Electronic Supplementary Information

Synergy between Quantum Confinement and Chemical Functionality of Graphene Dots Promote Photocatalytic H_2 Evolution

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Supporting information for:

(1) TEM images of NGODs;

(2) Atomic force microscopic analysis of NGOD5;

(3) Full-range XPS spectra of NGODs;

(4) FTIR spectra of NGODs;

(5) Raman spectra of NGODs;

(6) PL excitation spectra of NGOD suspensions;

(7) PL spectra of NGOD suspensions under various excitation wavelengths;

(8) Bandgap determination for NGODs;

(9) UPS analysis for VBM and E_F levels of NGODs;

(10) Absolute optical absorption spectra of NGOD suspensions.

1. TEM images of NGODs

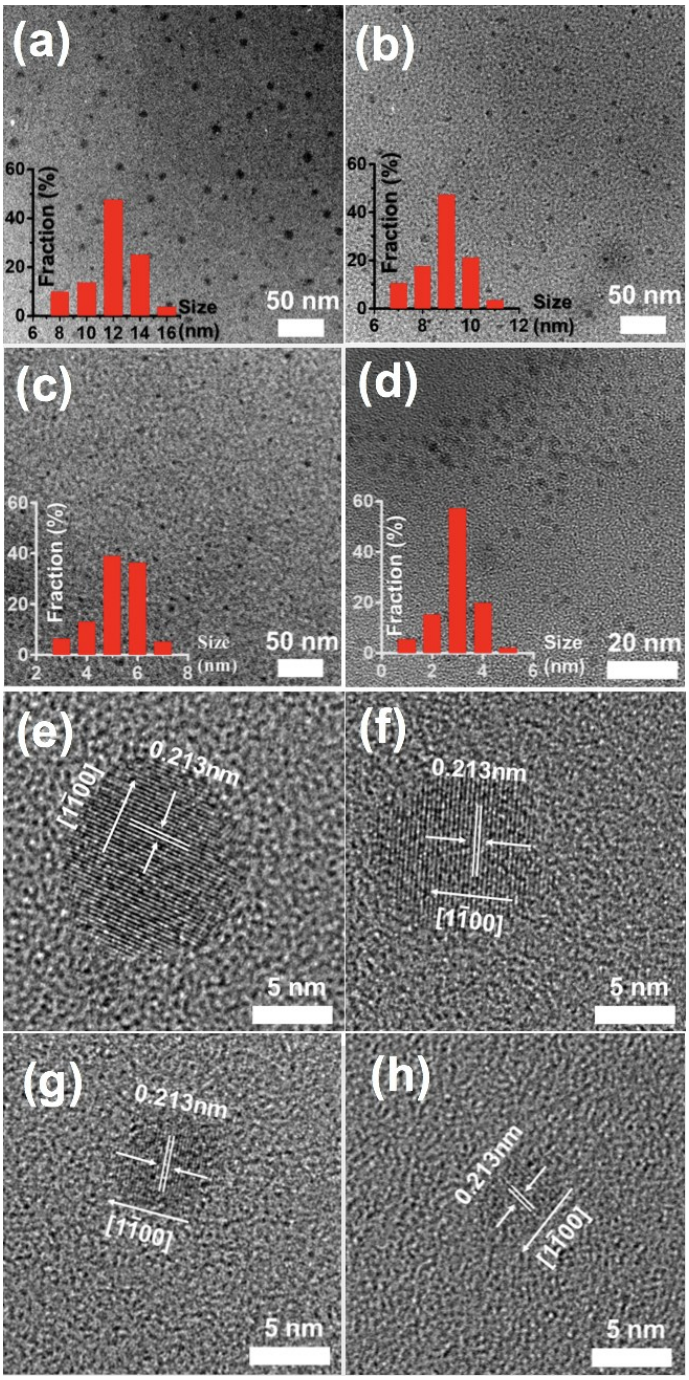

Fig. S1 Morphology and crystal structure of the NGOD specimens. TEM images of (a) NGOD12, (b) NGOD9, (c) NGOD5, and (d) NGOD3 with the insets showing the histogram of the size distribution. HRTEM images of (e) NGOD12, (f) NGOD9, (g) NGOD5, and (h) NGOD3, showing graphene $\{1\bar{1}00\}$ lattice planes with a d-spacing of 0.213 nm.

