**Ambient plasma synthesis of TiO$_2$@graphite oxide nanocomposites for efficient photocatalytic hydrogenation$^\dagger$**

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A graphite oxide (GO) layer with ordered ultrafine TiO$_2$ particles was synthesized using an ambient heterogeneous spark and the resulting materials displayed enhanced photocatalytic activity for hydrogen production. The ability of the TiO$_2$@GO nanocomposites to produce hydrogen was significantly greater than that of spark-produced TiO$_2$ particles, and even of p25-TiO$_2$ and p25-TiO$_2$@large reduced graphene oxide (LrGO). Even though nanoscale rGO hybridization with TiO$_2$ nanoparticles resulted in the highest performance in hydrogenation, this ambient plasma synthesis of TiO$_2$@GO composites nevertheless did make an appropriate structure for the photocatalytic performance comparable to that of p25-TiO$_2$@LrGO without individual chemical preparation of rGO.

**Introduction**

Photocatalytic technology could supply a feasible way to alleviate energy and environmental problems through splitting water for hydrogen production and degrading toxic pollutants.\(^1,2\) Semiconductor photocatalysis, one of the most promising technologies, is mainly applied to clean hydrogen energy production and environmental remediation applications.\(^3\) Titanium oxide (TiO$_2$), due to its cheapness, nontoxicity, effectiveness, and photostability, is becoming more popular for use with various semiconductor materials.\(^4\) Unfortunately, because of its large band gap of 3.2 eV, it can utilize only a very small UV fraction (\(~\leq 4\)% of available solar light; hence, it has aroused great interest for extending the photoresponse of TiO$_2$ to the visible light region for better solar light utilization. Another major limitation for achieving high photocatalytic activity is the rapid recombination of charge carriers. The charge pair recombination, which is faster than the interfacial charge transfer, reduces the quantum efficiency of photocatalysis.\(^5\)

Numerous efforts have been made in the last few decades to improve the photocatalytic activity of semiconductor photocatalysts. Aside from tuning their nanostructure and chemical composition, hybrid catalysts prepared by immobilization of the photocatalytic nanoparticles on appropriate substrates have been explored because of the significantly improved performance observed on such composites,\(^6-8\) among them, the potential role of carbon materials as additives and supports (i.e., conjugated carbon materials) for the immobilization of photocatalyst nanoparticles has recently attracted considerable attention\(^9-11\) because of the high efficiencies reported for carbon-photocatalyst composites on the photodegradation of a variety of pollutants in both the liquid and the gas phase.\(^12-16\)

Conjugated carbon materials such as carbon nanotubes, fullerenes, graphene, and graphite are excellent candidates for improving the transport of photocarriers during photocatalysis through the formation of electronic interactions with photocatalyst nanoparticles.\(^17\) Among them, carbon nanotubes, fullerenes, and graphenes are more expensive than graphite because they require complex manufacturing processes.\(^4\) Graphite oxide (GO) is a member of conjugated carbon materials that have a lamellar structure and has attracted great interest among researchers owing to some of its potential applications for electrochemical devices, catalysis, energy storage, and adsorption, and furthermore, GO is the most readily available, inexpensive, and suitable for mass production.\(^18\) However, GO produced through a harsh oxidation treatment of graphite sheets is usually used as the starting material in most studies.\(^19\) Moreover, its hybridization with photocatalyst nanoparticles requires additional batch chemical steps and control of the preparation of the nanoparticles,\(^20\) and thus it is still a challenge to prepare the hybrid photocatalysts in a lesser waste and continuous synthesis manner.

The present work introduces an ambient heterogeneous spark discharge to assemble TiO$_2$@GO nanocomposites for enhancement of photocatalytic hydrogen production. In our previous work, we reported the creation of different carbonaceous nanostructures by controlling the conditions of heterogeneous spark discharges.\(^21\) This is the first attempt to synthesise in situ oxidized metal–carbon nanostructures in a
continuous gas-phase manner without using any wet chemical steps under ambient conditions. A graphite–titanium spark configuration in an N$_2$–CO$_2$–O$_2$ atmosphere was employed to produce TiO$_2$@GO nanocomposites, and the nanocomposites were separated using mechanical filtration. Finally, they were employed as photocatalysts to produce hydrogen. The as-formed TiO$_2$@GO nanocomposites exhibited significantly higher photocatalytic activity than that from commercial and spark-produced TiO$_2$ nanoparticles. The mechanism of enhanced photocatalytic activity is based on the high migration efficiency of photoinduced electrons at the TiO$_2$–GO interface, which is due to the electronic interaction between both materials. We also evaluated the photocatalytic stability of the nanocomposites by repeating the experiment five times for stronger confirmation.

