Supporting Information:

Predicted Structures of the Active Sites Responsible for the Improved Reduction of Carbon Dioxide by Gold Nanoparticles

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simulation methods

We used LAMMPS (1 Feb 2014 version)[1] with the USER-REAXC package and fix qeq/reax.[2] for the Molecular Mechanics (MM) Dynamics simulations. A Nose-Hoover thermostat was used to control the temperature with a damping parameter of 100 time steps.

To grow a gold (Au) nanoparticle (NP), we used a zigzag carbon nanotube (CNT) with a diameter of 8.39 nm as the catalysis support, which was kept fixed during all the simulations. The Embedded-atom-model (EAM) [3] was used to describe the interaction between Au atoms, and a Lennard-Jones (LJ) potential was used to describe the interaction between Au and the CNT. The temperature for the growth simulation was 300K, and the deposition rate for the growth simulation was 3.0 Å ns^{-1}. The time step was 1 fs. After 35 ns of growth simulation, an Au NP with a normal thickness of about 10 nm was obtained on the CNT support. Annealing simulations were carried out to heal the defect and increase the grain size. Each annealing cycle included 10 ps cook-off simulation from 300 K to 1200 K, 5 ps NVT simulation at 1,164 K, 10 ps annealing from 1,164 K to 300 K and 15 ps NVT simulation at 300 K. After 120 annealing cycles, a fully crystallized Au NP formed on CNT support. In the annealing trajectory, the Au-NP structure after 63 annealing cycles is mostly close to the experimental structure, which was further refined by using 20 ps ReaxFF reactive force field (ReaxFF) simulation at 300K using a previous published Cu-C ReaxFF parameters.[4] The time step for the reactive force field (ReaxFF) simulations was 0.25 fs.

Quantum mechanics calculations were performed with VASP package [5-7], using the PBE flavor[8] of DFT and the projector augmented wave (PAW) method[9] to account for core-valence interactions. The kinetic energy cutoff for plane wave expansions was set to 400 eV. The Methfessel-Paxton smearing of second order with a width of 0.2 eV was applied. The convergence criteria are 1×10^{-5} eV energy differences for solving the electronic wave function. All geometries (atomic coordinates) are converged to 1×10^{-2} eV/Å for maximal components of forces.

Cluster models for VASP calculations were cut from the simulated nanoparticle using a cut-off of 8 Å taking the selected site as a center. We consider that this provides an accuracy 0.02 eV while keeping the computational cost modest. For cluster calculations, a 20 Å cubic box was used, and only gamma point was considered in these calculations. All the Au atoms were fixed in cluster calculations.

Debyer, (freely available on https://github.com/wojdyr/debyer), was used to calculate the diffraction pattern for the synchrotron x-ray source. QSTEM (freely available on http://qstem.org/) was used to simulate the TEM images.

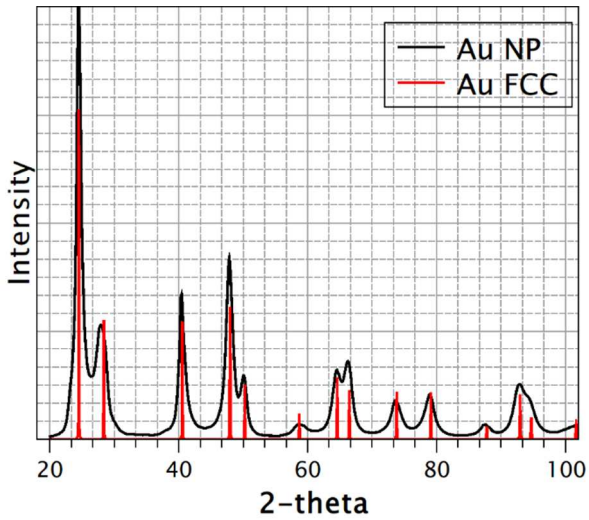

Figure S1. The simulated XRD-diffraction pattern.

