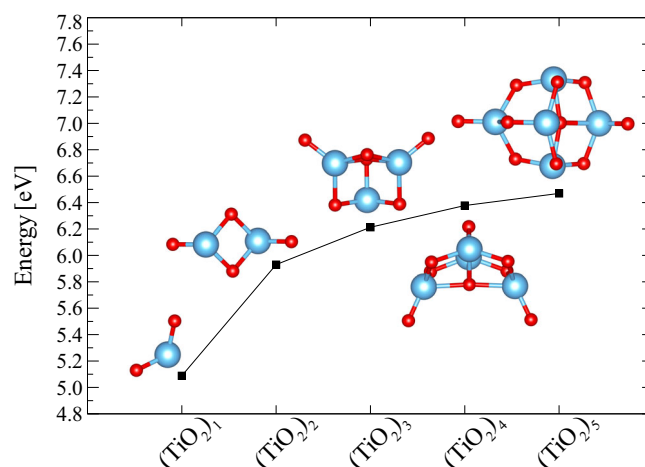


FIGURE 1 Calculated cohesive energy per atom in dependence on the titania cluster size. The insets show the geometric structure of the energetically most favorable neutral TiO₂ clusters. Blue and red spheres represent Ti and O atoms, respectively. The solid line is to guide the eye [Color figure can be viewed at wileyonlinelibrary.com]

All ground state structures of TiO_2 clusters are found to be nonmagnetic.

As shown in Table 1, we calculate both vertical and adiabatic electron affinities (EA_v and EA_{ad}) and ionization energies (IE_v and IE_{ad}) for the TiO_2 clusters. The EA_{ad} and IE_{ad} are in a fair agreement with the experimentally reported data.^[58–61] Here, it has to be mentioned that isomers with high electron affinity rather than those with the lowest energy may be selectively observed in photoemission experiments.^[63]

The calculated HOMO-LUMO energy gaps for the various clusters depend strongly on the level of theory: GGA, HSE, and ΔSCF predict value between 1.55–2.89, 3.06–4.27, and 6.7–8.07 eV, respectively. DFT-GGA provides systematically the lowest values, as expected from the neglect of the electron self-energy.^[88] The partial inclusion of exact exchange in hybrid DFT leads to distinct gap widening in hybrid DFT. Even larger values, which are in fact consistent with the order of magnitude expected from the measured ionization energies and electron affinities, are obtained from the ΔSCF calculations. The latter method does account for electronic many-body effects and may thus be considered to yield the most reliable data. Neither of the computational methods used here shows a monotonous decrease of the HOMO-LUMO energy gap with increasing cluster size, as one might expect from the quantum confinement effect.^[97] The reason for this might be the small size of the clusters studied here. Therefore, the excitation energies are strongly affected by surface and symmetry effects.

The $\text{O}_2/\text{H}_2\text{O}$ oxidation potential and the H^+/H_2 reduction potential equal -4.44 and -5.67 eV on the physical (0 and 1.229 V on the electrochemical) scale at $\text{pH} = 0$, respectively.^[98] As shown in Figure 2, the respective values are well within the HOMO-LUMO gap obtained within ΔSCF , that is, the energies of photogenerated holes (electrons) of TiO_2 clusters are lower (higher) than the electrochemical potential of the $\text{O}_2/\text{H}_2\text{O}$ (H^+/H_2) redox couple. Thus, TiO_2 clusters in

principle have a suitable electronic structure for the solar water splitting. Furthermore, the charge density separation of HOMO and LUMO by location at the corner and center of clusters mitigates the probability of electron-hole recombination (see Figure S2). The optical gaps of the TiO_2 clusters vary between 2.09 and 2.86 eV and are thus measurably smaller than the optical gaps of TiO_2 bulk in its rutile ($E_g = 3.0\text{--}3.4$ eV) and anatase phase ($E_g = 3.2\text{--}3.6$ eV).^[59,99,100] Thus, they are more responsive to visible light. As shown in Table 1, the optical gaps of the TiO_2 clusters are quite close to the bare DFT HOMO-LUMO energy gaps, indicating the near cancellation of the quasiparticle gap opening and Coulomb attraction of electrons and holes. We calculate large exciton binding energies of about 5.98, 5.13, 4.25, 4.53, and 4.07 eV in $(\text{TiO}_2)_1$, $(\text{TiO}_2)_2$, $(\text{TiO}_2)_3$, $(\text{TiO}_2)_4$, and $(\text{TiO}_2)_5$ clusters, respectively. The results show that in particular the small clusters have a strong electrostatic electron-hole pair interaction, indicating a significant quantum confinement effect in TiO_2 clusters. Furthermore, the large Stokes shift shows that there is strong exciton-phonon coupling, which increases with cluster size.

3.2 | TiO_2 clusters on pristine graphene

Next, the interaction of the TiO_2 clusters with pristine GR is investigated. Depending on cluster size and symmetry, up to hundred start configurations were used to determine the optimum binding geometry. In any case, it is found that the TiO_2 clusters bond preferentially with Ti to the GR surface. The adsorbed TiO_2 clusters only negligibly strain the GR structure. The most favorable adsorption configurations are shown in Figure 3. They are largely consistent with previous theoretical results,^[67–69] with remaining differences related to the neglect of vdW forces or limitations with respect to the number of starting configurations in previous studies.

TABLE 1 The calculated parameters for neutral TiO_2 clusters^a

	E_{Coh} (eV)	$\Delta\rho_{\text{Ti-O}}$ (e [−])	EA_v (eV)	EA_{ad} (eV)	$\text{EA}_{ad}^{\text{exp}}$ (eV)	IE_v (eV)	IE_{ad} (eV)	$\text{IE}_{ad}^{\text{exp}}$ (eV)	$E_{\text{HL}}^{\text{GGA}}$ (eV)	$E_{\text{HL}}^{\text{HSE}}$ (eV)	$E_{\text{HL}}^{\Delta\text{SCF}}$ (eV)	$E_{\text{Op}}^{\Delta\text{SCF}}$ (eV)	Δ_{ST} (eV)	E_b^{ex} (eV)
$(\text{TiO}_2)_1$	5.09	0.8	1.58	1.61	1.59 (3) ^{b,c}	9.65	9.50	9.5 (1) ^d	2.05	3.52	8.07	2.09	0.51	5.98
$(\text{TiO}_2)_2$	5.92	0.8–0.9	1.64	1.83	2.10 (8) ^b , 2.06 (5) ^c	9.63	9.42	10.0 (5) ^e	2.89	4.27	7.99	2.86	1.24	5.13
$(\text{TiO}_2)_3$	6.21	0.7–0.8	2.59	2.89	2.9 (1) ^b , 2.78 (10) ^c	9.29	9.17	–	1.55	3.06	6.70	2.45	1.27	4.25
$(\text{TiO}_2)_4$	6.37	0.7–1.0	2.17	2.85	3.3 (2) ^b , 3.00 (15) ^c	9.55	9.40	–	2.44	4.09	7.38	2.85	1.66	4.53
$(\text{TiO}_2)_5$	6.46	0.8–1.0	2.40	2.85	3.15 (20) ^c	9.33	9.08	–	2.31	3.79	6.93	2.86	1.68	4.07

^aThe cohesive energy per atom, E_{Coh} ; the charge donation from Ti to O, $\Delta\rho_{\text{Ti-O}}$; the vertical and adiabatic electronic affinities, EA_v and EA_{ad} ; the vertical and adiabatic ionization energies, IE_v and IE_{ad} ; experimental electron affinities and ionization energies, $\text{EA}_{ad}^{\text{exp}}$ and $\text{IE}_{ad}^{\text{exp}}$; $E_{\text{HL}}^{\text{GGA}}$, $E_{\text{HL}}^{\text{HSE}}$, and $E_{\text{HL}}^{\Delta\text{SCF}}$ are HOMO-LUMO energy gaps based on GGA, HSE and ΔSCF , respectively; $E_{\text{Op}}^{\Delta\text{SCF}}$ is optical gap based on ΔSCF ; the Stokes shift, Δ_{ST} ; the exciton binding energy, E_b^{ex} . Numbers in parentheses represent estimated experimental uncertainties in the last digits.

