

# Substantially enhanced Raman signal for inorganic-organic nanocomposites by ALD-TiO<sub>2</sub> capping

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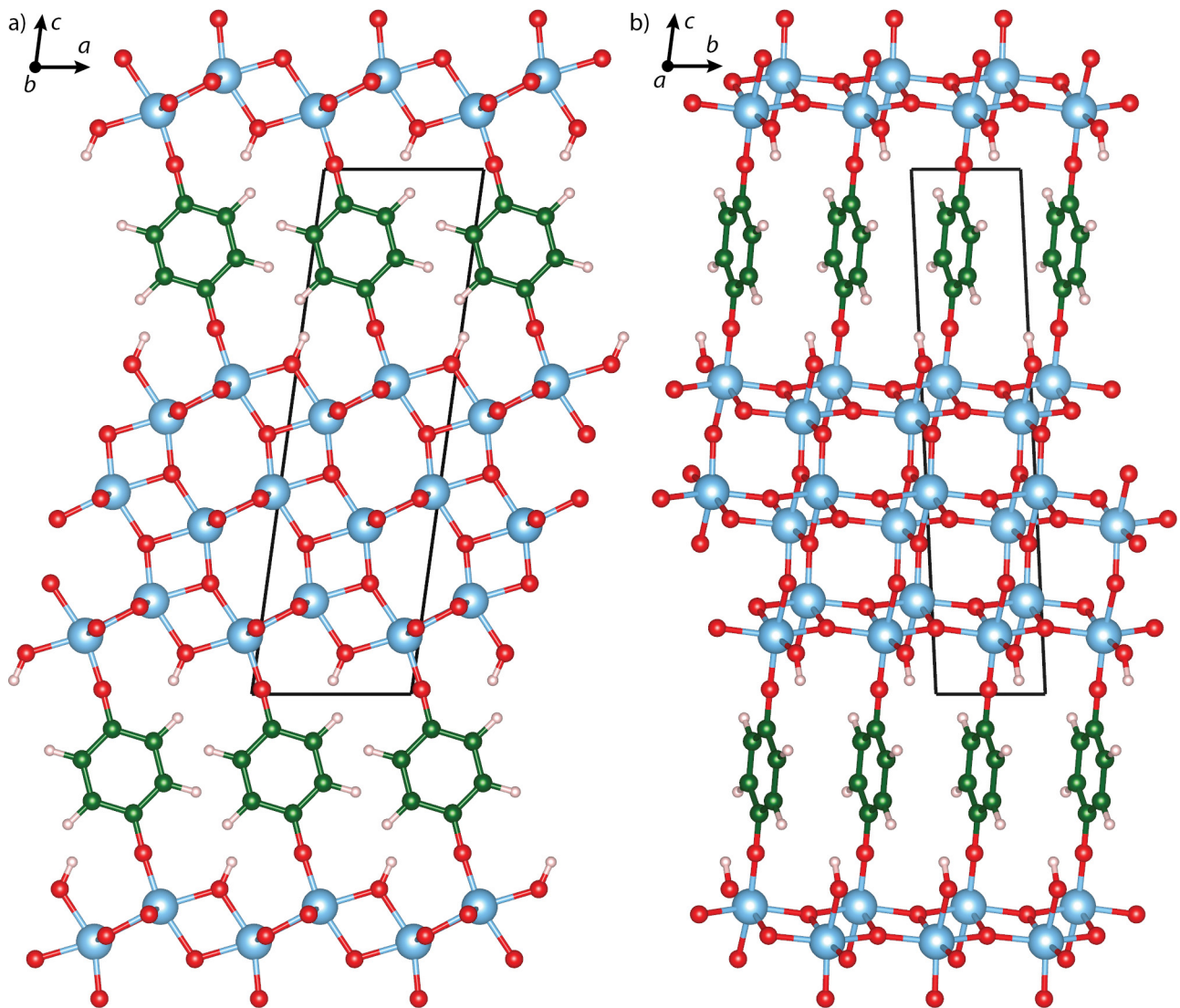
## 1. Supporting information for the quantum chemical calculations