Results and discussion

The gas temperature inside the spark channel was increased beyond a critical value of 4000 K, which was sufficient to sublime parts of the titanium and graphite electrodes. The duration of each spark was very short and the vapors cooled rapidly downstream of the spark. This formed a supersaturation resulting in particle formation through nucleation–condensation. The total number concentration (TNC), geometric mean diameter (GMD), and geometric standard deviation (GSD) of the TiO$_2$ particles, which were measured using a scanning mobility particle sizer (SMPS, 3936, TSI, US), were $9.04 \times 10^6$ particles cm$^{-3}$, 22.7 nm, and 1.63, respectively, as shown in Fig. 1. TiO$_2$@GO nanocomposites were formed near the spark channel by incorporating titanium with graphite under an oxygen existing environment. We verified the incorporation of TiO$_2$ particles with GO layers by measuring the size distributions of GO and TiO$_2$@GO in the gas-phase. Table S1† summarizes the size distribution measurements of GO and TiO$_2$@GO. The TNC, GMD, and GSD of the TiO$_2$@GO case were $7.61 \times 10^6$ particles per cm$^3$, 19.6 nm and 1.63, respectively. The analogous data for GO were $4.84 \times 10^3$ cm$^{-3}$, 73.8 nm, and 2.92, respectively. The size distribution of TiO$_2$@GO was rather similar to that of TiO$_2$ particles compared to that of GO, and there was no bimodal distribution character, implying that GO was nearly quantitatively incorporated with TiO$_2$, to form TiO$_2$@GO nanocomposites.

Low- and high-magnification transmission electron microscopy (TEM, JEM-3010, JEOL, Japan) images (Fig. 2) show the morphology of TiO$_2$ and TiO$_2$@GO samples. Specimens were prepared for examination using TEM by direct electrostatic gas-phase sampling at a sampling flow rate of 1.0 L min$^{-1}$ and an operating voltage of 5 kV using a Nano Particle Collector (NPC-10, HCT, Korea). The TEM images reveal that the TiO$_2$ particles were agglomerates ($\sim$20 nm in lateral dimension) of several primary particles, which is consistent with the SMPS data (measured agglomerated TiO$_2$ particles) noted in Table S1.† As shown in the inset of TiO$_2$, about 0.35 nm size of the lattice fringe of TiO$_2$ can be observed, which can be indexed to the (101) plane of the tetragonal structure. The crystalline structure of TiO$_2$ was further analyzed using X-ray diffraction (Fig. S1a†). When the heterogeneous spark discharge was employed, most TiO$_2$ particles were attached to the GO layers, resulting in TiO$_2$@GO nanocomposites. It seems that the co-condensation of the vapors resulted in carbon incorporation with TiO$_2$ particles during the spark process. The production yield of TiO$_2$@GO nanocomposites from the ambient plasma synthesis is approximately 83.4%. The yield was determined by the area fraction of TiO$_2$@GO-to-all particles in the TEM image. The TEM image shows the larger sizes of the nanocomposites owing to gathering individual nanocomposites during the direct electrostatic gas-phase sampling. Nevertheless, the GO layers were clearly seen and had a $d$-spacing of about 0.44 nm (see the inset). The increased basal spacing of GO (vs. a graphite layer) was verified by X-ray diffraction measurements.

![Fig. 1](image1.png)  
**Fig. 1** Size distributions of spark-produced individual TiO$_2$ and GO particles and their incorporated nanostructures (TiO$_2$@GO) in the gas-phase. Standard deviations are noted in Table S1†.