^bSee Table 3 in Wu and Wang^[58].

^cSee the value of Adiabatic Detachment Energies of anions TiO_2^- clusters in Table 1 in Zhai and Wang^[59], which represents Adiabatic Electronic Affinities of neutral TiO_2 clusters.

^dSee Hildenbrand^[60].

^eSee Balducci et al.^[61].

FIGURE 2 Calculated energies of the highest occupied and lowest unoccupied molecular orbitals, E_{HOMO} and E_{LUMO} , of titania clusters in relation to the redox reactions of water splitting [Color figure can be viewed at wileyonlinelibrary.com]

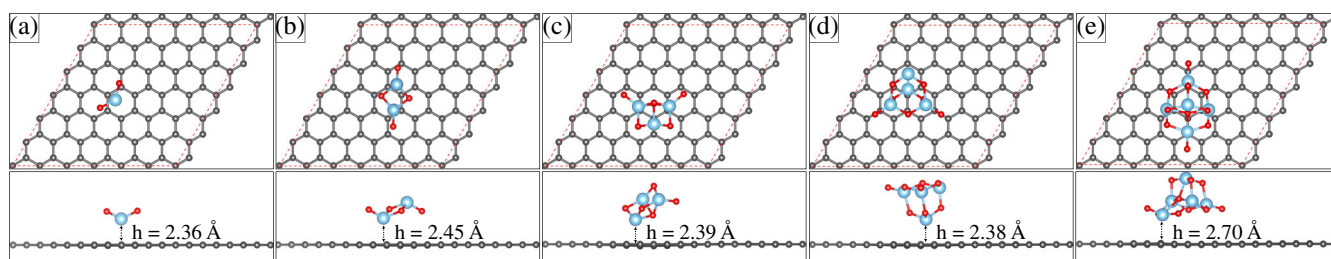
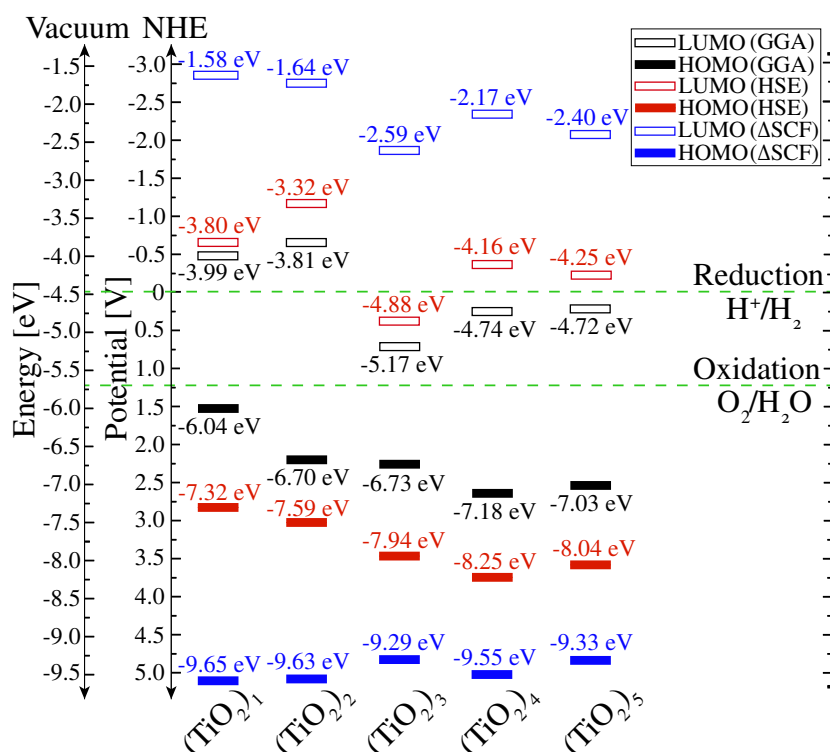


FIGURE 3 Top and side views of the energetically most favorable $(\text{TiO}_2)_n/\text{graphene}$ configurations within the (6×6) supercell for (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, and (e) $n = 5$. Blue, red, and dark gray spheres represent Ti, O, and C atoms, respectively. The dashed line represents the hexagonal unit cell [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 The calculated parameters for TiO_2 clusters on GR^a

	h (Å)	$E_b^{w-\text{vdW}}$ (eV)	$E_b^{wo-\text{vdW}}$ (eV)	$\Delta\rho_{\text{GR-TiO}_2}$ (e^-)	E_g^{GGA} (eV)	E_g^{HSE} (eV)
$(\text{TiO}_2)_1/\text{GR}$	2.36	1.08	0.72	0.1	14	28
$(\text{TiO}_2)_2/\text{GR}$	2.45	1.22	0.68	0.1	38	52
$(\text{TiO}_2)_3/\text{GR}$	2.39	1.56	0.98	0.2	45	66
$(\text{TiO}_2)_4/\text{GR}$	2.38	1.41	0.83	0.2	36	53
$(\text{TiO}_2)_5/\text{GR}$	2.70	1.04	0.27	0.1	6	6

^aThe GR- TiO_2 cluster distance, h ; the binding energy with and without vdW correction, $E_b^{w-\text{vdW}}$, and $E_b^{wo-\text{vdW}}$; the charge transfer from GR to TiO_2 clusters, $\Delta\rho_{\text{GR-TiO}_2}$, E_g^{GGA} , and E_g^{HSE} are band gaps based on GGA and HSE, respectively.

The vertical distance of the nearest atoms between TiO_2 clusters and GR varies between 2.36 and 2.70 Å; see Table 2 and Figure 3. As shown in Table 2, upon adsorption there is an electron transfer from GR to the TiO_2 clusters of the order of 0.1–0.2 e^- . Thus, the induced electric field at the interface may enhance the photoactivity of TiO_2

clusters by improving the electron-transfer rate and providing more reaction active sites for the degradation of environmental pollutants.^[101,102] Still, there is only little charge overlap between the GR π electrons and the adsorbate (see Figure S3). This is consistent with the total energy findings that demonstrate a sizeable contribution of