2. Atomic force microscopic analysis of NGOD5

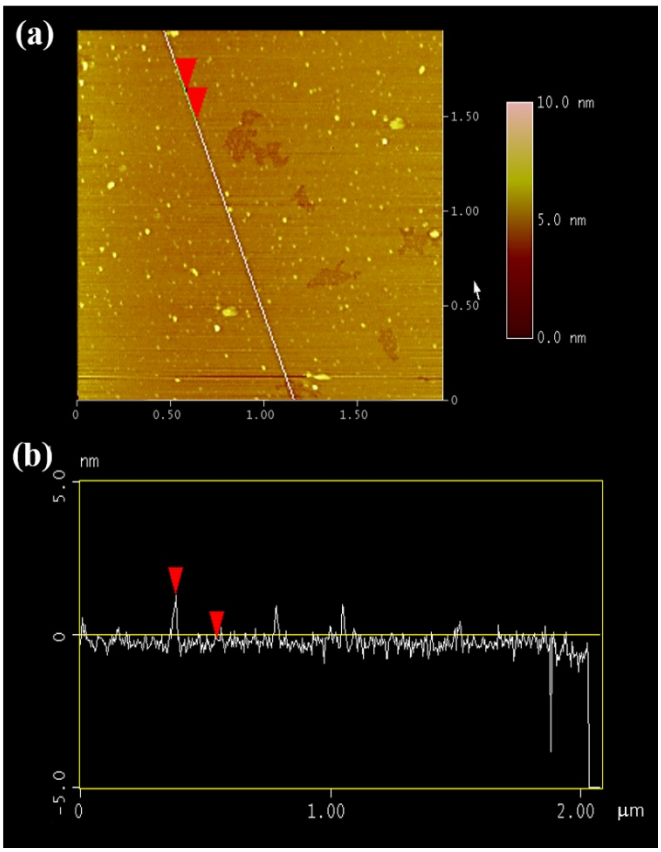

Fig. S2 Topographic analysis of NGOD5. (a) Atomic force microscopic image of NGOD5 distributed on a mica substrate. (b) The height profile along the line of panel a.

