Supporting Information

Decoration of graphene quantum dots on TiO$_2$ nanostructures: Photosensitizer and cocatalyst role for enhanced hydrogen generation

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Synthesis of graphene quantum dots (GQDs)

Synthesis of GQDs was done following our previous work \cite{32}. In brief, 100 mg of NaOH was added to 60 mL of ethylacetoacetate under constant stirring for 30 min. followed by filtration. 200 mg of graphite powder was added to the filtrate and sonicated for 2 h using a 20 kHz probe sonicator (Sonics Vibra Cell, USA). Once the solution has cooled down, the mixture was centrifuged and the supernatant was filtered through 0.22 µm syringe filter. The filtrate was then dialyzed using 3.5 kDa membrane to yield the GQDs solution.

Photocatalytic H₂ generation experiments

The experiments were carried out in a 185 mL quartz reactor equipped with a gas-tight rubber septum and a top loading port, used for both out gassing and sampling. 50 mL of 5 vol% glycerol aqueous solution containing 5 mg of the catalyst was stirred for 30 min in the absence of light to ensure homogenous dispersion of the catalyst. To maintain an inert atmosphere, quartz reactor was evacuated by purging with high-purity N₂ gas (99.999% pure). Natural solar light irradiation was employed for photocatalytic activity experiments continuously for 4 h with an average light intensity of 80,000±1000 lx. The generated H₂ gas was collected hourly and analysed using a gas chromatograph (GC), equipped with a thermal conductivity detector (TCD) and a molecular sieve/5A column, at 70 °C, using N₂ as the carrier gas. Identical conditions were maintained for both control and blank (without catalyst) experiments. To check the lifetime of the catalyst for prolonged usage, recyclability experiments were carried out for 4 cycles, wherein each cycle of experiments were carried out for 4 h under solar light irradiation. After completion of the first cycle, the reactor was covered with aluminium foil to protect it from light and remained airtight overnight under ambient conditions. In the experiment before the first recycle, the gaseous products in the reactor were evacuated, followed by purging with dry N₂, and the absence of H₂ and O₂ was verified by analysing with a gas chromatograph and then irradiating with solar light for 4 h. The same procedure was repeated for all 4 recycles.