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Introduction

A gel is considered to be a substance that consists of a solid scaffold with long chain molecules that cross-link to form an interconnected network which encloses a continuous liquid phase (water in the case of a hydrogel). Hydrogels made of natural and synthetic polymers are mainly used for biomedical applications which include drug delivery and tissue engineering whilst hydrogels consisting of TiO_2 nanofiber and nanoparticle composites are used mainly for lead, dye and wastewater treatment applications.¹⁻⁴

Recently, there is a growing interest in the composition of TiO₂ and carbon based nanomaterials to enhance photocatalytic performance.⁵⁻⁸ Zhang *et al.* reported the photocatalytic H₂ production of TiO₂-graphene composites by studying the effects of graphene loading content and calcination conditions on the photocatalytic performance.⁵ The results show that the photocatalytic performance of 0.1 g $\rm TiO_2$ with 5.0 wt% graphene composites was 8.6 μ mol h⁻¹ (86 μ mol h⁻¹ g⁻¹) from Na₂S-Na₂SO₃ aqueous solution under UV-vis light irradiation. Wong et al. investigated the 1-dimensional TiO₂ nanotube and nanobelt structures of different structural phases with various graphene loading% composites for photocatalytic H₂ production.⁶ The optimal H₂ production was from anatase TiO₂ nanotube/5 wt% graphene composite producing 550 µmol h⁻¹ g⁻¹ under UV-vis light irradiation. Xiang et al. studied graphene-TiO₂ nanosheet composites for

Green chemistry synthesis of a nanocomposite graphene hydrogel with three-dimensional nanomesopores for photocatalytic H₂ production[†]

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In this work, we have developed a nanocomposite graphene hydrogel (NGH) based on green chemistry, employing vitamin C (VC) to attain a supramolecular 3D network of hybrid nanostructured materials. Here, it is shown that the hydrogel is an appropriate and robust host for stable a TiO₂ semiconductor catalyst sensitized with visible light responsive nanostructured particles. The NGH is tailored with well-defined nano-mesopores, a large surface area, a highly dispersive nanosheet–nanorods–nanoparticle composite, and enhance visible light absorption. Finally, we demonstrate practical applications of utilizing the NGH with water containing pores for photocatalytic H_2 production. An important pragmatic consideration of using a NGH is the ease of separation and recovery of the nanosized catalyst after the photoreaction which would otherwise require extensive and expensive nanofiltration.

photocatalytic H_2 evolution from a methanol-water solution.⁷ The optimal graphene content was found to be 1.0 wt% with a H_2 production rate of 736 µmol h^{-1} g⁻¹ and a quantum efficiency of 3.1%.

Graphene an important form of carbon allotrope, is gaining prevalence because of the industrial scalability, low cost (solution processable) and ease of hybridizing with other materials. Other benefits include visible light absorption, light weight, high specific surface area and outstanding chemical/ electrical stability characteristics which are advantageous for catalysis applications. Due to its myriad of benefits, composites of two-dimensional (2D) assemblies of graphene sheets with metal oxide and metal nanostructures have been explored.5-8 However, to meet the demands of catalysis requirements of possessing a high surface area, porous structure and superior electrical conductivity, it is desirable to assemble the composite into a 3D framework.^{9,10} Forming a 3D interconnected framework (hydrogel) forms (i) desirable pores which facilitate liquid/gas access and diffusion, (ii) superior charge generation and collection of interconnected electrical pathways and (iii) conceptually ideal open structure for integration with other functional nanomaterials. Moreover, the size reduction of a photocatalyst to the nanoscale is often carried out to increase the reactive surface area, which brings about the difficulty in recovery after the catalysis process. However, constructing a catalyst into a 3D hydrogel allows ease of separation and recovery which would otherwise require extensive and expensive nanofiltration.

However, till-date no report has focused on the preparation and functionality of NGHs, 3D macroscopic assembled graphene sheets consisting of a photostable TiO₂ and Au

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Fig. 1 Schematic representation of the synthetic procedures for synthesizing NGH and NGH-Au.

nanostructure for photocatalytic H_2 production. Here, we demonstrated a NGH based on green chemistry, employing VC to attain a supramolecular 3D network of hybrid nanostructured materials. The NGH possesses novel physicochemical properties, well-defined nano-mesopores, a large surface area, a highly dispersive composite, and enhanced visible light absorption characteristics. Next, we demonstrated proof of concept for practical applications by utilizing the NGH with water containing pores for water splitting to produce and possibly uptake H_2 .