3. Full-range XPS spectra of NGODs

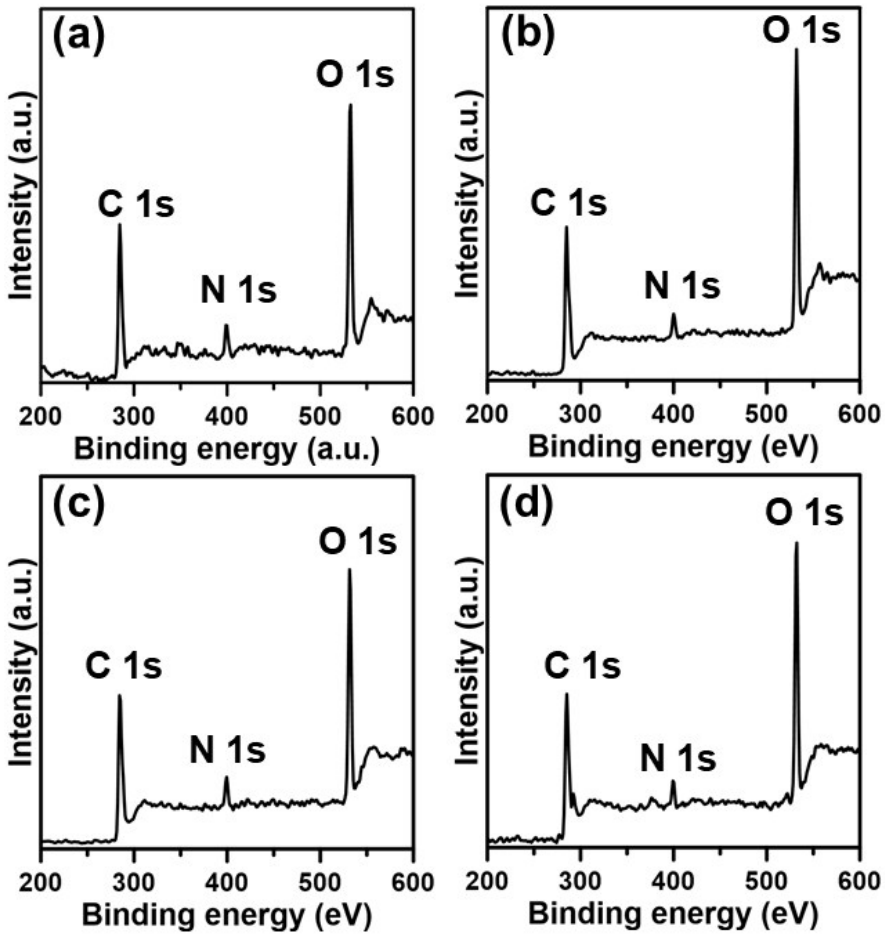

Fig. S3 Full-range XPS spectra of the NGOD specimens: (a) NGOD12, (b) NGOD9, (c) NGOD5, and (d) NGOD3.

4. FTIR spectra of NGODs

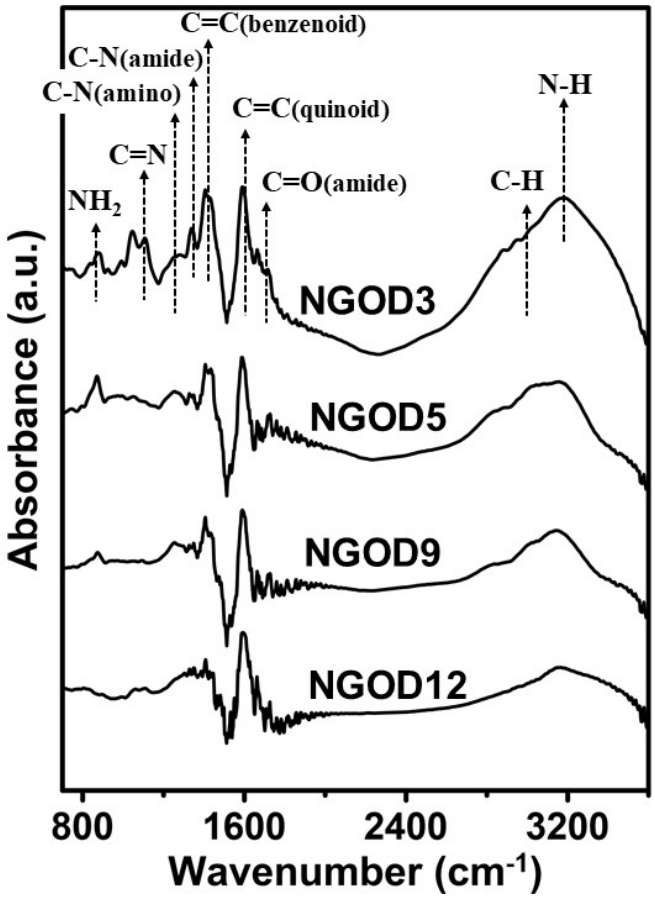

Fig. S4 FTIR absorption spectra of the NGOD specimens.

