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Supplementary Information for Publication

Ambient plasma synthesis of TiO_2@graphite oxide nanocomposites for efficient photocatalytic hydrogenation

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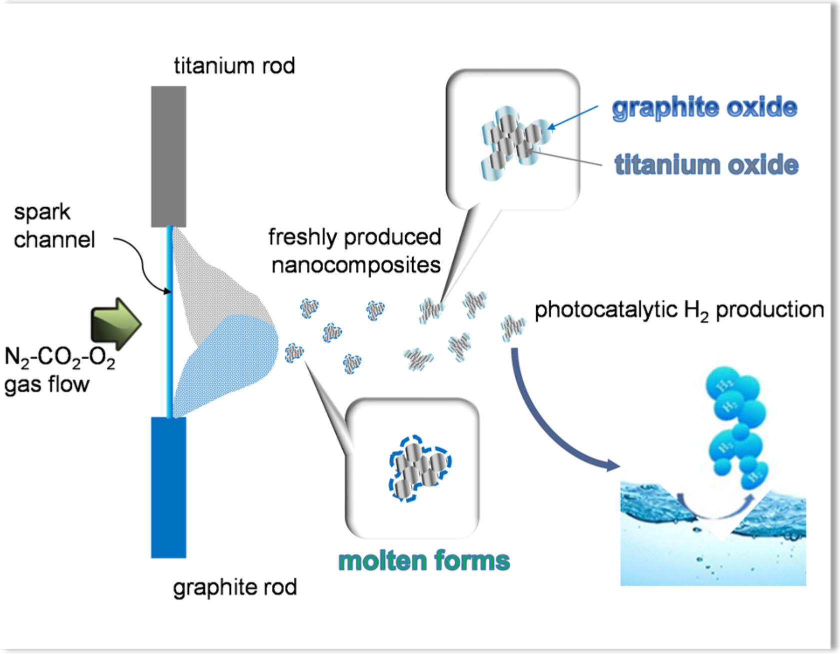
Experimental Procedure

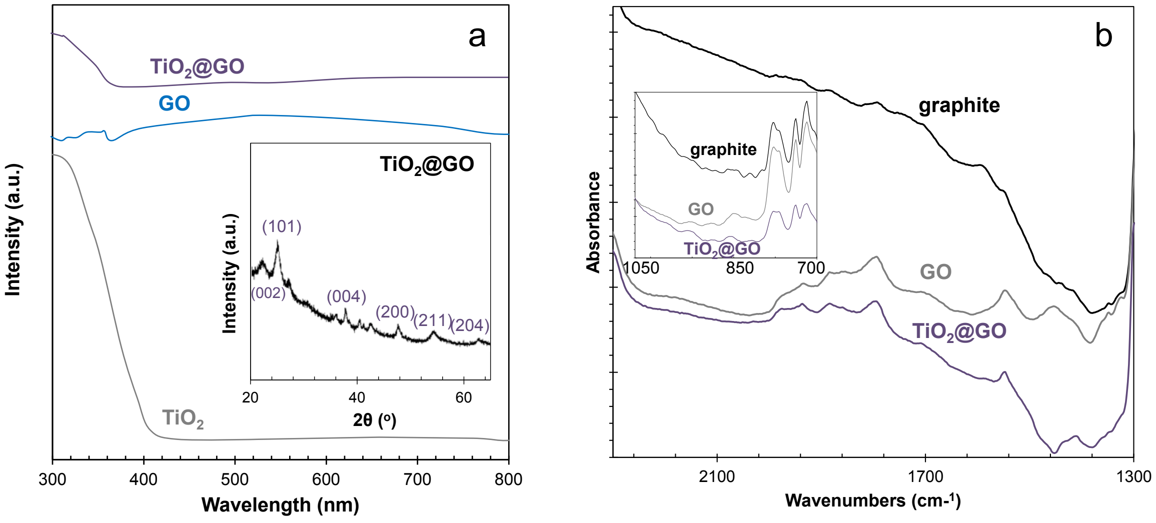
As shown in **Scheme S1**, a spark was generated between titanium and graphite carbon rods (diameter: 3 mm, length: 100 mm, Nilaco, Japan) inside a reactor within a 95 vol% N_2, 4.5 vol% CO_2, and 0.5 vol% O_2 environment (with a relative humidity of 85%) at standard temperature and pressure. Recently, new methods have been employed to prepare graphitic sheets using an electrical discharge in a CO_2/H_2 gaseous environment.[s1,s2] The specifications of the spark discharge were as follows: resistance, 0.5 MΩ; capacitance, 1.0 nF; loading current, 2.8 mA; applied voltage, 3.6 kV; and frequency, 1226 Hz. The flow rate of the gases was controlled by mass flow controllers (Kofloc, Japan), and the total flow rate was 2.8 L min^{-1}. To minimize agglomeration of primary TiO_2 particles, positively ionized gas was injected into the spark chamber because an electrostatic repulsion between unipolar ions on the primary TiO_2 particles surface may minimize the unwanted agglomeration.[s3] The resulting TiO_2@GO nanocomposites were separated from the flow *via* mechanical filtration. They were set aside in a clean booth to keep them in powder form.