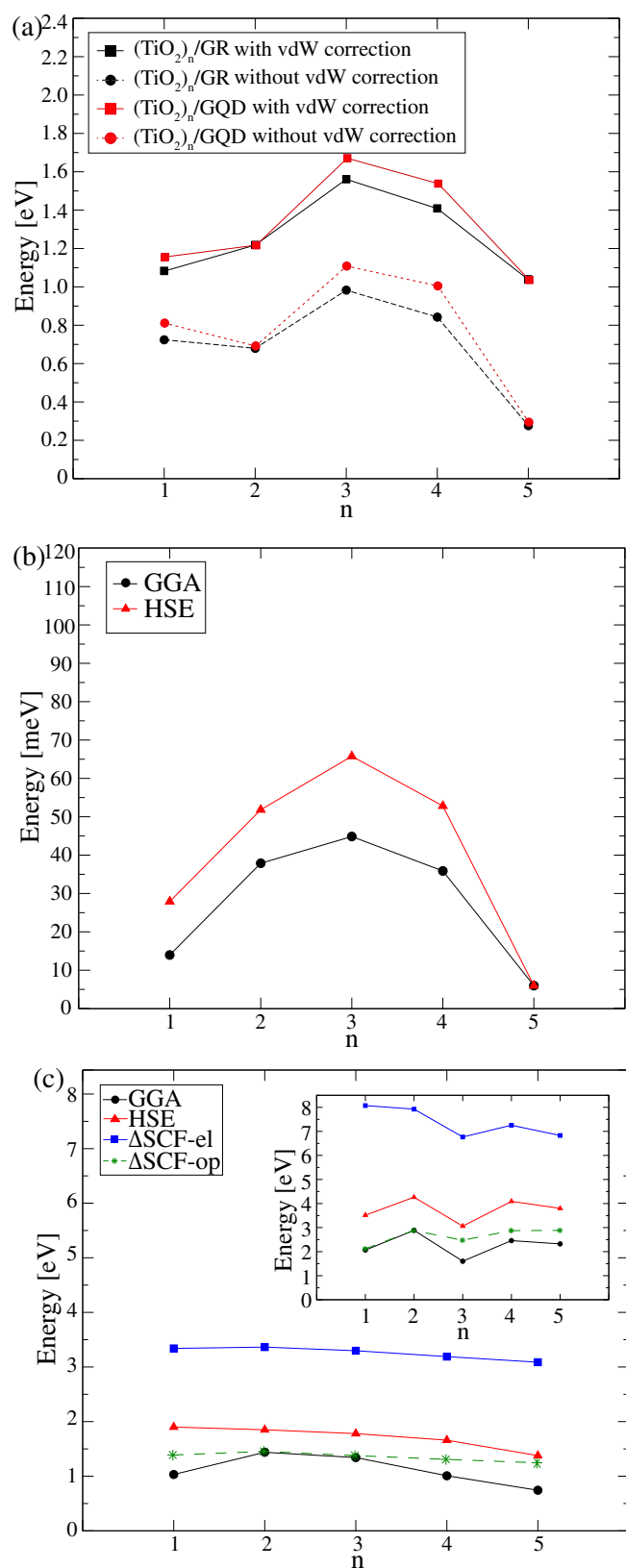


FIGURE 4 (a) Calculated binding energy of GR and GQD adsorbed $(\text{TiO}_2)_n$ clusters. (b) Band gap of GR adsorbed $(\text{TiO}_2)_n$ clusters. (c) HOMO-LUMO energy gap and the optical gap of GQD adsorbed $(\text{TiO}_2)_n$ clusters. The inset shows the HOMO-LUMO energy gap and optical gap of the isolated titania clusters for comparison. The solid lines are to guide the eye [Color figure can be viewed at wileyonlinelibrary.com]

vdW forces to the binding between pristine GR and TiO_2 clusters, see Figure 4a.

The perturbation by the adsorbed TiO_2 clusters leads to a splitting of the GR linear bonding and antibonding π bands (Dirac cone) at the Fermi level (see Figure S4 and Figure 4b). The symmetry break in the carbon lattice opens a small band gap. However, considering the calculated values, one word of caution is in order: The calculations are performed using periodic boundary conditions describing a (6×6) GR unit cell. The band gap opening will not only depend on the cluster size, but also increase with decreasing unit cell size corresponding to increasing cluster coverage.

The projected density of states (PDOS) of $(\text{TiO}_2)_n/\text{GR}$, shown in Figure 5, shows that both valence band (VB) and conduction band (CB) states mainly originate from the GR carbon atoms, and that the characteristic V shape of the graphene PDOS at the Dirac point is almost conserved with the exception of the small band gap opening. However, there is a notable contribution of $(\text{TiO}_2)_n$ clusters states to the total DOS that increases with cluster size for the CB and decreases with cluster size for the VB. There is a partial hybridization between GR and $(\text{TiO}_2)_n$ VB and CB states as seen in the band decomposed charge density (see the last column of Figure S4).

3.3 | TiO_2 clusters on graphene quantum dot

Finally, the TiO_2 cluster interaction with GQDs is explored. The electronic character of GR is changed from semimetal to semiconductor and depends on the flake size due to the quantum confinement. The stable structure of GQD depends on their size, shape, and temperature. The hexagonal GQDs with an armchair edge are thermodynamically more stable than other GQD forms.^[103] Hexagonal-like GQDs have already been synthesized in the diameter range of 1.65–21 nm (~ 2.1 – 317.3 nm² surface area) by chemical exfoliation from graphite nanoparticles.^[104] Thus, we use the hexagonal armchair GQD as a model system. Since GQDs from bottom-up synthesis are generally hydrogen passivated,^[105] the quantum dot edges in our models are passivated by hydrogen in order to saturate the dangling bonds.

At first, bare and $(\text{TiO}_2)_1$ decorated GQD of various sizes (~ 1 – 13 nm²) were explored with respect to the equilibrium geometry, total energy, and band gap (see Figure S5). The experimental HOMO-LUMO band edges (~ -3.3 to -5.7 eV vs. vacuum level) and band gap (~ 2.4 eV) for the coil GQD (~ 60 carbon rings)^[106] are, respectively, in reasonable agreement with the present ΔSCF results (-2.69 to -5.22 eV vs. vacuum level and 2.53 eV for $\text{C}_{222}\text{H}_{42}$ GQD [91 carbon rings]). Furthermore, for the $\text{C}_{114}\text{H}_{30}$ GQD, the theoretically predicted electronic band gap (3.51 eV) and exciton binding energy (1.37 eV) obtained from many-body perturbation theory^[107] are in fair agreement with the respective ΔSCF results of 3.45 and 1.93 eV calculated here for the identical system. Obviously, both the HOMO-LUMO energy gap and the optical gap of the GQDs depend strongly on their size. They gradually decrease with increasing GQD's size (see Figure S5 and Table S1). The optical gaps of bare and $(\text{TiO}_2)_1$

FIGURE 5 The total and projected density of states for the adsorbed $(\text{TiO}_2)_n$ cluster (a) $n = 0$, (b) $n = 1$, (c) $n = 2$, (d) $n = 3$, (e) $n = 4$, and (f) $n = 5$ with the GR. Note the (decimal) logarithmic scale [Color figure can be viewed at wileyonlinelibrary.com]