The simulated XRD-diffraction pattern of Au NP shows peaks of FCC Au. The widened peak of Au NP is due to the Nano-size effect.

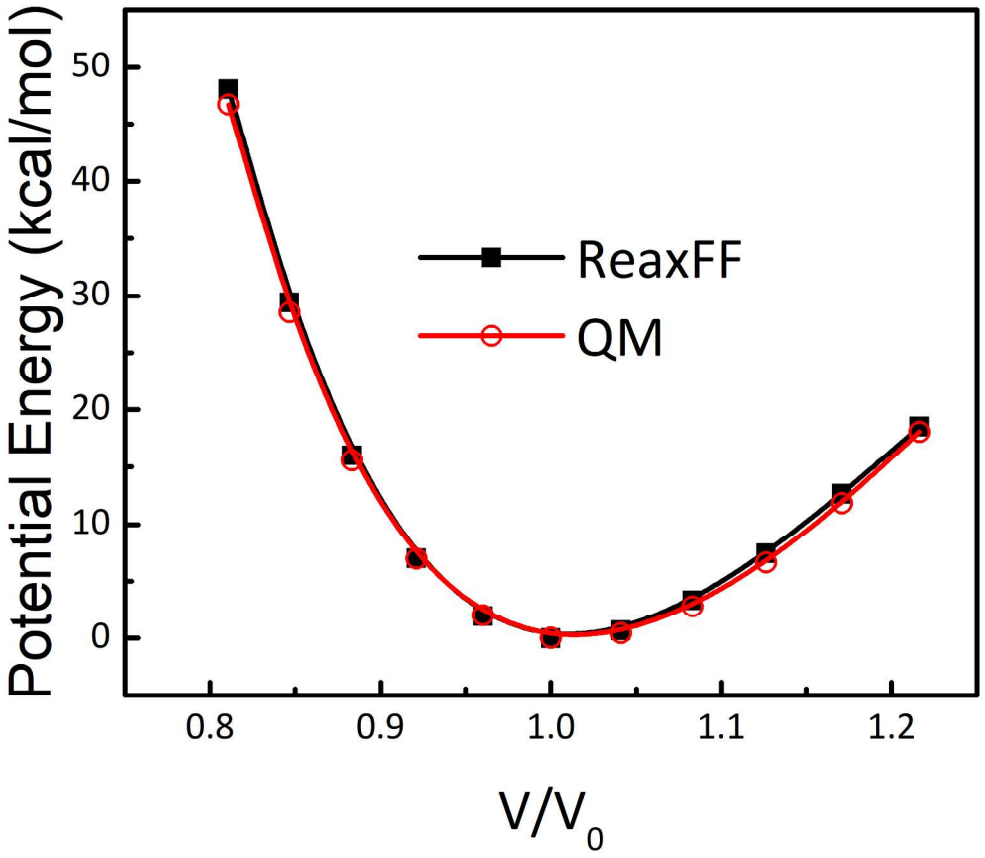

Figure S2. Comparison of the equation of state of FCC Au between ReaxFF and QM.