SCHEME 1 Ambient heterogeneous spark discharge to synthesize TiO_2@GO nanocomposites in the gas-phase for photocatalytic applications. Ultrafine ZnO or WO_3 particles were also incorporated with thin GO layers *via* the same method

To measure photoelectrochemical responses, 5 mg of TiO_2@GO nanocomposites were dispersed in 5 mL of ethanol. After 10 min of sonication, the nanocomposites were coated onto a 2 cm^2 indium-tin oxide glass electrode and dried at 25 ^oC. The prepared electrodes, saturation calomel electrode, and platinum (Pt) electrode were chosen as the working, reference, and counter electrodes, respectively. The electrolyte was a 0.5 M L^{-1} Na_2SO_4 aqueous solution. The working electrode was irradiated horizontally by a high-pressure mercury lamp (160 W) with different wavelengths (320-450 nm). Photocatalytic hydrogen production was carried out in aqueous suspension under visible light (>390 nm). The filtered light was collected in the headspace of the closed reactor and analyzed by a gas chromatograph (3000, Agilent, US) with a thermal conductivity detector and argon used as the carrier gas.

FIGURE S1

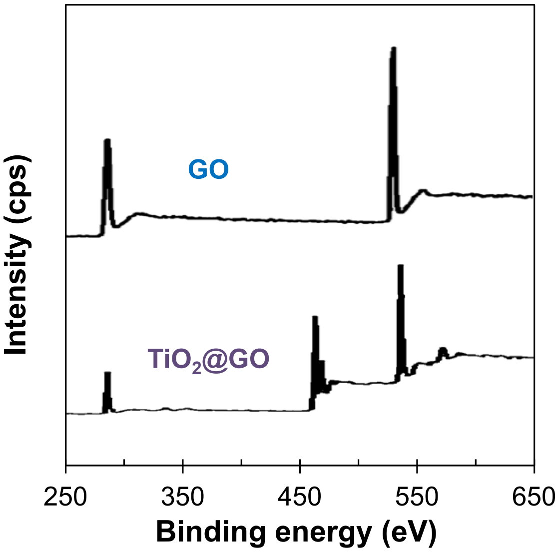


(a) UV-vis spectra of the TiO_2, GO and TiO_2@GO samples and XRD profile (inset) of TiO_2@GO sample. (b) FTIR spectra of the graphite, GO and TiO_2@GO samples.

The UV-vis spectrum of TiO_2@GO shows an absorption edge of ~380 nm, which coincides with the literature value of anatase of *ca.* 387 nm.[s4] Incorporation of TiO_2 with the GO leads to an absorption in the visible region. The broad absorption at the visible region should be ascribed to the conjugated structure in the GO covering in the nanocomposite. The X-ray diffractometry pattern peaks at 2θ = 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, and 62.7° crystalline planes of TiO_2 (inset of Fig. S1a), in agreement with the anatase form (JCPDS file No. 00-021-1272). In addition, graphite flakes of the GO precursor were detected, as indicated by the (002) reflection at 2θ = 26.5°, and the slight diffraction peak appears at *ca.* 45° corresponding to the (100) plane of the graphite, indicating TiO_2 crystallites deposited on a GO surface. Fig. S1b displays Fourier transform infrared spectra (IFS 66/S, Bruker Optics, Germany) of graphite, GO, and TiO_2@GO samples. All the samples exhibit a broad IR peak at around 1500 cm^{-1} corresponding to the C=C vibrations, and GO and TiO_2@GO additionally show carboxyl C=O (~1800 cm^{-1}), COOH (~1700 cm^{-1}), hydroxyl C-OH (~1400 cm^{-1}), and epoxy stretching (~950 cm^{-1}) groups. On the other hand, graphite shows a featureless spectrum at the given absorbance scales. The spectrum of the GO was not significantly changed after the incorporation of TiO_2 particles, but new bands at around

900 cm^{-1} correspond to Ti-O and TiO_2 stretching,[s5] clarifying that TiO_2 nanocrystals exist within the nanocomposites. This incorporation may be of significance to transfer carriers and induce a synergistic effect to enhance photocatalytic activity.

FIGURE S2



XPS spectra of GO and TiO_2@GO.

Fig. S2 shows the X-ray photoelectron spectra of the GO and TiO_2@GO specimens. The GO spectrum shows the binding energy (BE) peaks of C 1s at 286 eV and O 1s at 532 eV. After incorporation with TiO_2, the spectrum shows the Ti 2p peak at 458 eV, accompanied by the C 1s and O 1s peaks. These results imply that when the heterogeneous spark discharge was employed, most TiO_2 particles were incorporated with the GO particles, resulting in TiO_2@GO nanocomposites. It seems that the separated condensation and subsequent incorporation of the vapors result in the TiO_2@GO composites through the spark process.

TABLE S1 A summary of the size distributions of spark-produced individual TiO_2 and GO particles their incorporated nanostructures (TiO_2@GO) in the gas-phase

Case	GMD (nm)	GSD (-)	TNC (particles cm^{-3})
TiO_2	22.7	1.63	9.04×10^6
GO	73.8	2.92	4.84×10^3
TiO_2@GO	19.6	1.63	7.61×10^6

TABLE S2 A summary of the size distributions of spark-produced ZnO and WO_3 nanoparticles, and their hybridized nanostructures with thin GO layers (ZnO@GO and WO_3@GO) in the gas-phase

Case	GMD (nm)	GSD (-)	TNC ($\times 10^7$ particles cm^{-3})
ZnO	39.3	1.63	1.52
ZnO@GO	29.4	1.60	1.52
WO_3	11.4	1.54	0.23
WO_3@GO	13.0	1.57	0.41

SUPPORTING REFERENCES

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