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COMMUNICATION

Building a Bridge from Papermaking to Solar Fuels

Zaiyong Jiang,[#] Xinhan Zhang,[#] Wei Sun, Deren Yang, Paul N. Duchesne, Yugang Gao, Zeyan Wang, Tingjiang Yan, Zhimin Yuan, Guihua Yang, Xingxiang Ji, Jiachuan Chen,* Baibiao Huang, Geoffrey A. Ozin**

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Abstract: *Black liquor, an industrial waste product of papermaking, is primarily used as a low-grade combustible energy source. Despite its high lignin content, the potential utility of black liquor as a feedstock in products manufacturing, remains to be exploited. Demonstrated here in is the use of black liquor as a primary feed-stock for synthesizing graphene quantum dots that exhibit both up-conversion and photoluminescence when excited using visible/near-infrared radiation, thereby enabling the photosensitization of ultraviolet-absorbing* TiO_2 *nanosheets. In addition, these graphene quantum dots can trap photo-generated electrons to realize the effective separation of electron-hole pairs. Together, these two processes facilitate the solar-powered generation of* H_2 *from* H_2O*, and CO from* H_2O-CO_2*, using broadband solar radiation.*

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Black liquor is a major waste product of industrial papermaking.[1] It is composed primarily of lignin, together with small amounts of hemicellulose and sodium salts (*i.e.*, hydroxides and sulfides).[2] Today, black liquor is utilized as a low-grade combustible energy source, despite being is considered environmentally unsound and resource-inefficient.[3] In the Kraft papermaking process, every ton of pulp produced results in 10 tons of black liquor.[4] Such levels of waste generation *via* papermaking is the worldwide norm.[5,6] The vision of a sustainable papermaking process is imagined in this work: the transformation of black liquor from a liability to a resource for producing value-added products.[7,8]

In recent years, polycyclic aromatic hydrocarbons (PAHs) have been shown to be useful precursors for synthesizing graphene quantum dots (GQDs) with appealing optical properties.[9-11] Biomass from agriculture and forestry, is available

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in large quantities and is rich in PAHs, making it a useful precursor for producing GQDs.[12-15] Thus, in the work described herein it is proposed that lignin-rich black liquor, could serve as a useful feed-stock for the large-scale production of GQDs, thereby significantly increasing the value of this waste product.

This proposition is reduced to practice by employing black liquor sourced GQDs as a visible/near infrared up-conversion sensitizer and electron collector, thus enabling ultraviolet-absorbing TiO_2 nanosheets to function as a broadband photocatalyst, generating H_2 from H_2O, and CO from H_2O and H_2O-CO_2, under solar irradiation.

The GQDs were prepared using poplar sulfate black liquor lignin, as shown in **Figure 1a**. Inspired by the method for processing biomass, we isolated the lignin-rich portion and then applied oxidative cleavage and aromatic refusion procedures. The synthesized GQDs could be uniformly dispersed in water without signs of sedimentation for several months, indicating their high colloidal stability. As discussed below, a combination of various spectroscopic tools demonstrated the characteristic features of GQDs, indicating the success of the aforementioned transformation.

The morphology of the GQDs was characterized via transmission electron microscopy (TEM), see representative image **Figure 1b and Figure S1**, revealing that they were uniformly dispersed with sizes in the range of 2 to 6 nm. High-resolution TEM imaging, see **Figure 1c**, revealed a lattice spacing of approximately 0.205 nm, which was close to that of graphene (100) planes.[16] The height of the GQDs was further measured by atomic force microscopy (AFM), see **Figure 1d-e**, yielding values of 0.3 to 2.1 nm. As far as we know, these GQDs are the first ever prepared *via* using the black liquor from papermaking.

