

Electronic Supplementary Information (ESI)

Green chemistry synthesis of nanocomposite graphene hydrogel with three-dimensional nano-mesopores for photocatalytic H₂ production application†

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Experimental Details

Synthesis of TiO₂ nanorods, 2D RGO TiO₂ and Nanocomposite hydrogel (NGH)

0.34 g of TiO₂ anatase powder was mixed with an amount of 10 M of aqueous NaOH. The mixture was stirred for 1 h to get a homogenous mixture before it was transferred to a Teflon-lined stainless steel autoclave and heated in an oven at 110 °C for 48 h. The precipitate was then mixed with 20ml of 1M of HCl, stirred for 24 h and finally rinsed dried to form TiO₂ nanorods. Then 4.2 mM of HAuCl₄, 0.42 M of urea and 0.1g of TiO₂ nanorods were added into 10ml DI water and stirred for 2 h at 80 °C water bath. The mixture was then calcinated at 300 °C for 4 h to obtain TiO₂ nanorods-Au nanoparticles. Subsequently, 0.25g of VC was added into 10 ml Graphite oxide (GO) (produced by modified Hummers method¹) aqueous dispersion (0.2 mg/ml) and 30 mg of TiO₂ nanorods/TiO₂ loaded Au nanoparticles and heated to 90°C for 1.5 to 4 hr to obtain NGH and NGH-Au respectively. 2D RGO TiO₂ is prepared based on the same procedure without the addition of Au nanoparticles and VC (which is essential for formation of 3D hydrogel).

Materials Characterizations

Scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 6700F field-emission operating at 15kV. X-ray photoelectron spectroscopy (XPS), VG ESCALAB 220I-XL system equipped with an Mg K α x-ray source was employed chemical composition studies. X-ray diffraction (XRD) was carried out on a Philips X-ray diffractometer with Cu K α radiation ($\lambda=1.541\text{\AA}$). Absorption spectra were obtained using a Shimadzu UV-3600 UV-vis spectrophotometer. Brunauer- Emmett-Teller (BET) measurements were conducted using Quantachrome Nova 1200 with N₂ as the adsorbate at liquid nitrogen temperature. Raman

spectra were measured using Raman spectroscopy (Renishaw inVia Raman microscope) with VIS (488 and 633 nm) and UV (325 nm) lasers. H₂ uptake was measured using pressure-Composition Isotherm Measurement with the AMC four-channel Gas Reaction Controller (4-ch GRC). Electrochemical impedance spectroscopy (EIS) was performed using a PARSTAT 4000 from Princeton. The electrolyte used was 0.1M Na₂SO₄ in deionized water. H₂ evolution measurements were carried out using 30 mg of hydrogel and 10 ml DI water (10% methanol) contained in a quartz vial and illuminated with a 300W Xe lamp (Excelitas, PE300BFM). The reaction mixture was purged with Ar gas for 15 min prior to measurements. The reaction mixture was syringe drawn (100 μl) to sample the gas composition using gas chromatographer (Shimadzu, GC-2014AT).

H₂ adsorption of NGH

Figure S1 shows pure TiO₂, 2D RGO-TiO₂ and 3D NGH were irradiated with Xenon lamp for 2h before removing them from the lamp. This is followed by mechanically agitation in a conventional ultrasonic bath for duration of 90 min while H₂ that were trapped and released were intermittently measured at 30, 60 and 90 min. It is noted that the pure TiO₂ and 2D graphene sheets TiO₂ composite show lower H₂ content as compared to the 3D NGH. Architecturing a 3D interconnected framework (hydrogel) forms desirable pores which facilitate adsorption of H₂.

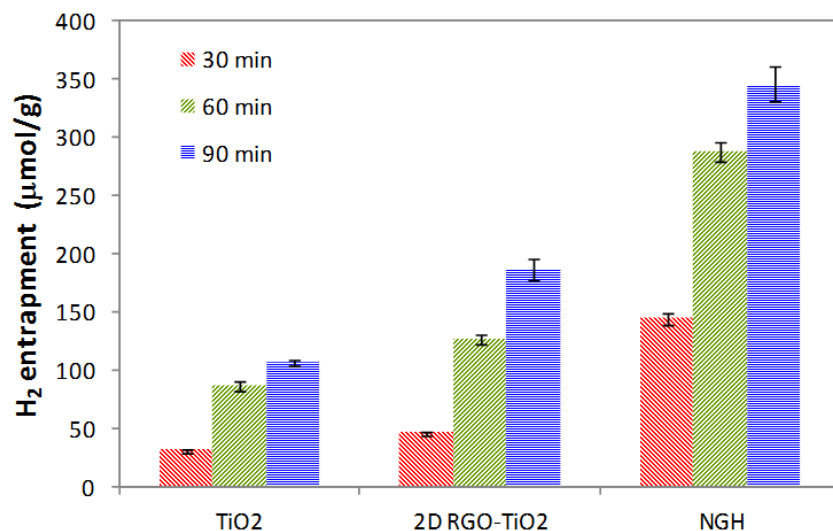


Figure S1: H₂ adsorption in pure TiO₂, 2D RGO-TiO₂ and NGH.