5. Raman spectra of NGODs

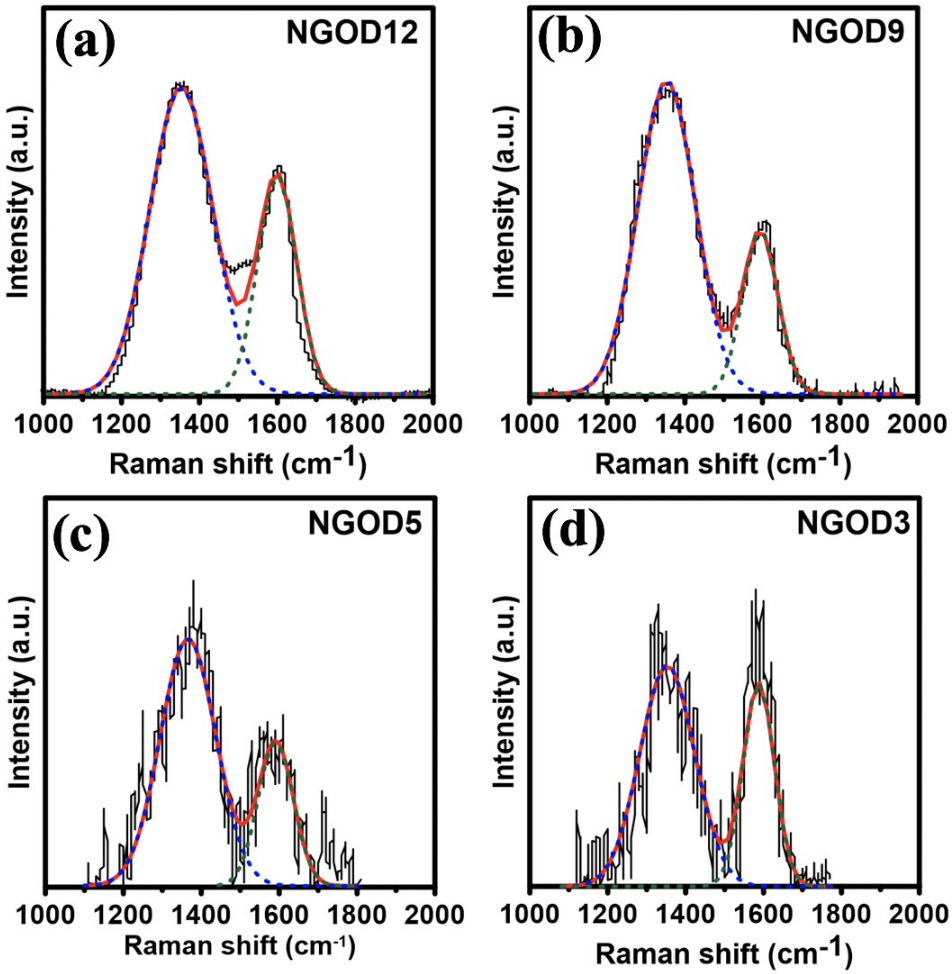

Fig. S5 Raman spectra of the NGOD specimens: (a) NGOD12, (b) NGOD9, (c) NGOD5, and (d) NGOD3. All the Raman spectra were obtained by subjecting the specimens to 532-nm laser excitation. The blue and red lines simulated the fitted D-band and G-band peaks, respectively.

6. PL excitation spectra of NGOD suspensions

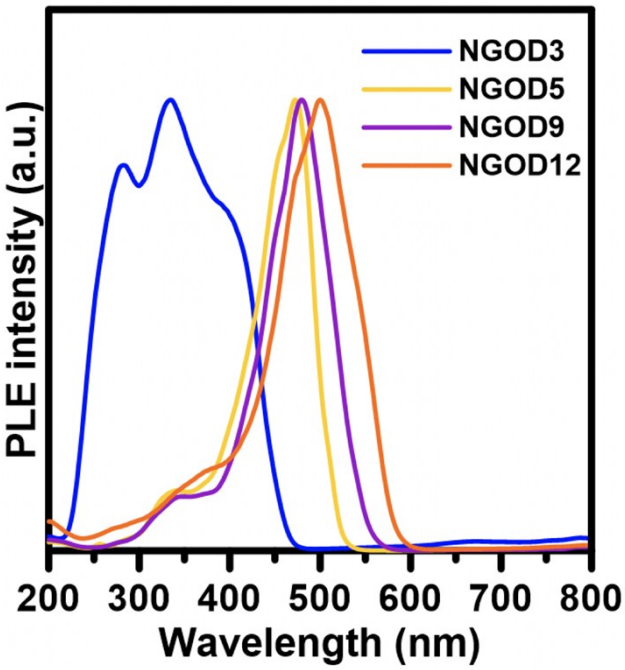

Fig. S6 PL excitation (PLE) spectra of the NGOD aqueous suspensions.