Results and discussion

The synthetic procedures (see ESI†) for synthesizing NGH and NGH–Au are illustrated in Fig. 1. Pre-dispersed graphite oxide (GO) sheets, VC with respective TiO_2 nanorods and Au nanoparticle loaded TiO_2 nanorods were mixed to obtain a homogeneous suspension. The suspensions were left undisturbed/unstirred at 55–90 °C in a conventional oven under atmospheric pressure for 100 min. Time-evolution studies (Fig. 2a) showed that an initial brown solution turns black after 40 min. Further reaction time of 100 min shows aggregation of the GO nanosheets and TiO_2 nanorods to form the NGH which floats at the water surface. The functional groups (–OH and –COOH) form hydrogen bonds with the VC



Fig. 2 (a–b) Time-evolution studies of NGH and NGH–Au with VC respectively. (c) NGH consists of pores that absorb water to form a gel-phase which remains stable upon inversion of the vial containing gel. SEM images of the supercritically dried (d) GH and (e) NGH. The pore sizes are in the sub to several micrometers range while the pore walls are thin/semi-transparent.

reducing agent under appropriate conditions, and leads to the assembly of GO sheets thus forming the hydrogel.¹¹ The water in which the hydrogel is suspended is observed to be completely transparent and clear, which suggests that all the composite has self-assembled and been incorporated into the hydrogel. In Fig. 2b, the graphene and Au nanoparticle loaded TiO₂ nanorods solution turns from dark purplish to black which suggests homogeneous interfacing of the Au nanoparticle loaded TiO₂ nanorods with graphene sheets. In both cases, a distinct color change to dark grey/black solution proves the successful reduction of GO, where partial restoration of the π -network within the carbon structure has occurred.¹² Essentially, the GO has been reduced to graphene and has self-assembled into a composite hydrogel driven by the π - π stacking interaction of the graphene sheets. The photograph in Fig. 2c shows the uptake of water within the NGH which is stable even upon inversion of the vial containing gel. The 3D NGH framework consists of pores/cages that facilitate the absorption of a large amount of water. Scanning electron microscopy (SEM) images of the supercritically dried graphene hydrogel (GH) reveals numerous pores formed after physical cross-linking of graphene sheets into an interconnected network (Fig. 2d). A similar porous structure is observed for the NGH sample along with the TiO₂ nanorods (Fig. 2e). The pore sizes are in the range of sub micrometer to several micrometers while the pore walls are thin/semitransparent.

The Brunauer-Emmmett-Teller (BET) specific surface area and porous structure characteristics of the supercritically dried NGH were determined using nitrogen isothermal adsorption. Fig. 3a displays a nitrogen adsorption/desorption isotherm which exhibits an H3 hysteresis loop observed at relative pressure (P/P_0) close to unity, suggesting the presence of large mesopores and macropores.13 The specific surface area is 327 m² g⁻¹ which is significantly higher than the reported graphene aerogel ($\sim 117 \text{ m}^2 \text{ g}^{-1}$).¹⁴ It is believed that the large specific surface area facilitates a better access and diffusion of the liquid and gaseous reactants which is beneficial for photocatalytic reactivity. However, the obtained surface area is lower compared to the graphene aerogel $(\sim 2000 \text{ m}^2 \text{ g}^{-1})$ formed by covalent carbon cross linking based on resorcinol-formaldehyde sol-gel chemistry.15 This may be due to the effect of different methods of synthesizing and processing of the materials where sonication of the GO dispersion and addition of resorcinol-formaldehyde will both result in a higher degree of GO exfoliation which then yields a higher surface area than NGH. It is noteworthy that the application of this work does not require drying of the NGH can be used directly for water splitting which reduces the cost and time needed for material processing. The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method. Fig. 3b shows the pore volume of 1.9 cm³ g⁻¹ with the corresponding bimodal size distributions of 3.9 and 24 nm for the meso- and nanopores.