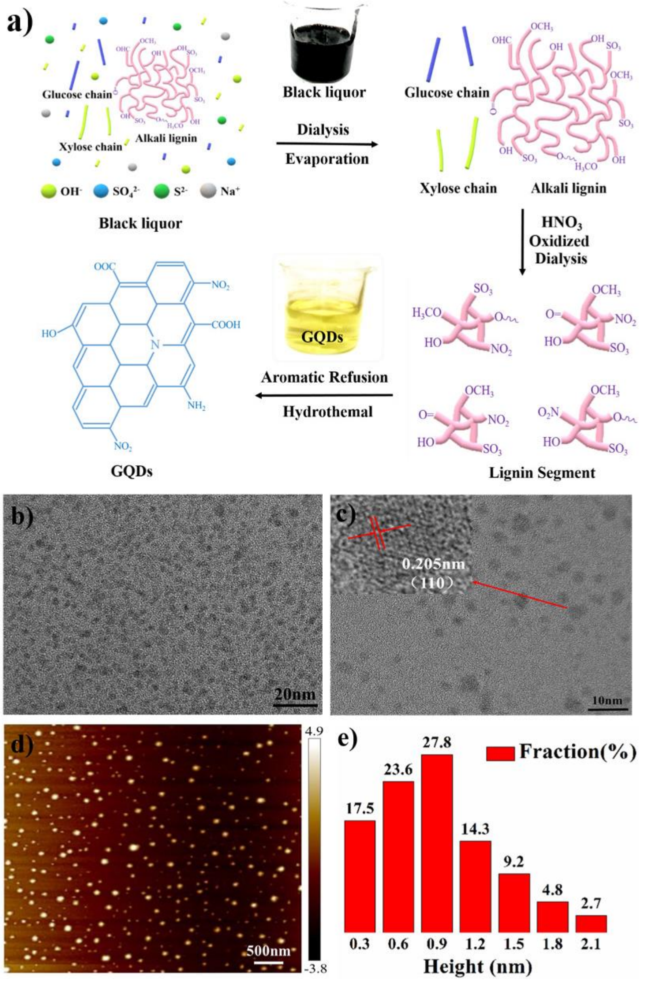

Figure 1. (a) Synthetic steps for producing GQDs from black liquor generated *via* papermaking; (b-f) Morphology and size distribution of GQDs, (b) TEM and (c) HR-TEM images of the GQDs; (d) AFM image and (e) height distributions of GQDs by AFM.

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The power X-ray diffraction (PXRD) pattern of GQDs, shown in **Figure S2a**, exhibited a graphene oxide (001) peak at 2θ = 12.9° and a graphite peak at 2θ = 28.9°.[17] The interlayer spacings are 6.86 Å and 3.09 Å, respectively, corresponding well with the PXRD peaks of graphene oxide and bulk graphite. Raman spectroscopy, **Figure S2b**, reveals two diagnostic peaks of graphene at 1375 cm^{-1} and 1588 cm^{-1}, corresponding to the D peak (sp^3 C) and the G peak (sp^2 C), respectively.

X-ray photoelectron spectroscopy (XPS) of the GQDs (**Figure S2c-f**) revealed three types of carbon: C=C/C-C, C-N and C-O/C=O. Four distinct nitrogen environments were also observed in these samples: C-N-C (399.9 eV), $N\text{-}(C)_3$ (400.9 eV), N-H (402.0 eV) and N-O (406.3 eV).[18] The C-N bond in the C 1s spectrum is indicative of nitrogen doping of the GQDs by nitric acid. The O 1s peaks contributions, observed at 531.6 eV (C=O), 532.1 eV ($-NO_2$) and 533.1 eV (C-O), indicated some oxidative cleavage of lignin bonds during the synthesis of the GQDs from the black liquor, likely by nitric acid.[13] Oxygen- and nitrogen-containing functional groups in the GQDs exist as mid-gap states, which can act as capture centers for excitons and the source of PL described below.[19]

The GQDs also exhibited some anticipated diagnostic optical properties. Under 365 nm UV excitation, a notable blue-green down-conversion photoluminescence (PL) was observed in **Figure 2a**. The PL was dependent on the excitation wavelength and could be tuned in the range of 430 to 520 nm (**Figure 2b**). The GQDs also displayed up-conversion PL, **Figure 2c**, which has been ascribed to multiphoton excitation.[20] The UV-Vis absorption spectrum of GQDs, **Figure 2d**, has an optical adsorption edge around 450 nm. Together, both the optical properties and well-known electrons-capturing properties of the GQDs allow them to function in a broadband composite photocatalyst for generating H_2 and CO from H_2O and $H_2O\text{-}CO_2$, as described below.