7. PL spectra of NGOD suspensions under various excitation wavelengths

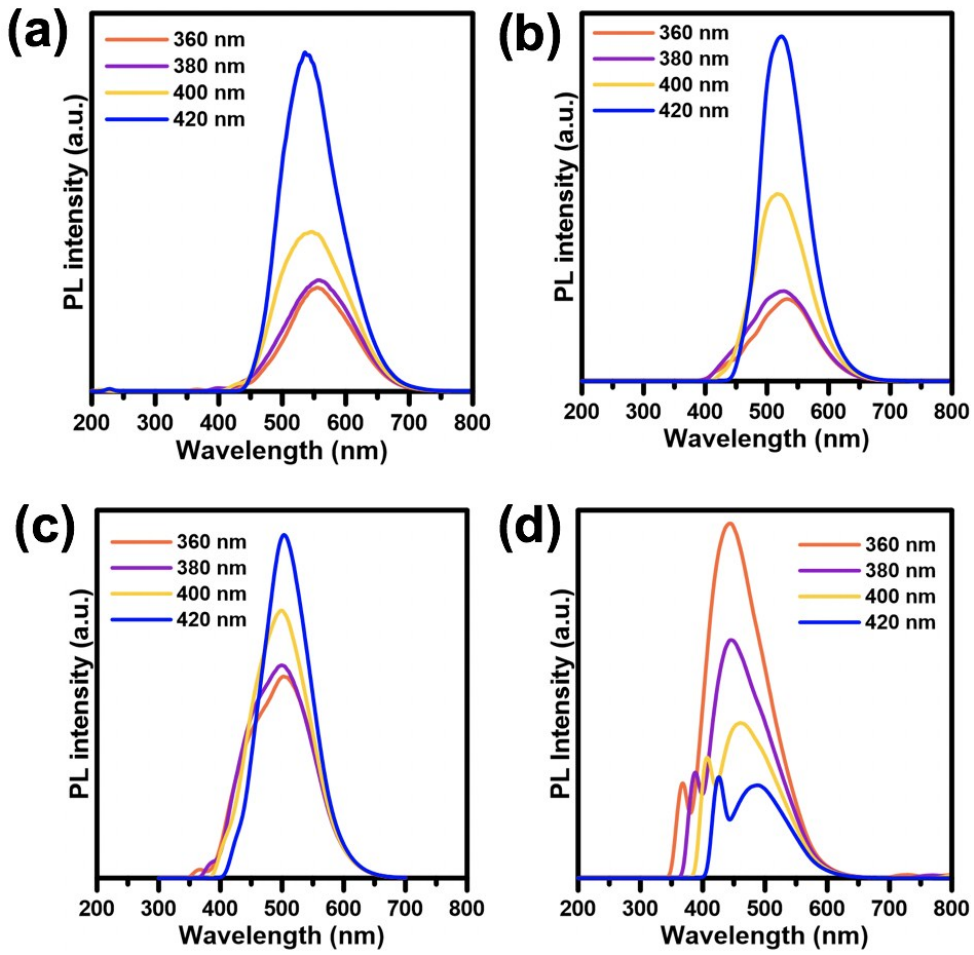

Fig. S7 PL excitation spectra of the NGOD aqueous suspensions under various excitation wavelengths. The NGOD specimens are (a) NGOD12, (b) NGOD9, (c) NGOD5, and (d) NGOD3.