### 1.1 Studied TiO<sub>2</sub>-HQ hybrid structure

We derived an atomistic structural model for a TiO<sub>2</sub>-HQ hybrid structure starting from the bulk TiO<sub>2</sub> anatase structure (space group *I4<sub>1</sub>/amd*, six atoms in the primitive cell). The lattice parameters predicted for the bulk TiO<sub>2</sub> anatase at the DFT-PBE0/SVP level of theory are in agreement with the experimental values ( $a = 3.7845 \text{ \AA}$  and  $c = 9.5143 \text{ \AA}$ ).<sup>1</sup> The difference between the experimental and calculated lattice parameters  $a$  and  $c$  is  $-0.9\%$  and  $+2.0\%$ , respectively, in line with previous theoretical studies carried out using DFT methods.<sup>2</sup>

Considering that TiO<sub>2</sub>(101) is the most stable and frequently exposed surface of anatase,<sup>3</sup> we created our atomic-level model of the TiO<sub>2</sub>-HQ hybrid structure by cutting a three-layer (101) slab of TiO<sub>2</sub> from the bulk anatase (resulting lattice parameters of the 2D slab:  $a = 5.53 \text{ \AA}$ ;  $b = 3.75 \text{ \AA}$ ). The three-layer (101) slab includes one layer of fully six-coordinated Ti and three-coordinated O atoms in the middle, while the surface layers contain five-coordinated Ti atoms and two-coordinated O atoms.<sup>3</sup> The coordination of the Ti and O atoms in the surface layers can be fulfilled by introducing organic hydroquinone (HQ) molecules between two (101) slabs (HQ = benzene-1,4-diol, HO-C<sub>6</sub>H<sub>4</sub>-OH). The H atom of the OH group of HQ is transferred to the two-coordinated surface-O atom and the organic molecule forms Ti-O-C<sub>6</sub>H<sub>4</sub>-O-Ti bonds with the five-coordinated surface-Ti sites (Figure S1).

After a full structural optimization, the lattice parameters of the resulting TiO<sub>2</sub>-HQ hybrid structure are  $a = 5.49 \text{ \AA}$ ;  $b = 3.76 \text{ \AA}$ ;  $c = 17.14 \text{ \AA}$ ;  $\alpha = 89.99^\circ$ ;  $\beta = 97.38^\circ$ ;  $\gamma = 110.02^\circ$  (full unit cell coordinates listed below). Harmonic frequency calculation shows the structure to be a true local minimum. The electronic band gap of the TiO<sub>2</sub>-HQ hybrid structure is 2.6 eV (the band gap of TiO<sub>2</sub> anatase at the same level of theory is 4.1 eV, in line with previous theoretical studies<sup>2</sup>).



**Figure S1.** Optimized geometry of the  $\text{TiO}_2$ -HQ hybrid structure used for simulating the Raman spectrum (unit cell denoted with black lines). a) Structure viewed along the  $b$  axis. b) Structure viewed along the  $a$  axis. Color code: Blue: Ti; Red: O; Green: C; white: H.