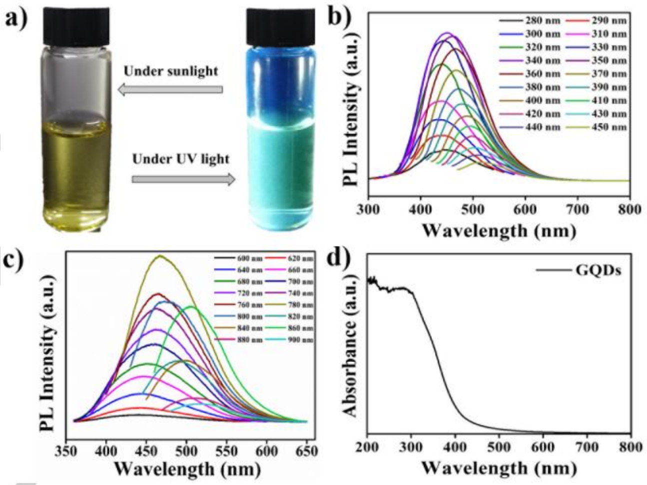

Figure 2. (a) Photographs taken of a GQDs suspension while illuminated by sunlight or a 365 nm UV light, (b) PL spectra of GQDs excited from 280 nm to 450 nm, (c) Up-conversion PL spectra of GQDs excited from 600 nm to 900 nm, (d) Ultraviolet-visible (UV-Vis) absorption spectrum of GQDs.

With this background information regarding the synthesis-structure-property relations of black-liquor-derived GQDs, their function and utility in H_2O and $H_2O\text{-}CO_2$ photoreduction was explored.

Different quantities of GQDs were first

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immobilized on the surface of TiO_2 nanosheets and subsequently reduced using $NaBH_4$ to improve the conductivity of graphene.[21] For comparison, the pristine TiO_2 nanosheets (henceforth denoted TiO_2) were also treated using the same amount of $NaBH_4$. In both cases, residual $NaBH_4$ was removed via washing with de-ionized water. The expected splitting of H_2O to produce H_2 and O_2 was not initially observed; therefore, methanol (CH_3OH) was employed as a sacrificial reagent for H_2 evolution. For this process, it is well-documented that the H_2 is evolved reductively *via* the reaction of photoelectrons by H_2O, while CH_3OH is oxidized *via* the reaction of photo-generated holes.[22, 23]

The results shown in **Figure 3a, 3c** demonstrate a significant enhancement of the CO_2 to CO and H_2O to H_2 reduction activities of GQDs/TiO_2 over those of TiO_2 under UV-Vis irradiation, with 0.6 wt% GQDs/TiO_2 exhibiting the best overall rates. The pristine rectangular TiO_2 nanosheets shown in the TEM images of **Figure 3e** were observed to have average widths and lengths of 50 nm and 100 nm, respectively. GQDs immobilization on the TiO_2 nanosheets is seen to be fairly uniform, see **Figure 3f and Figure S3**, with essentially no change in nanosheets morphology. The stability of the most active 0.6 wt% GQDs/TiO_2 sample can be seen from the reproducibility of the H_2 and CO evolution reactions shown in **Figure 3b and Figure 3d**. Isotopic $^{13}CO_2$ tracing experiments analyzed using gas chromatography-mass spectroscopy (GC-MS) confirmed that the photogenerated ^{13}CO originated from the reduction of $^{13}CO_2$, **Figure S4**. In addition, the PXRD and Raman spectra of used samples, shown in **Figure S5,** revealed no obvious changes in the morphology or crystallinity of TiO_2 after immobilizing the GQDs.