8. Bandgap determination for NGODs

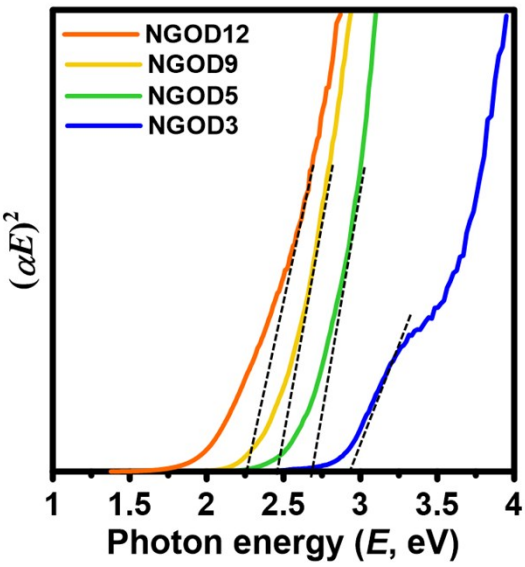

Fig. S8 Plots of $(\alpha E)^2$ against photon energy (E) for the NGOD suspensions converted from the absorption spectra of Fig. 4b. α is the absorbance.

9. UPS analysis for VBM and E_F levels of NGODs

We identified the VBM level of the NGODs deposited on silicon substrate by using UPS equipped with He I light irradiation. The following equation was used for UPS analysis:

$$E_B + E_k + \varphi = 21.2$$

where E_B is the binding energy measured from the Fermi level, E_k is the kinetic energy of electrons, φ is the work function of the NGODs, and 21.2 eV is the energy of the He I light.

The VBM and E_F can be calculated using the following equations:

$$\text{VBM} = 21.2 - (E_{B2} - E_{B1})$$

$$E_F = 21.2 - E_{B2}$$

where E_{B2} is the secondary cutoff binding energy in the UPS spectra, in which the E_k of the excited electrons is equal to 0, and E_{B1} represents the difference between the Fermi and VBM levels. **Fig. S6** shows the UPS spectra of the NGODs. The E_{B1} can be determined using the intercepts of the extrapolated straight lines on the abscissa at low binding energy. The E_{B2} can be estimated using the secondary cutoff values ($E_k = 0$ eV) in the UPS spectra, obtained from the intercepts of the extrapolated straight lines on the abscissa at high binding energy. The UPS widths are the difference between E_{B2} and E_{B1}. As presented in the above two equations, we determined the VBM and E_F levels relative to the vacuum by subtracting the width of the UPS spectra ($E_{B2} - E_{B1}$) and electron onset at high binding energy in the UPS spectra, respectively, from the excitation energy (21.2 eV).