Fig. 3 (a) Type IV nitrogen adsorption/desorption isotherms which indicates that the NGH is mesoporous. (b) BJH pore size distribution with corresponding bimodal pore diameters of 3.9 and 24 nm. XPS spectra of deconvoluted C1s of (c) GO (d) GH and (e) NGH. The inset of 3d shows the chemical structure of VC. (f) Ti2p XPS spectrum of NGH.

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The deconvoluted C1s X-ray photoelectron spectroscopy (XPS) spectrum of the GO sample indicates the presence of various carbon bonds namely C-C (284.6 eV), C-O (286.5 eV), and C=O (288.1 eV), corresponding to sp^2 aromatic rings, epoxy/alkoxy, and carbonyl groups, respectively (Fig. 3c). The inset shows the chemical structure of GO. The C1s spectra of GH and NGH (Fig. 3d and f) display similar peaks except that the peak intensities of oxygen containing functionality, predominantly the C-O peaks are of lower intensity than the GO sample. A significant decrease of the C-O peak in comparison with the original GO sample, reflects the reduction of GO to graphene. It is noted that the GH shows the presence of an additional peak at 289.7 eV which is attributed to O-C=O, also reported for another VC reduction of GO.¹⁶ The inset shows the chemical structure of VC which contains many oxygen-containing functional groups wherein the electrons in the double bond, hydroxyl group lone pair, and the carbonyl double bond form a conjugated system. The carbonyl group is responsible for the existence of the additional peak. The XPS results show that VC is an effective reducing agent; a good alternative to hydrazine which is an aggressive chemical that can potentially introduce defects into graphene.¹⁷ It has been shown that hydrazine reduced GO consists of covalently linked C-N species17 whilst VC reduced GO shows only oxygen-

containing species consistent with a mild yet effective reduction reaction. It is observed that the GH is further reduced with the addition of TiO_2 nanorods *via* interactions with the TiO_2 surface hydroxyl groups to undergo charge transfer.¹⁸ Fig. 3f shows the NGH sample with the presence of Ti $2p_{3/2}$ at 459.1 eV and the Ti $2p_{1/2}$ at 464.4 eV due to the incorporation of TiO₂ nanorods into the GH.

Fig. 4a shows the Raman spectrum of GO, GH, or NGH which display two characteristics peaks around 1350 and 1590 cm⁻¹, attributed to the D and G bands of carbon, respectively.¹⁹ The G band is related to graphitic carbon while the D band is associated with the disorder-induced structural defects of graphitic domains.¹⁹ The intensity ratio (I_D/I_G) of GO was determined to be 0.79, while that of GH or NGH was higher at 1.33 and 1.32 respectively, which signifies partial restoration of the disordered graphene sheets upon reduction with VC.²⁰ It is noted that the Raman spectra of GH and NGH have similar peak positions and $I_{\rm D}/I_{\rm G}$ which implies that the graphene supramolecular network is well-preserved even after TiO2 nanorods integration. The successful reduction of GO using VC is further reflected with the X-ray diffraction (XRD) studies. Fig. 4b shows the XRD patterns of GO, GH and NGH. The GO has a large interlayer distance of 8.5 Å ($2\theta = 10.4^{\circ}$) relative to graphite (3.36 Å) due to the presence of hydroxyl, epoxy, and



Fig. 4 (a) Raman spectra of GO, GH, and NGH which display two characteristics peaks around 1350 and 1590 cm⁻¹, attributed to the D and G bands of carbon, respectively. (b) XRD spectra of GO, GH, and NGH. The interlayer spacings of GO and GH are 8.5 Å and 3.8 Å respectively. (c–d) TEM images of TiO₂ nanorods homogeneously dispersed onto the graphene sheets. (e) High resolution TEM images show that the NGH is composed of 3 to 6 layers of graphene sheets which are well-interfaced with anatase phase TiO₂ nanorods.