## 1.2 Full computational details

The TiO<sub>2</sub>-HQ structure was investigated using the PBE0 hybrid density functional method (DFT-PBE0).<sup>4,5</sup> The calculations were carried out with the CRYSTAL14 program package,<sup>6,7</sup> utilizing all-electron, Gaussian-type basis sets derived from the molecular Karlsruhe basis sets.<sup>8</sup> A split-valence + polarization (SVP) level basis was applied for all atoms (detailed basis set listings are given below). In the structural optimizations, both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. The reciprocal space was sampled using 4x6x1 and 6x6x6 Monkhorst-Pack-type *k*-point grids for TiO<sub>2</sub>-HQ and bulk TiO<sub>2</sub> anatase, respectively.<sup>9</sup> For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Default optimization convergence thresholds were applied in structural optimizations and the default numerical integration grid (XLGRID) was used for the integration of the exchange-correlation functional. The  $\Gamma$ -point harmonic vibrational frequencies were obtained by using the computational scheme implemented in CRYSTAL<sup>10,11</sup> and the Raman intensities were calculated using the analytical coupled perturbed Hartree-Fock/Kohn-Sham method.<sup>12,13</sup> The predicted Raman wavenumbers have been scaled by a factor of 0.95 to account for the overestimation typical for *ab initio* harmonic frequencies.<sup>14,15</sup> The Raman intensities have been calculated for a polycrystalline powder sample (total isotropic intensity in arbitrary units). The final spectrum was obtained by using pseudo-Voigt peak profile (50:50 Lorentzian:Gaussian) and FWHM of 32 cm<sup>-1</sup>. The structural figures were prepared using the VESTA visualization program.<sup>16</sup>

### 1.3 Unit cell coordinates of the TiO<sub>2</sub>-HQ hybrid structure

Lattice parameters (Å) and fractional atomic coordinates are listed below in the CRYSTAL input format:

```
Space group number
Minimal set of lattice parameters a,b,c,α,β,γ
Number of non-equivalent atoms in the asymmetric unit
<atomic number> <fractional x> <fractional y> <fractional z>

1
5.49425297 3.76250090 17.13841402 89.985761 97.384890 110.021168
32
22 9.310598296776E-02 -4.411138768021E-01 1.112626460428E-01
22 4.370895433917E-01 -2.695658324629E-01 3.210946039299E-01
22 -2.272455060361E-01 -1.018630110414E-01 -4.717040353174E-01
22 -2.907132077006E-01 -1.326934266758E-01 1.781625031309E-01
22 4.494483638152E-02 3.450920732143E-02 3.853623384033E-01
22 3.889334635351E-01 2.061680517617E-01 -4.048084855168E-01
8 -2.211501650259E-01 4.017023419449E-01 1.666206205827E-01
8 1.148166073536E-01 -4.306040754702E-01 3.727421148012E-01
8 4.530887619090E-01 -2.617179655447E-01 -4.195863052714E-01
8 -6.019482618716E-02 4.823819836748E-01 9.280763861746E-03
8 3.552464865959E-01 -3.101283516346E-01 2.111321684879E-01
8 -3.091741459452E-01 -1.426538833345E-01 4.197125938136E-01
8 3.354868639823E-02 2.845524827025E-02 -3.714662222131E-01
8 2.895627934359E-02 2.682407376103E-02 1.260416934290E-01
8 3.672220020512E-01 1.956381366928E-01 3.337187652752E-01
8 -2.967957993248E-01 3.633785400835E-01 -4.601620256210E-01
8 4.484923665754E-01 -2.633953032454E-01 7.792369678966E-02
8 -2.087797669462E-01 -9.228710073367E-02 2.867442077706E-01
8 1.267983041781E-01 7.523587678506E-02 4.953262109443E-01
8 -4.577737688233E-01 2.827293490647E-01 -3.028253934580E-01
6 -3.618934497614E-01 3.309035901595E-01 -2.272970376932E-01
6 -9.234238385099E-02 4.657239205561E-01 -2.034761971329E-01
6 7.420977130215E-03 -4.841952426984E-01 -1.244594896109E-01
6 -1.560720170232E-01 4.342416872537E-01 -6.624793987912E-02
6 -4.256222063671E-01 2.994315793733E-01 -9.006871975184E-02
6 4.746142549854E-01 2.493506220364E-01 -1.690851922261E-01
1 3.866748187833E-02 -4.689046414298E-01 -2.480598583552E-01
1 2.165871984229E-01 -3.795796795232E-01 -1.071622504752E-01
1 4.433687809292E-01 2.340773237579E-01 -4.548488779035E-02
1 2.654484870483E-01 1.447310132152E-01 -1.863822908007E-01
1 -1.970198455475E-02 1.829789844353E-03 -3.198966339598E-01
1 -4.982612735287E-01 -2.365299449598E-01 2.635344159477E-02
```

## 1.4 Basis sets listed in CRYSTAL14 input format

The following SVP-level basis sets were used in the DFT-PBE0 calculations:

**H, C, O:** We applied the basis sets we have previously derived from the molecular def-SVP (*J. Phys. Chem C* **2015**, *119*, 13105–13114).