![Fig. 2](image2.png)  
**Fig. 2** Low- and high-magnification TEM images of TiO$_2$ (20 ± 4.4 nm) and TiO$_2$@GO (26 ± 8.6 nm) samples.
interspacing of 0.34 nm) is related to the accommodation of various oxygen species and to the changes in the carbon hexahedron grid plane, indicating that the graphite was efficiently oxidized. While the boundary of TiO₂ particles within the nanocomposites was a little bit ambiguous probably due to agglomeration between TiO₂ and GO particles.

Fig. 3a gives the photoelectricity results of the TiO₂ and TiO₂@GO samples using a photocurrent test with a cutoff filter. The potential of the working electrode against the Pt counter electrode is set at 0.0 V. It was observed that there was a fast and uniform photocurrent response to each turn-on and off event in both electrodes. TiO₂ showed a maximum photocurrent in the UV range that is located at ~330 nm, while no significant photocurrent was generated under visible irradiation. Interestingly, TiO₂@GO showed a broad but much more intense photocurrent peak covering the range to 450 nm, thus extending into the visible range. Its maximum signal appeared at ~350 nm, 20 nm red-shifted from that of TiO₂. The photocurrent density of the TiO₂ and TiO₂@GO samples was 0.02 and 0.11 mA cm⁻² (0.83 and 4.14 × 10⁻⁴ A in photocurrent, inset) at 350 nm wavelength, respectively. The current of TiO₂ was enhanced more than five times by incorporation with GO. The high photocurrents measured in the nanocomposites are related to a higher density of photogenerated electrons recovered at the back contact of the electrical circuit likely as a result of efficient charge carrier separation; this indicates that the incorporation of GO plays an important role in the photoelectrochemical response of the nanocomposites, and anticipates a potentially higher photocatalytic activity of the nanocomposites. The time profiles of hydrogen production are compared among samples in Fig. 3b. Compared with p25-TiO₂, TiO₂, and GO, TiO₂@GO enhanced the hydrogen production performance. p25-TiO₂ had a size of 32.4 nm, a specific surface area of 52 m² g⁻¹, and an anatase : rutile ratio of 82 : 18. The specific surface areas of TiO₂, GO, and TiO₂@GO are 126.4, 100.8, and 225.2 m² g⁻¹, respectively. Incorporation between TiO₂ and GO was the most suitable to form void areas due to a significant difference in the morphology. The p25-TiO₂ shows a slightly larger hydrogen production than the spark produced TiO₂ particles, and this might have originated from the difference in the anatase : rutile ratio (69 : 31 for spark produced TiO₂). The hybridization assisted the photocatalysis by withdrawing electrons and subsequently retarding the charge pair recombination. Previous studies have also explained that the enhanced photocatalytic activity of the TiO₂@GO hybrid materials is mainly attributed to the inhibition of charge recombination.⁴ In the present case, the incorporation of GO with ultrafine TiO₂ particles did make an appropriate structure for enhanced photocatalytic performance. Therefore, the photo-generated conduction band electrons in TiO₂ could be more easily transferred to GO layers, because there is good contact between the TiO₂ surface and the GO layer. Further, even after five cycles (inset of Fig. 3b), we found that the hydrogen production performance reduced only by ca. 8% from 44.7 to 40.8 μmol h⁻¹, suggesting that the nanocomposites have good stability and reusability. The quantum yield (QY) of the photocatalytic production of hydrogen \( [\text{QY}(\%) = (2 \times R/I) \times 100] \) at 420 nm in wavelength was approximately 9.3%. The presence of GO on the surface of TiO₂ could inhibit the photocorrosion phenomenon and enhance the stability of the TiO₂ photocatalyst greatly. On the other hand, the slight decrease in the performance among the cycles is probably attributed to the aggregation of TiO₂ particles on the GO layers after several runs, which results in the decrease in surface area, and finally leads to the decrease in photocatalytic activity. In addition, about 85% of carbon was produced when the polarity of spark electrodes was switched as Ti: cathode – C: anode, and the hydrogen production was significantly smaller (~7.4 μmol h⁻¹) than that from the present work. A further
study for precisely controlling the ratio between TiO$_2$ and GO for the most efficient hydrogen production via ambient spark discharge is in progress.