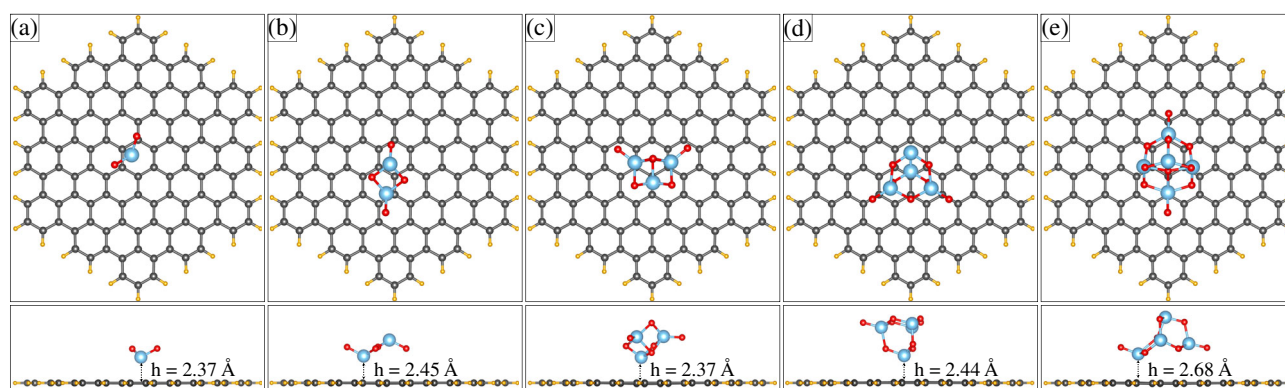
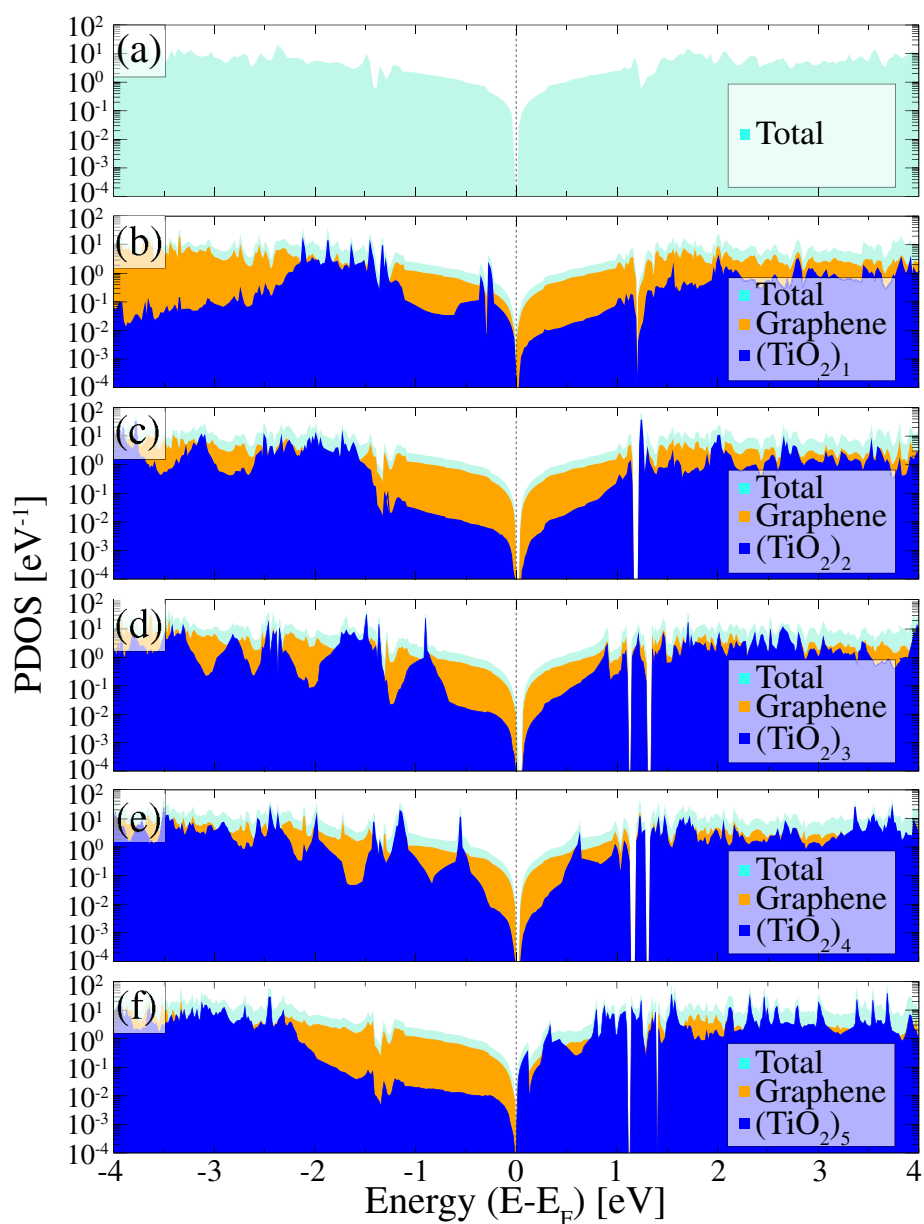


FIGURE 6 Top and side views of the energetically most favorable $(\text{TiO}_2)_n/\text{GQD}$ configurations for (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, and (e) $n = 5$. Blue, red, dark gray, and orange spheres represent Ti, O, C, and H atoms, respectively [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 The calculated parameters for TiO₂ clusters on GQD^a

	<i>h</i> (Å)	<i>E_b^{w-vdW}</i> (eV)	<i>E_b^{wo-vdW}</i> (eV)	$\Delta\rho_{\text{GQD-TiO}_2}$ (e ⁻)	<i>E_{HL}^{GGA}</i> (eV)	<i>E_{HL}^{HSE}</i> (eV)	<i>E_{HL}^{ΔSCF}</i> (eV)	<i>EA_v</i> (eV)	<i>EA_{ad}</i> (eV)	<i>IE_v</i> (eV)	<i>IE_{ad}</i> (eV)	<i>E_{Op}^{ΔSCF}</i> (eV)	Δ_{ST} (eV)	<i>E_b^{ex}</i> (eV)
(TiO ₂) ₁ /GQD	2.37	1.15	0.81	0.2	1.03	1.90	3.37	2.40	2.43	5.77	5.75	1.41	0.16	1.96
(TiO ₂) ₂ /GQD	2.45	1.22	0.69	0.1	1.44	1.85	3.38	2.31	2.33	5.69	5.68	1.46	0.09	1.92
(TiO ₂) ₃ /GQD	2.37	1.67	1.11	0.2	1.37	1.78	3.34	2.54	2.60	5.88	5.86	1.40	0.05	1.94
(TiO ₂) ₄ /GQD	2.44	1.53	1.00	0.2	1.05	1.66	3.26	2.67	2.74	5.93	5.91	1.38	0.30	1.88
(TiO ₂) ₅ /GQD	2.68	1.03	0.29	0.1	0.74	1.41	3.18	2.49	2.63	5.67	5.66	1.35	0.33	1.83

^aThe GQD-TiO₂ cluster distance, *h*; the binding energy with and without vdW correction, *E_b^{w-vdW}* and *E_b^{wo-vdW}*; the charge transfer from GQD to clusters; $\Delta\rho_{\text{GQD-TiO}_2}$, *E_{HL}^{GGA}*, *E_{HL}^{HSE}*, and *E_{HL}^{ΔSCF}* are HOMO-LUMO energy gaps based on GGA, HSE, and ΔSCF, respectively; the adiabatic electronic affinity and ionization energy, *EA_{ad}* and *IE_{ad}*; *E_{Op}^{ΔSCF}* is optical gap based on ΔSCF; the Stokes shift, Δ_{ST} ; the exciton binding energy, *E_b^{ex}*.

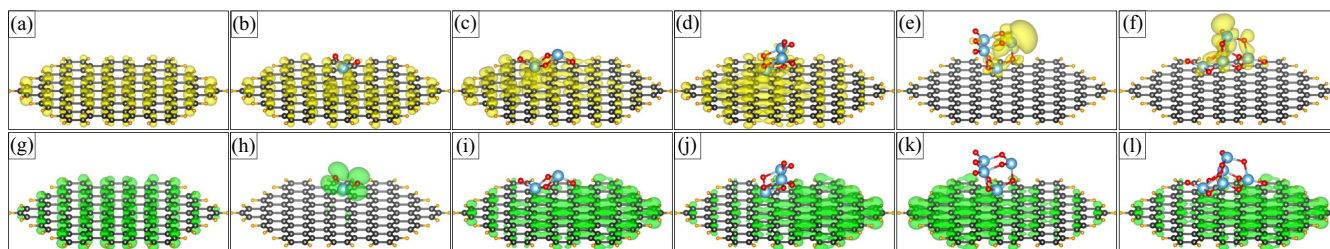


FIGURE 7 The decomposed charge density of (a–f) the lowest unoccupied and (g–l) highest occupied molecular orbital, respectively, LUMO and HOMO energy levels of (TiO₂)_n clusters (*n* = 0–5) on the surface of GQD. The isosurface level of charge density is taken to be that at $67.5 \times 10^{-5} \text{ e}^-/\text{\AA}^3$ ($1 \times 10^{-4} \text{ e}^-/\text{Bohr}^3$) [Color figure can be viewed at wileyonlinelibrary.com]

decorated GQS larger than about 3 nm² are energetically essentially below the spectral range of visible light.

Therefore, we focus in the following on a GQD with 3.18 nm² surface, consisting of 114 carbon and 30 H atoms. This GQD is used to study the adsorption of (TiO₂)_n clusters. By using a variety of plausible starting configurations, we arrived at the models shown in Figure 6, which describe the most favorable geometry for each cluster size. It can be seen that the TiO₂ clusters bond to the GQD similarly as to pristine GR. This also holds for structural details such as the vertical distance between TiO₂ clusters and pristine GR, see Table 3 and Figure 6.