**Ti:** The molecular def-SVP basis set was used as the starting point. The diffuse outermost s-exponents in the Ti basis were increased from 0.025 and 0.066 to 0.12 and 0.24, respectively. The exponent of the p-type polarization function was changed from 0.10 to 0.12 and the outermost s and p functions were then combined into a single sp-type function to increase the efficiency of the CRYSTAL code.

### Hydrogen

```
1 3
0 0 3 1.0 1.0
  16.405375868      0.19682158000E-01
  2.4682873851     0.13796524000
  0.60403963859     0.47831935000
0 0 1 0.0 1.0
  0.160000000000    1.00000000000
0 2 1 0.0 1.0
  0.80              1.00000000000
```

### Carbon

```
6 5
0 0 5 2.0 1.0
  1238.4016938     0.54568832082E-02
  186.29004992     0.40638409211E-01
  42.251176346     0.18025593888
  11.676557932     0.46315121755
  3.5930506482     0.44087173314
0 0 1 2.0 1.0
  0.56046415662    1.00000000000
0 1 1 0.0 1.0
  0.230000000000    1.0 1.0
0 2 3 2.0 1.0
  11.852514432     0.38387871728E-01
  2.5673213956     0.21117025112
  0.79737433183     0.51328172114
0 3 1 0.0 1.0
  0.800000000000    1.00000000000
```

### Oxygen

```
8 5
0 0 5 2.0 1.0
  2266.1767785     -0.53431809926E-02
  340.87010191     -0.39890039230E-01
  77.363135167     -0.17853911985
  21.479644940     -0.46427684959
  6.6589433124     -0.44309745172
0 0 1 2.0 1.0
  0.84197953374    1.00000000000
0 1 1 0.0 1.0
  0.280000000000    1.0 1.0
0 2 3 4.0 1.0
  17.808254450     0.43394573193E-01
  3.8854243945     0.23094120765
  1.0579384045     0.51375311064
0 3 1 0.0 1.0
  1.200000000000    1.00000000000
```

### Titanium

```
22 9
0 0 6 2.0 1.0
  42961.512185     .39127635355E-02
  6450.9759169     .29969820489E-01
  1467.7210915     .14836352707
  414.20997355     .51347285324
  134.48715840     1.0335365483
  46.122209796     .77854233930
0 0 3 2.0 1.0
  89.447762543     -.28385401259
  10.223346060     1.6772785333
  4.1353774271     1.2411928456
0 0 3 2.0 1.0
  6.7896181452     -.78399994518E-02
  1.1106730691     .25495493019E-01
  0.47565975578     .16061172892E-01
0 0 1 2.0 1.0
  0.24              1.00000000000
0 1 1 0.0 1.0
  0.12              1.0 1.0
0 2 5 6.0 1.0
  522.03684782     .19754179642E-01
  122.68649489     .14460677619
  38.572903611     .54669004165
  13.672169319     1.0531647540
  5.0118529359     .69111213363
0 2 3 6.0 1.0
  2.4131928282     .75803437136
  0.93252270050     1.3036241399
  0.35429058390     .53638653300
0 3 4 2.0 1.0
  23.465125957     .26536380115E-01
  6.3332593832     .13796453963
  2.0766489946     .35312644228
  0.69027361954     .48647124166
0 3 1 0.0 1.0
  0.21088738554     .33026314258
```

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