In order to evaluate the feasibility of the synthesized TiO$_2$@GO, hydrogenation performances between the present composites and the TiO$_2$@reduced graphene oxide (rGO, MKN-SLG-F, M K Impex Corp., Canada) were tested. Hence, we further prepared different setups for fabricating TiO$_2$@rGO and p25-TiO$_2$@large rGO (LrGO, G250, Sinocarbon, China) composites. According to a previous study, the size of TiO$_2$@graphene is one of the critical parameters for efficient hydrogen production, and thus we employed TiO$_2$@rGO and p25-TiO$_2$@LrGO as representative comparators. In the case of TiO$_2$@rGO, we employed the BR method to fabricate nanoscale TiO$_2$@rGO composites since there are better contacts between the TiO$_2$ surface and rGO flakes. Briefly, a spark discharge between Ti rods (TI-452564, Nilaco, Japan) under air flow was employed to produce aerosol TiO$_2$ nanoparticles, and the particle laden flow was employed as the operating gas for atomizing the rGO solution (rGO in ethanol). The TiO$_2$ particles passed over the orifice of the collision atomizer, most TiO$_2$ particles were deposited onto the rGO flakes, resulting in TiO$_2$@rGO hybrid nanocomposites. The morphology of p25-TiO$_2$@LrGO (also shown in Fig. 4a) reveals a dispersion in the LrGO matrix, which has a tendency to locate along the wrinkles and edges of the graphene sheets. The time profiles of hydrogen production are compared among samples in Fig. 4b. Compared with TiO$_2$@rGO, TiO$_2$@GO shows a lower performance for hydrogen production. The nanoscale rGO hybridized structure further assisted the photocatalysis by withdrawing electrons and subsequently retarding the charge pair recombination. Nevertheless, the present TiO$_2$@GO shows a comparable performance to p25-TiO$_2$@LrGO for hydrogen production, which might be ascribed to the morphological difference between p25-TiO$_2$@LrGO (only a small fraction of the TiO$_2$ surface is in direct contact with LrGO) and TiO$_2$@GO (significantly smaller TiO$_2$ particles on graphitic layers). This implies that the ambient plasma synthesis of TiO$_2$@GO composites did make an appropriate structure for the comparable photocatalytic performance without individual
preparation of rGO. After five cycles (Fig. 4c), we found that the hydrogen production performances of TiO$_2$@rGO and p25-TiO$_2$@LrGO were reduced by ca. 7% and 5%, suggesting that the rGO hybridization also has good stability and reusability. On the other hand, the slight decreases in the performance are also shown in rGO hybridization cases, which imply that the rGO hybridization did not show a significant better stability in repetitive use.

As a significant expansion of this work, Fig. 5 shows the size distributions, morphologies, and photocatalytic activities of other nanocomposites from different spark configurations (zinc–graphite and tungsten–graphite under identical operation conditions) to verify the generalizability of the heterogeneous spark discharge. As shown in Fig. 5a, even though the other nanocomposites display different intrinsic size distributions, due to different material combinations, the size distributions of the metallic nanoparticles converged toward the nanocomposite size distribution (refer to Fig. 1), and there was no bimodal distribution character. This implies that the heterogeneous spark discharge may induce an appropriate incorporation of GO with metallic nanoparticles. Details of the size distributions are summarized in Table S2.† Fig. 5a also shows that the morphologies of ZnO@GO and WO$_3$@GO nanocomposites consisted of ZnO and WO$_3$ nanocrystals, although the spark electrodes for the synthesis were changed.

Conclusions

We developed for the first time a continuous gas-phase synthesis of TiO$_2$@GO nanocomposites through an ambient heterogeneous spark discharge without any wet chemical preparation steps, and we also tested their photocatalytic activities. The unique hybrid structure enabled enhanced contact between GO and TiO$_2$ and facilitated efficient electron transfer for enhanced photocatalytic activities for hydrogen production. We believe that this provides new perspectives and useful information for the design of low-cost and more efficient photocatalysts for energy production and environmental remediation.

Notes and references