The TiO₂ clusters are slightly stronger bonded to the GQD than to GR. Van der Waals forces constitute again a large fraction of the cluster GQD interaction, see Figure 4a. The Bader charge analysis (cf. Table 3) shows an electron transfer from the GQD to the TiO₂ clusters of about 0.1–0.2 e⁻, similar to the absorption of titanium clusters on pristine graphene. Similar is also the small charge density overlap at the interface (see Figure S6).

The GQD TiO₂ charge transfer upon bonding can be understood from their different ionization energies, see Figure S7. Upon combining the clusters and the GQDs, the respective Fermi levels align, electrons are transferred across the interface, and an electric field builds up. The relative positions of the TiO₂ cluster and GQD HOMO and LUMO states are affected in such a way that for some configurations, for example, (TiO₂)₁, (TiO₂)₄, and (TiO₂)₅ a transfer of photoelectrons

across the interface can be expected. This will enhance their lifetime and thus photocatalytic activity. This holds in particular if there is only weak hybridization between the cluster and GQD HOMO and LUMO states, as observed, for example, for (TiO₂)₄ and (TiO₂)₅, cf. Figure 7. Compared to the bare (TiO₂)_n clusters, both the HOMO-LUMO quasi-particle gaps as well as the optical gaps of GQD bonded clusters are substantially reduced, cf. Figure 4c and Table 3. A strong reduction also occurs in the respective Stokes shifts. Interestingly, no clear trends with respect to the (TiO₂)_n cluster size emerge, neither with respect to the spatial localization nor the relative energy of the photoactive states. Given that there are more (TiO₂)_n cluster configurations observed than the minimum energy structures considered here,^[63] and given that there are countless additional graphene quantum dot structures and binding geometries, a wide variety of excitation and charge transfer scenarios can be expected.

4 | CONCLUSIONS

In this study, the structural, electronic, and optical properties of neutral TiO₂ clusters and TiO₂ clusters adsorbed on pristine graphene and graphene quantum dots were studied by density-functional theory. Compared to bulk titania, the optical band gap of the TiO₂ clusters is much reduced and resides in the spectral range of visible light. A

further reduction occurs upon adsorption on graphene and graphene quantum dots, which is dominated by van der Waals interaction. In addition to the red-shifted absorption, also a spatial separation of photoexcited charge carriers will occur for many binding scenarios, further enhancing the photocatalytic activity of the hybrid material in comparison to its individual components. The electronic properties of the hybrid material depend sensitively on the size of the respective constituents and are highly system-specific. This allows for tuning and optimizing the material with respect to its desired properties, for example, for specific excitation wavelengths.

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SUPPORTING INFORMATION

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Supplemental Material for:
Photocatalytic Properties of Graphene-Supported Titania Clusters
from Density-Functional Theory

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(Dated: 18 May 2020)

I. Schematic Diagram of the Electron-Hole Pair Excitation Mechanism

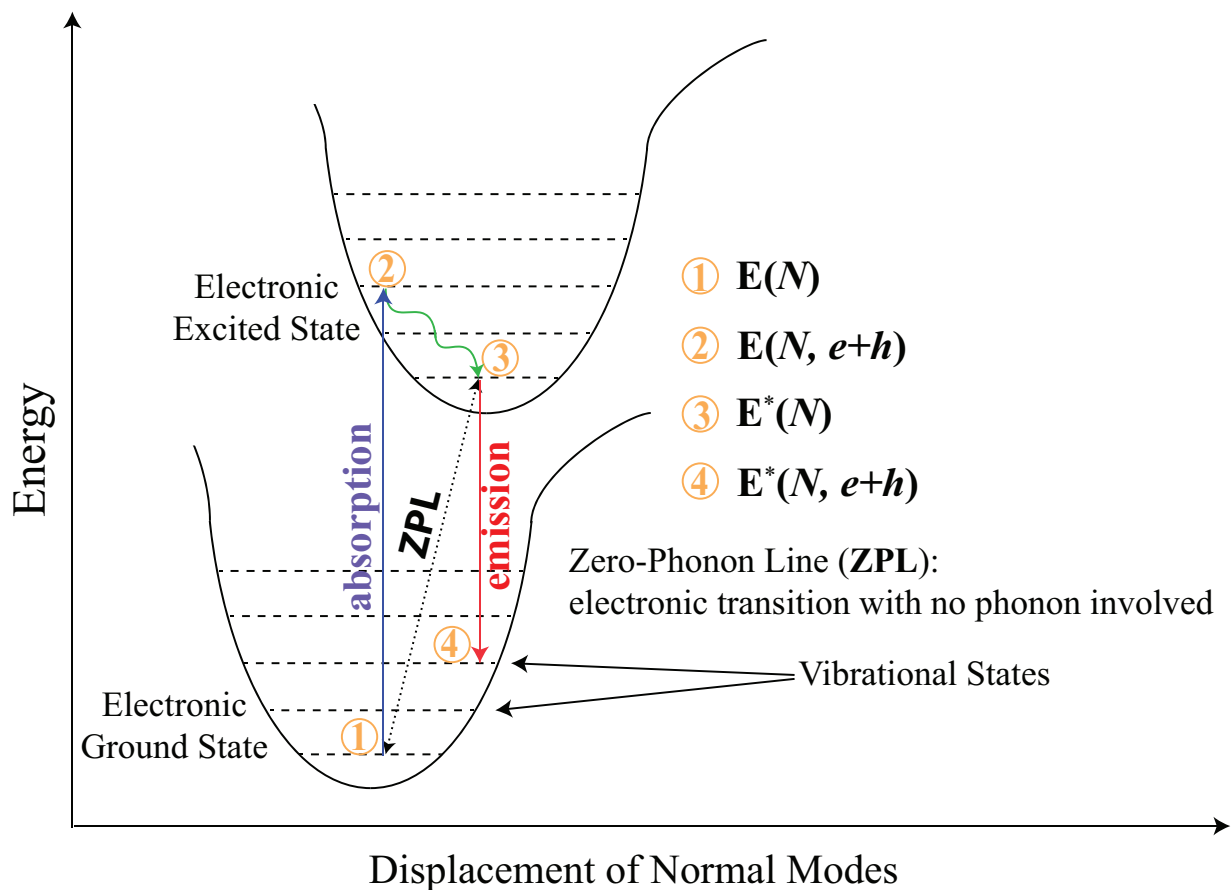


Figure S1: (Color online) Scheme illustrating the excitation energy calculations performed in the present work.

II. The Geometric and Electronic Properties of $(\text{TiO}_2)_n$ Clusters, and Its Combination with Pristine graphene and graphene Dot.

