Electronic Supplementary Information

Photocatalytic Reforming of Sugar and Glucose into H2 over Functionalized Graphene Dots

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Supporting information for:
(1) A sustainable carbon cycle producing solar H2;
(2) TEM images of catalysts;
(3) Full-range and S 2p XPS spectra of catalysts;
(4) XPS spectra of SGODs;
(5) FTIR spectra of catalysts before and after reaction;
(6) PL spectra and time-resolved PL decay curves of catalysts;
(7) Fitting parameters of the PL decay curves;
(8) UPS analysis of catalysts;
(9) Solution-pH dependence of H2 production;
(10) H2 production over bare SNGODs under irradiation;
(11) H2 production over Pt-deposited TiO2 under irradiation.
1. A sustainable carbon cycle producing solar H₂

Scheme S1 Photocatalytic reforming of glucose into H₂ and photosynthesis in plants constitute a sustainable carbon cycle that produces a clean solar fuel.
2. TEM images of catalysts

![TEM images of catalysts](image)

**Fig. S1** TEM images of (a) NGODs and (b) SNGODs with the insets showing the histograms of size distribution. High-resolution TEM images of (c) an NGOD and (d) an SNGOD, showing the graphene \{1\overline{1}00\} lattice planes with a d-spacing of 0.213 nm.
3. Full-range and S 2p XPS spectra of catalysts

**Fig. S2** Full-range XPS spectra of (a) NGODs and (b) SNGODs, and (c) S 2p XPS spectrum of SNGODs.
4. XPS spectra of SGODs

Fig. S3 XPS spectra of the SGODs: (a) full-range, (b) C 1s, and (c) S 2p.
5. FTIR spectra of catalysts before and after reaction

Fig. S4  FTIR spectra of the NGODs and SNGODs: (a) before-reaction and (b) after a 60-h photocatalytic reaction.
6. PL spectra and time-resolved PL decay curves of catalysts

**Fig. S5** (a) PL spectra of the NGOD and SNGOD aqueous suspensions under 405-nm excitation. (b) Time-resolved PL decay curves of the NGOD and SNGOD aqueous suspensions excited by a 405-nm laser.
7. Fitting parameters of the PL decay curves

Table S1. The fitting parameters of the PL decay curves (Fig. S5b) excited using a 405-nm laser. The PL emission wavelength for detection coincides with the PL peak wavelength, which is 540 nm as shown in Fig. S5a.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$\tau_{ave}$ (ns)</th>
</tr>
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<tr>
<td>NGOD</td>
<td>1.8</td>
<td>5.9</td>
<td>40</td>
<td>60</td>
<td>5.2</td>
</tr>
<tr>
<td>SNGOD</td>
<td>2.0</td>
<td>7.3</td>
<td>23</td>
<td>77</td>
<td>6.9</td>
</tr>
</tbody>
</table>
8. **UPS analysis of catalysts**

We identified the tVB level of the NGODs and SNGODs 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 \( (E_F) \), \( E_k \) is the kinetic energy of electrons, \( \varphi \) is the work function of the NGODs, and 21.2 eV is the energy of the He I light.

The tVB and \( E_F \) can be calculated using the following equations:

\[
tVB = 21.2 - (E_B^2 - E_B^1) \\
E_F = 21.2 - E_B^2
\]

where \( E_B^2 \) is the secondary cutoff binding energy in the UPS spectra, in which the \( E_k \) of the excited electrons is equal to 0, and \( E_B^1 \) represents the difference between the \( E_F \) and tVB levels. **Fig. S6** shows the UPS spectra of the NGODs and SNGODs. The \( E_B^1 \) can be determined using the intercepts of the extrapolated straight lines on the abscissa at low binding energy. The \( E_B^2 \) can be estimated using the secondary cutoff values \( (E_k = 0 \text{ eV}) \) 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 \( E_B^2 \) and \( E_B^1 \). As presented in the above two equations, we determined the tVB level relative to the vacuum by subtracting the width of the UPS spectra \( (E_B^2 - E_B^1) \) from the excitation energy (21.2 eV).
Fig. S6 UPS spectra of (a) NGODs and (b) SNGODs. The tVB energy levels with respect to the Fermi levels 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 give the secondary electron onset binding energy. The UPS widths (black lines) can be determined by these two intercept binding energies, and the tVB can be calculated by subtracting these widths from the excitation energy (21.2 eV).
9. **Solution-pH dependence of H₂ production**

**Fig. S7** The solution-pH dependence of H₂ production from photocatalytic reforming of sugar and glucose. The solutions contained 5 wt% Pt-deposited SNGODs and were irradiated by visible light (420 nm < \( \lambda < 800 \) nm) at an intensity of 35 mW cm\(^{-2}\) over a period of 12 h.
10. **H₂ production over bare SNGODs under irradiation**

**Fig. S8** Time course of H₂ production from a sugar (0.35 mol L⁻¹) aqueous solution (at pH of 10) containing bare SNGODs (0.4 g) over a period of 72 h, with several interventions for evacuating the system. The system was irradiated by visible light (420 nm < λ < 800 nm) at an intensity of 35 mW cm⁻².
11. **H₂ production over Pt-deposited TiO₂ under irradiation**

![Graph showing the time course of H₂ production from sugar and glucose](image)

**Fig. S9** The time course of H₂ production from sugar and glucose (0.35 mol L⁻¹) aqueous solutions (at pH of 10) containing 5 wt% Pt-deposited TiO₂ (0.4 g) over a period of 36 h, with several interventions for evacuating the system. The TiO₂ sample was a commercially available TiO₂ powder (P25, Degussa, Japan). The system was irradiated by visible light (420 nm < λ < 800 nm) at an intensity of 35 mW cm⁻².