9. UPS analysis for VBM and EF levels of NGODs

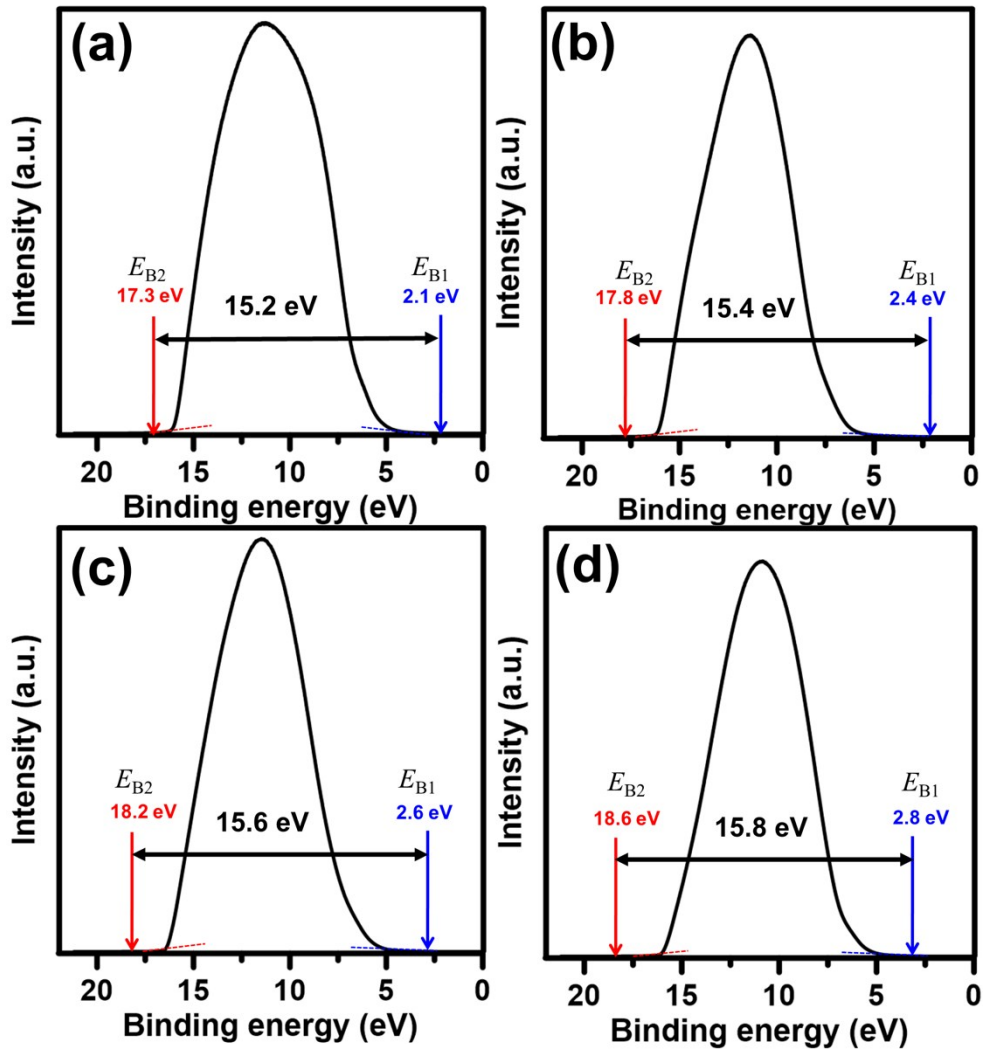

Fig. S9 UPS spectra of the NGODs specimens: (a) NGOD12, (b) NGOD9, (c) NGOD5, and (d) NGOD3. The E_{B1} values were determined from the intercepts of the extrapolated straight lines (blue dashed line) on the abscissa at low binding energy. The intersections of the tangent (red dashed line) with the abscissa at high binding energy gave the secondary electron onset binding energy, E_{B2}. The UPS widths (black lines) were the difference between E_{B1} and E_{B2}. The spectra were obtained under He I light irradiation at 21.2 eV.

10. Absolute optical absorption spectra of NGOD suspensions

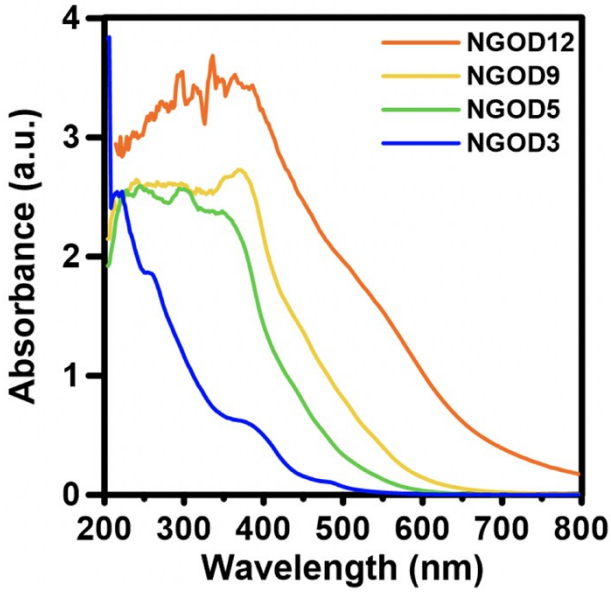

Fig. S10 Absolute optical absorbance spectra of the NGOD aqueous suspensions.