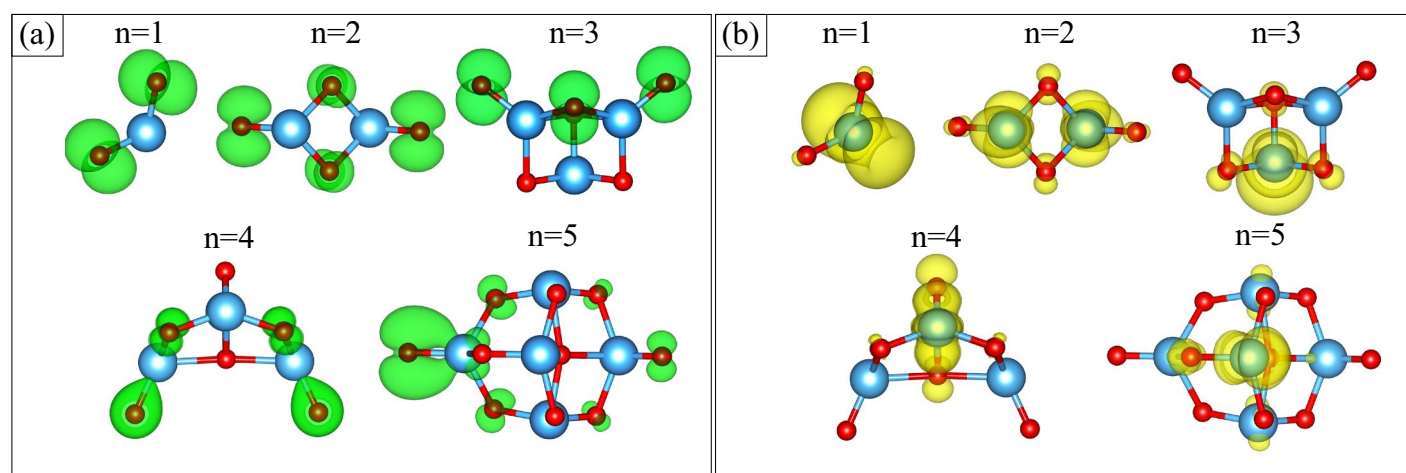


Figure S2: (Color online) The decomposed charge density plots of (a) the highest occupied molecular orbital (HOMO) and (b) the lowest unoccupied molecular orbital (LUMO) of $(\text{TiO}_2)_n$ clusters ($n=1-5$). The isosurface level of charge density is taken to be that at $67.5 \times 10^{-5} \text{ e}^-/\text{\AA}^3$ ($1 \times 10^{-4} \text{ e}^-/\text{Bohr}^3$).

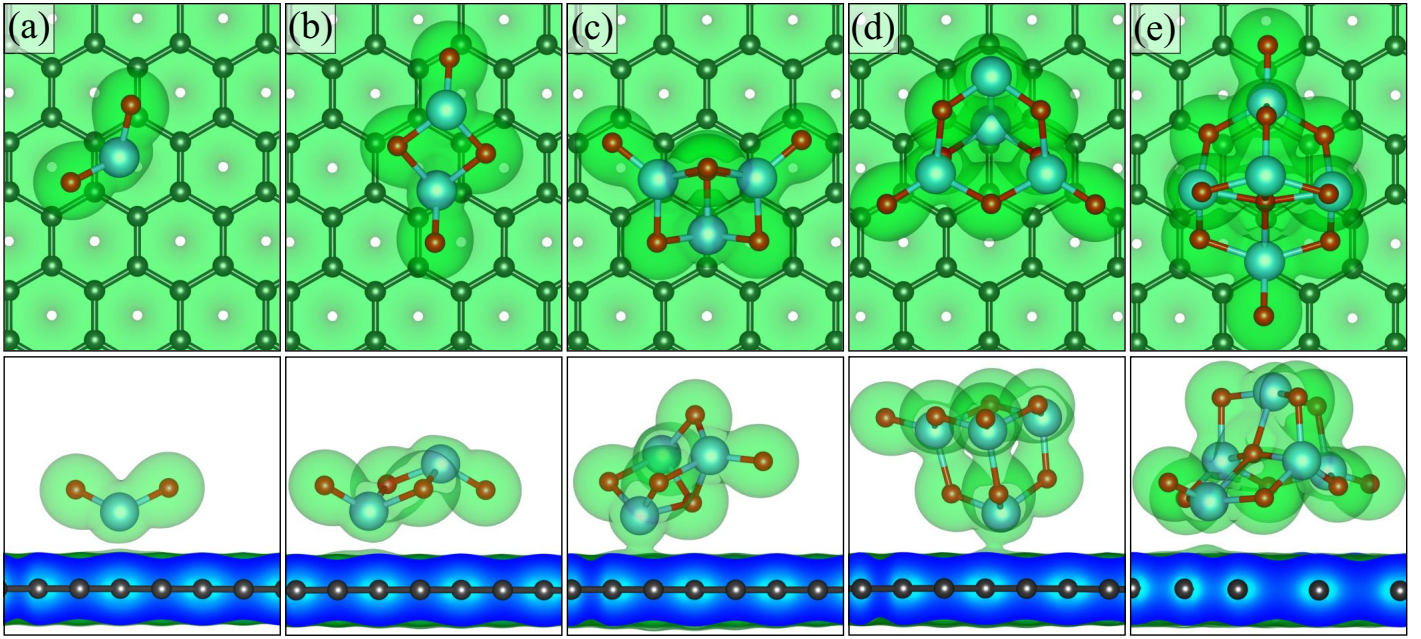


Figure S3: (Color online) The top and side views of the total charge density of $(\text{TiO}_2)_n$ clusters on the surface of graphene (GR) at (a) $n=1$, (b) $n=2$, (c) $n=3$, (d) $n=4$, and (e) $n=5$. The isosurface level of charge density is taken to be that at $0.169 \text{ e}^-/\text{\AA}^3$ ($0.025 \text{ e}^-/\text{Bohr}^3$).

Table SI: The calculated parameters for GQDs and $(\text{TiO}_2)_1$ cluster on the surface of GQDs.^a

	E_{Coh} (eV)	E_b (eV)	$E_{\text{HL}}^{\text{GGA}}$ (eV)	$E_{\text{HL}}^{\text{HSE}}$ (eV)	$E_{\text{HL}}^{\Delta\text{SCF}}$ (eV)	EA_v (eV)	EA_{ad} (eV)	IE_v (eV)	IE_{ad} (eV)	$E_{\text{Op}}^{\Delta\text{SCF}}$ (eV)	Δ_{ST} (eV)	E_b^{ex} (eV)	μ (μ_B)
$\text{C}_{42}\text{H}_{18}$	6.27	-	2.46	3.12	5.27	1.24	1.26	6.51	6.50	2.44	0.26	2.83	0
$\text{C}_{114}\text{H}_{30}$	6.77	-	1.53	1.95	3.45	2.19	2.20	5.64	5.63	1.52	0.11	1.93	0
$\text{C}_{222}\text{H}_{42}$	7.03	-	1.10	1.40	2.53	2.69	2.69	5.22	5.22	1.10	0.06	1.43	0
$\text{C}_{480}\text{H}_{60}$	7.39	-	0.76	0.95	1.77	3.11	3.11	4.88	4.88	0.76	0.02	1.01	0
$(\text{TiO}_2)_1/\text{C}_{42}\text{H}_{18}$	-	1.18	1.31	2.53	4.88	1.75	1.86	6.63	6.54	1.87	0.65	3.01	0
$(\text{TiO}_2)_1/\text{C}_{114}\text{H}_{30}$	-	1.15	1.03	1.90	3.37	2.40	2.42	5.77	5.76	1.41	0.16	1.96	0
$(\text{TiO}_2)_1/\text{C}_{222}\text{H}_{42}$	-	1.13	0.90	1.38	2.51	2.80	2.81	5.31	5.31	1.06	0.05	1.45	0
$(\text{TiO}_2)_1/\text{C}_{480}\text{H}_{60}$	-	1.12	0.72	0.94	1.71	3.19	3.19	4.90	4.90	0.75	0.02	0.96	0

^a The cohesive energy per atom, E_{Coh} ; the binding energy of $(\text{TiO}_2)_1$ cluster to GQDs, E_b ; $E_{\text{HL}}^{\text{GGA}}$, $E_{\text{HL}}^{\text{HSE}}$ and $E_{\text{HL}}^{\Delta\text{SCF}}$ are HOMO-LUMO energy gaps based on GGA, HSE and ΔSCF , respectively; the vertical electronic affinity and ionisation energy, EA_v and IE_v ; the adiabatic electronic affinity and ionisation energy, EA_{ad} and IE_{ad} ; $E_{\text{Op}}^{\Delta\text{SCF}}$ is optical gap based on ΔSCF ; the Stokes shift, Δ_{ST} ; the exciton binding energy, E_b^{ex} ; the magnetisation, μ .