Pressure-composition isotherm of NGH at room temperature and pressure range of 0 to 100 atm was carried out to affirm H₂ uptake capabilities of the NGH (figure S2). The H₂ adsorption of NGH was around 2.5 and 4.2 wt% at pressure of 50 and 100 atm respectively. The adsorption capacity of NGH at room temperature is comparable to GO-MWCNTS composite (2.6 wt %) while surpasses many other metal-organic frameworks (MOFs) and carbon based materials.² However, it was found that not all adsorbed H₂ desorbed when the samples were evacuated. The presence of hysteresis is possibly due to the trapping of adsorbed H₂ molecules in small cavities or mesopores such as interlayer graphene sheets (~3.8 Å). At the present stage, kinetics of H₂ adsorption may not be optimal but potentially tunable since it has been experimentally shown and calculated (first-principles calculations) that interlayer distance of graphene sheets plays an important role for optimal H₂ kinetics.³ In our case, the kinetics of H₂ adsorption is possibly determined not only by the H₂ molecules diffusing through the porous network of NGH but also through the lamellar interlayer graphene sheets. In general, high micropore volume and surface area are essential parameters for consideration of H₂ adsorption capacity which is well-taken into account in our architected NGH as it offers a more direct diffusion pathway and greater access to internal surfaces.

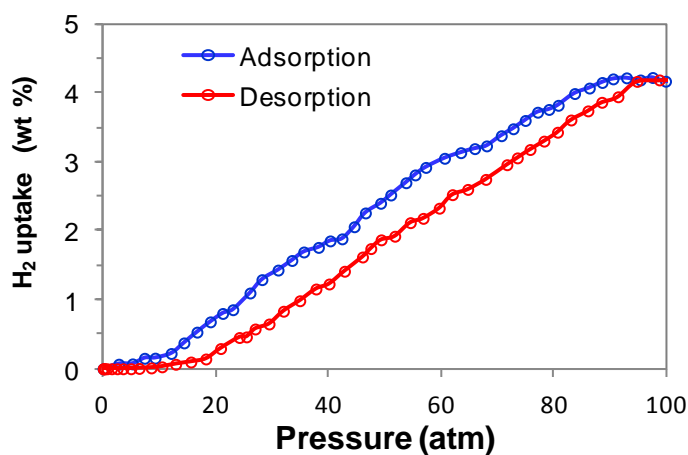


Figure S2: Pressure-composition H₂ isotherm of NGH at room temperature and pressure range of 0 to 100 atm.

Sonocatalysis H₂ production of NGH

It can be observed that purely mechanically agitated photocatalyst show low H₂ production (figure S3). The use of ultrasound for photocatalytic reaction (sonocatalysis) has been reported to produce H₂ as it promotes catalytic activity due to surface cleaning, particle size reduction and enhanced mass transport.⁴

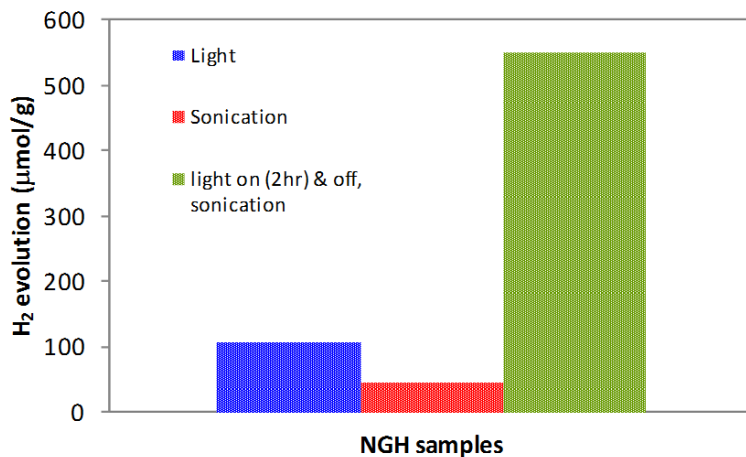


Figure S3: H₂ measurements after light irradiation, sonification and light irradiation (2 h) with sonification of NGH.

References:

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