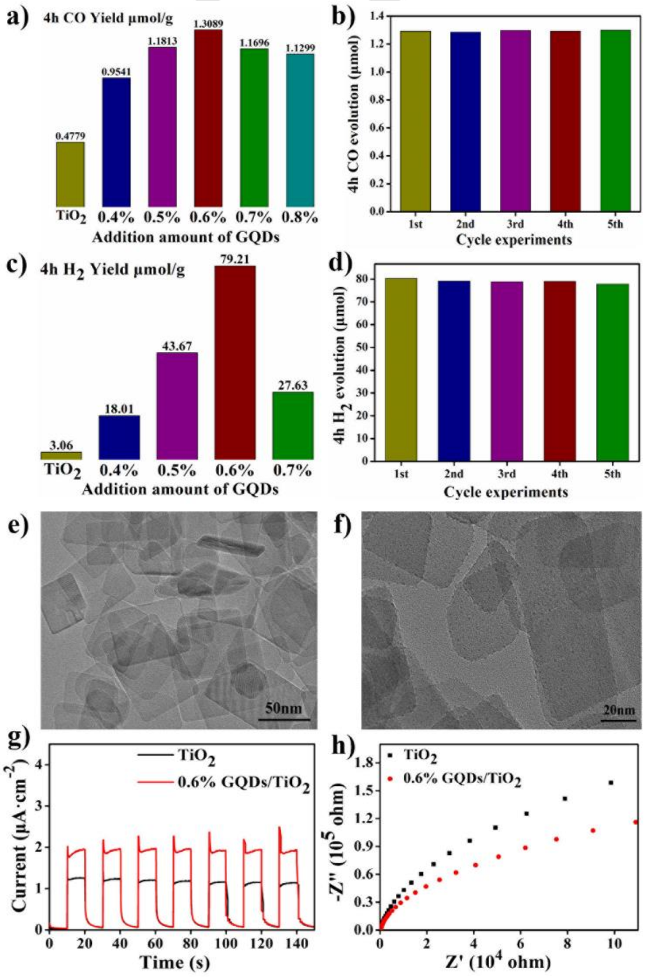

Figure 3. (a) Photocatalytic CO_2 reduction activities of GQDs/TiO_2 samples under UV-Vis light, (b) Cycling test results of CO_2 reduction photoactivity of 0.6wt% GQDs/TiO_2, (c) Photocatalytic H_2 evolution activity of TiO_2 and GQDs/TiO_2 samples, (d) Cycling test results of photocatalytic H_2 evolution activity of 0.6 wt% GQDs/TiO_2, (e) TEM image of pristine TiO_2

nanosheets, (f) TEM image of the 0.6 wt% GQDs/TiO_2, (g) Transient photocurrent responses of the TiO_2 and 6 wt% GQDs/TiO_2, (h) Electrochemical impedance spectroscopy (EIS) of TiO_2 and 6 wt% GQDs/TiO_2.

To explore the origin of the aforementioned enhancement, transient photocurrent and electrochemical impedance spectroscopy (EIS) experiments were performed, see **Figure 3g-h**. The photocurrent of GQDs/TiO_2 increased relative to pristine TiO_2, which implied GQDs can efficiently promote the separation of photo-generated electron-hole pairs. **Figure 3h** shows the arc radius of GQDs/TiO_2 in the EIS Nyquist plot was smaller compared with that of pristine TiO_2, again supporting the fact that the photogenerated electron-hole pairs could be well separated.[24-30] In addition, the UV-Vis spectra of GQDs/TiO_2 differed from that of TiO_2 showing a visible light absorption band from 400 to 600 nm from HOMO-LUMO excitations in GQDs, see **Figure S6**[31].