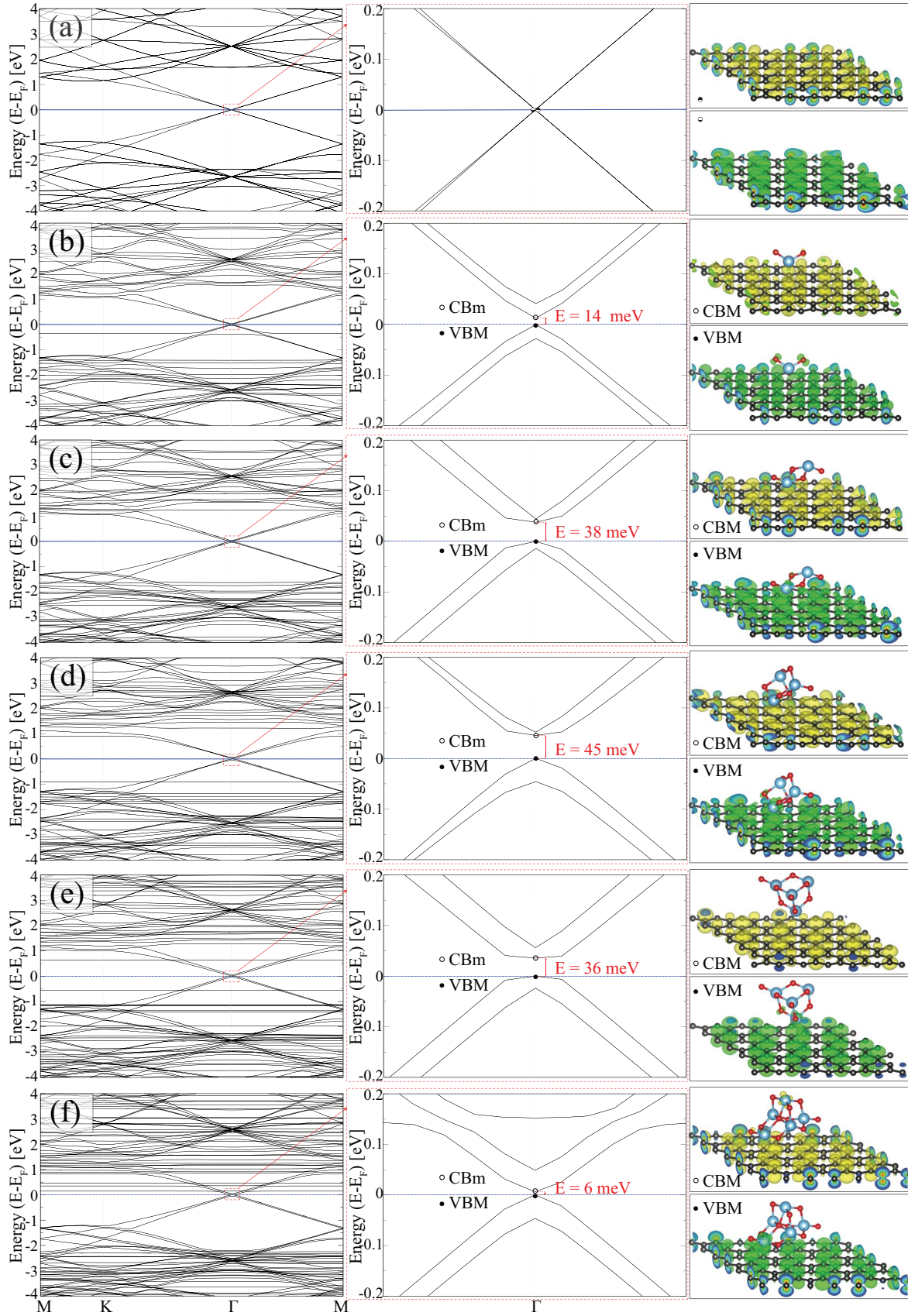


Figure S4: (Color online) The band structure and the decomposed charge density of valence band maximum (VBM) and conduction band minimum (CBM) of the $(\text{TiO}_2)_n$ clusters on the surface GR at (a) $n=0$, (b) $n=1$, (c) $n=2$, (d) $n=3$, (e) $n=4$, and (f) $n=5$. In the case of $(\text{TiO}_2)_n/\text{GR}$, the Dirac cone at the Γ and the folded bands due to the (6×6) GR supercell structure of the system are present in the plot. The second column views show the corresponding valence band maximum (VBM) and conduction band minimum (CBM) on an enlarged scale. The isosurface level of charge density is taken to be that at $67.5 \times 10^{-5} \text{ e}^-/\text{\AA}^3$ ($1 \times 10^{-4} \text{ e}^-/\text{Bohr}^3$).

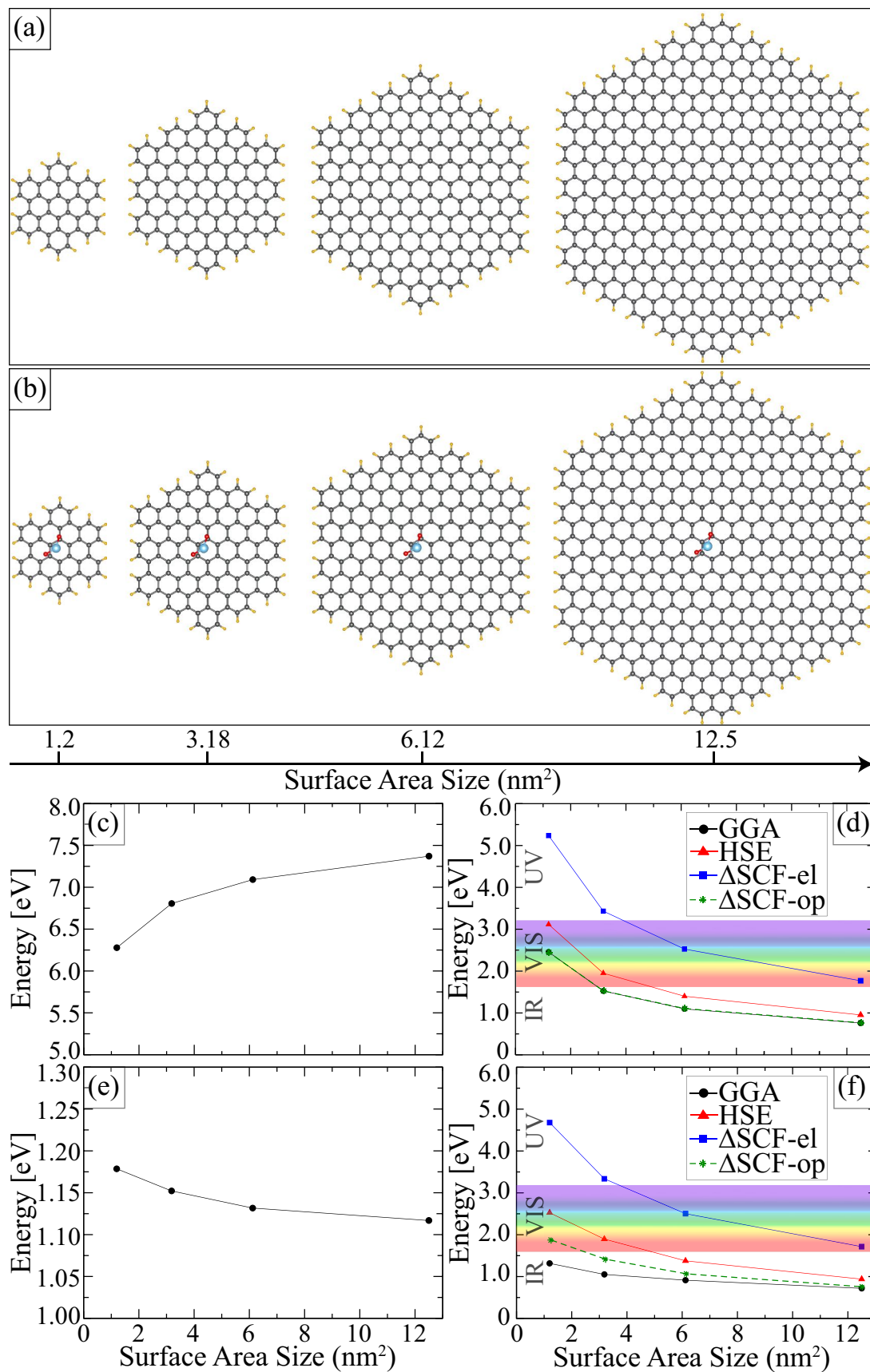


Figure S5: (Color online) The top views of (a) optimised hexagonal graphene quantum dot (GQD) with armchair edges and (b) the most favourable $(\text{TiO}_2)_1$ adsorption configuration on the respective GQD. Blue, red, dark grey, and orange spheres represent Ti, O, C, and H atoms, respectively. (c) The cohesive energy per atom and (d) the HOMO-LUMO energy gap and the optical gap of GQDs. (e) The $(\text{TiO}_2)_1$ bonding energy on the GQD and (f) the HOMO-LUMO energy gap and the optical gap of $(\text{TiO}_2)_1$ decorated GQDs. For comparison, the spectral energy of visible light (1.59-3.26 eV) is indicated.