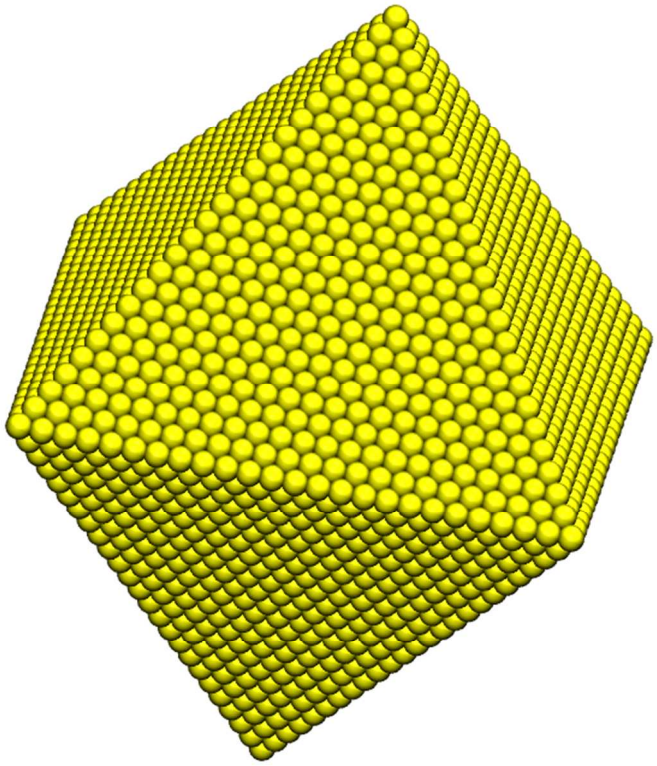

Figure S3. Au octahedral with a length of 6.93 nm (10,425 Au atoms), which consists of 2,024 facet sites (87.77%), 276 edge sites (11.97%) and six corner sites (0.26%).

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2017-06-25 16:33:21 : C|Au
 39
   50.0000
    9.5469
   26.5405
    1.5105
    6.6630
    0.0000
    1.0588
    4.6000
   12.1176
   13.3056
  -70.1292
    0.0000
   10.0000
    0.0000
   33.8667
    6.0891
    1.0563
    2.0384
    6.1431
    6.9290
    0.3989
    3.9954
    0.0000
    5.7796
   10.0000
    1.9487
    0.0000
    2.1645
    1.5591
    0.1000
    2.1365
    0.6991
   50.0000
    1.8512
    0.0000
    0.0000
    0.0000
    0.0000
    2.6962
 2    ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
           alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
           cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
           ov/un;val1;n.u.;val3,vval4
 C    1.3825   4.0000  12.0000   1.9133   0.1853   0.9000   1.1359
4.0000
      9.7602   2.1346   4.0000  33.2433  79.5548   5.8678   7.0000
0.0000
      1.2104   0.0000 199.0303   8.6991  34.7289  13.3894   0.8563
0.0000
     -2.8983   2.5000   1.0564   4.0000   2.9663   0.0000   0.0000
0.0000
```

```
 Au   2.0271   1.0000 196.9665   2.2078   0.3446   0.5126  -1.0000
1.0000
     11.9754   2.0434   1.0000   0.0000   0.0000   1.0082   8.9305
0.0000
     -1.0000   0.0000  92.5070   6.2293   5.2294   0.1542   0.8563
0.0000
    -24.7561   2.9867   1.0338   6.2998   2.5791   0.0000   0.0000
0.0000
 3      ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
                         pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
  1  1 156.5953 100.0397  80.0000  -0.8157  -0.4591   1.0000  37.7369
0.4235
         0.4527  -0.1000   9.2605   1.0000  -0.0750   6.8316   1.0000
0.0000
  1  2  66.7504   0.0000   0.0000   0.3297  -0.2000   0.0000  16.0000
0.1769
         0.1314  -0.2000  15.0000   1.0000  -0.1324   5.9552   0.0000
0.0000
  2  2 146.6542   0.0000   0.0000  -0.0295  -0.2000   0.0000  16.0000
0.3319
         0.2793  -0.2000  15.0000   1.0000  -0.1591   5.3892   0.0000
0.0000
 1    ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
  1  2   0.0673   1.9638   9.9501   1.9677  -1.0000  -1.0000
 4    ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
  1  1  1  67.2326  22.0695   1.6286   0.0000   1.7959  15.4141   1.8089
  1  1  2  58.3918  13.9641   2.0300   0.0000   1.2404   0.0000   2.2787
  1  2  1  71.3861   3.9232   2.1478   0.0000   1.1259   0.0000   2.1341
  1  2  2  20.0000   7.2189   1.6647   0.0000   0.9966   0.0000   1.2857
 1    ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
  1  1  1  1  -0.2500  11.5822   0.1879  -4.7057  -2.2047   0.0000
0.0000
  0    ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
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