With the collected results of this study one can propose a model for the photocatalytic CO and H_2 evolution reactions from CO_2-H_2O and H_2O respectively, as delineated in **Figure 4**.

In brief, GQDs/TiO_2 can be excited by UV-Vis irradiation to produce photo-generated electrons (e^-) and holes (h^+). As shown in **Figure 4a**, the photo-generated e^- in the conduction band of TiO_2 can be transferred to GQDs, where they reduce adsorbed CO_2 molecules to CO. Concurrently, the photogenerated h^+ can directly oxidize water molecules to O_2.[32-34] A similar process occurs for the reduction of adsorbed H_2O molecules to H_2 as shown in **Figure 4b**. Meanwhile, h^+ are consumed by the sacrificial methanol reagent. For both cases, the GQDs/TiO_2 faciliated separation of electrons and holes. Furthermore, the up-conversion PL of GQDs, can advantageously generate photoelectrons in TiO_2, thereby exploiting the wider visible/near-infrared wavelength range of sun-light and improving the photocatalytic efficiency.

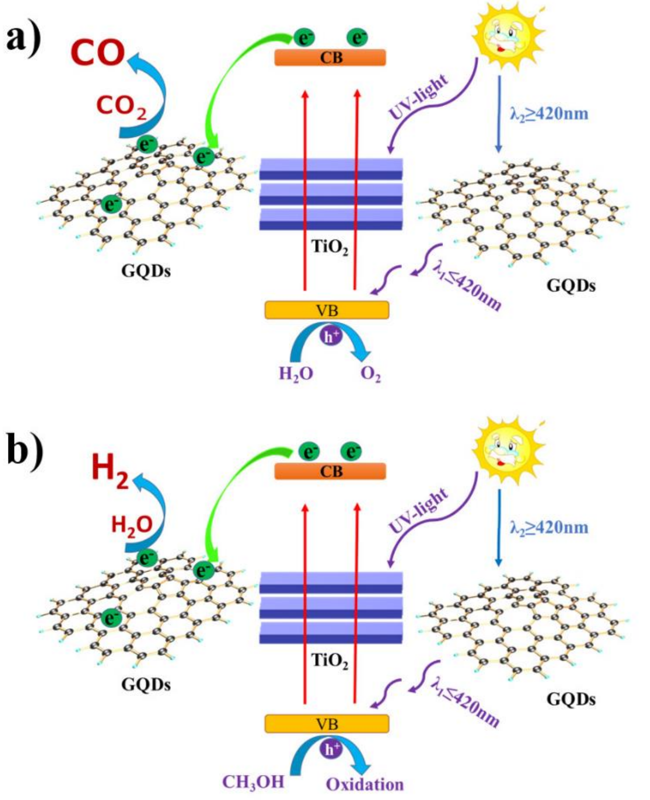

Figure 4. Schematic of the photocatalytic (a) CO_2-H_2O and (b) H_2O reduction pathways to CO and H_2 over GQDs/TiO_2 under UV-Vis light irradiation.

In summary, GQDs sourced from industrial black liquor have been successfully immobilized on the surface of TiO_2 nanosheets. Relative to pristine TiO_2, the resulting GQDs/TiO_2 catalysts exhibited a remarkable improvement in CO_2 and H_2O photoreduction activity by GQDs-TiO_2 under simulated solar light irradiation. The up-conversion and charge trapping abilities of the GQDs work synergistically to enhance the photocatalytic performance of GQDs/TiO_2 relative to TiO_2 alone.

Thus, the envisioned bridge between the black liquor of papermaking and fuels from the sun has been realized in this work, enabling the conversion of two waste products (black liquor and CO_2) into value-added products. As a result, this fundamental scientific advance shows great promise for such technological applications, and is certainly worthy of continued research and development to discover if it can indeed be reduced to practice.

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Keywords: Graphene quantum dots, Black liquor, Papermaking, Solar fuels, Photocatalytic CO_2 Reduction

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