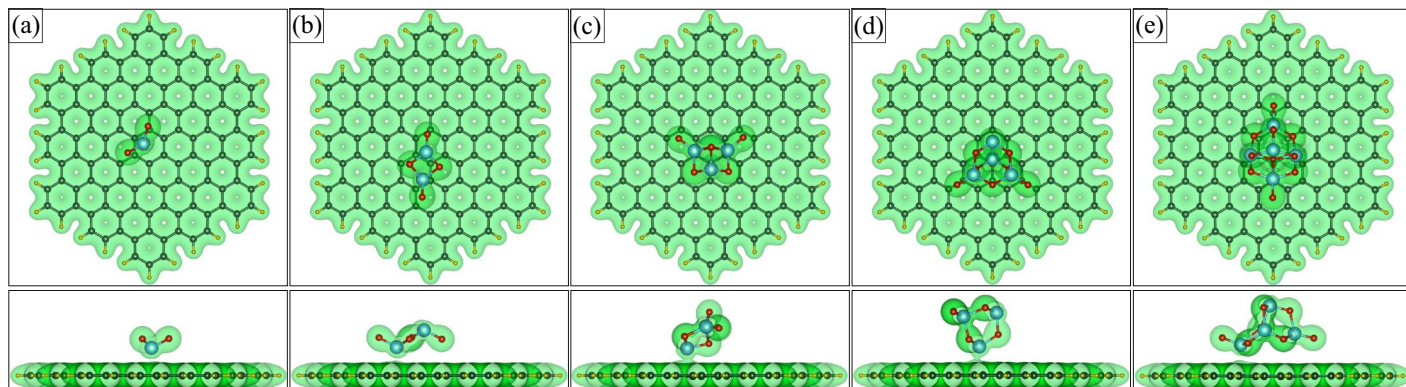


Figure S6: (Color online) The top and side views of the total charge density of $(\text{TiO}_2)_n$ clusters on the surface of GQD at (a) $n=1$, (b) $n=2$, (c) $n=3$, (d) $n=4$, and (e) $n=5$. The isosurface level of charge density is taken to be that at $0.169 \text{ e}^-/\text{\AA}^3$ ($0.025 \text{ e}^-/\text{Bohr}^3$).

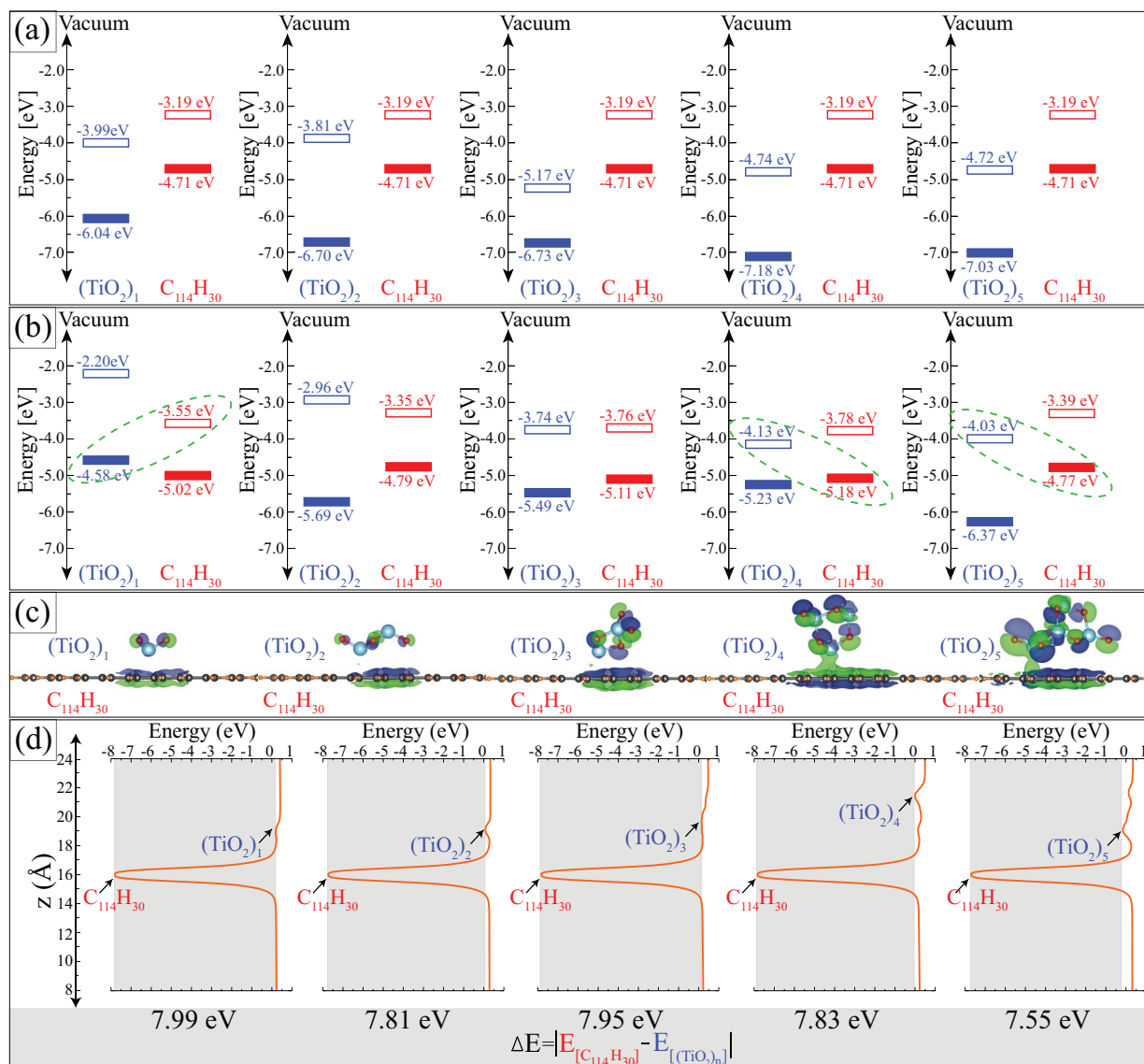


Figure S7: (Color online) HOMO-LUMO energy levels for (a) isolated and (b) combined $(\text{TiO}_2)_n/\text{GQD}$ systems calculated on the DFT-GGA level of theory. The charge density difference distribution $\Delta\rho$ between GQD and TiO_2 clusters. The green and blue colours represent the charge accumulation and depletion, respectively. The isosurface level of charge density is taken to be that at $0.067 \text{ e}^-/\text{\AA}^3$ ($0.01 \text{ e}^-/\text{Bohr}^3$). (d) Local electrostatic potential diagrams versus combine $(\text{TiO}_2)_n/\text{GQD}$ systems. ΔE is the electrostatic potential difference.