carbonyl groups.²¹ The large interlayer spacing of GO weakens the van der Waals interactions between the sheets, hence exfoliation down to a few layers of graphene sheets is feasible.22 The transmission electron microscopy (TEM) images complement the XRD results since it has been routinely observed that the GH samples comprise of 3-6 layers of graphene sheets. The GH spectra shows a broad diffraction peak at $2\theta = 23.4^{\circ}$ corresponding to a much smaller interlayer distance of 3.8 Å, which suggests a π -conjugated structure recovery upon VC reduction. The GH interplanar distance is larger than the graphite indicating the presence of residual oxygenated functional groups.23 Furthermore, the broad graphitic (002) plane of GH suggests a poor ordering of graphene sheets along their stacking direction since they are self-assembled into the 3D network in a random manner.²¹ As for the case of NGH, diffraction peaks due to TiO₂ anatase phase with characteristic (101), (004), (200), (105), (211), (204) planes were observed (JCPDS PDF 00-021-1272). The anatase TiO₂ (101) and graphene (002) XRD peaks are located at \sim 25.4° and 23.4° which resulted in fairly indistinguishable peaks.

The activity of a catalytic system is dependent both on the surface area available for the reaction as well as on the degree of photocatalyst dispersion. GO with its extremely high surface area makes a good support for dispersion of other nanomaterials in aqueous media. The feasibility of water splitting to produce H₂ by using TiO₂ nanoparticles on 2D graphene has been reported.^{24,25} Here, 1D TiO₂ nanorods are employed to allow better interfacial contact and also to enhance vectorial electron transport due to decreased grain boundaries.⁶ It is observed from the TEM images that TiO2 nanorods were homogeneously interfaced with the graphene sheets (Fig. 4ce). The TiO₂ nanorods have a diameter of \sim 10-30 nm, with lengths of several tens of nanometers. At higher resolution (Fig. 3f), it is evident that the NGH is composed of 3 to 6 layers of graphene sheets which are interfaced with TiO₂ nanorods. Strong chemical coupling between the graphene sheets and the TiO₂ nanorods is possible since H bonding or electrostatic interactions between the hydroxyl groups of TiO_2 and the functional groups of GO can be expected.²⁶ The lattice fringes of the TiO₂ nanorods with a d spacing of 0.35 nm can be assigned to the (101) lattice planes of the anatase phase.

In the past few decades, a significant understanding of noble metal co-catalysts loaded onto transition metal oxide semiconductor photocatalysts has been derived mainly from Pt.^{27,28} It has been proven that the Pt co-catalysts decreases the H_2 evolution overpotential and suppresses the recombination rate.²⁸ However, there is an increasing interest in Au/TiO₂ systems primarily in the field of heterogeneous catalytic oxidation which has recently extended to the photocatalysts field.²⁸ The development of stable and durable photocatalysts requires the co-catalyst to be chemically inert, especially towards water/photo corrosion. For this reason, noble Au metal nanoparticles are used in this work. When Au nanoparticles are deposited onto the TiO₂ photocatalyst, a color change from white to dark purplish was observed

(Fig. 1b). This is due to the characteristic surface plasmon of Au in a nanosized dimension which will promote a visible light photoresponse upon excitation. Fig. 5a and b show low resolution TEM images of a Au nanoparticle loaded TiO2 nanorods hydrogel (NGH-Au). The Au nanoparticles are fairly uniformly deposited on TiO₂ nanorods without aggregation. The higher resolution TEM image (Fig. 5c) shows the lattice fringes of the Au nanoparticles, well matched to the (111) planes of Au. The geometrical distribution of the Au nanoparticles showed a size range from 2.5-15 nm, and the mean diameter was approximately 10 nm (Fig. 5d). The deposition of the reasonably small Au nanoparticles ensures a catalytically active co-catalyst. It has been shown that the Au catalytic activity is derived from its nanometric dimensions and its reactivity progressively reduces with increasing the particle size, disappearing beyond 20 nm.²⁹ In addition to the tailoring of particle size and distribution, controlling other physicochemical parameters such as good interfacing with its support is equally important. An intimate interfacing of the TiO₂ nanorods, Au nanoparticles and graphene (Fig. 5c) will ensure favorable separation of photogenerated carriers and enhancement of the photocatalytic performance.

The XRD patterns of GH, NGH and NGH-Au are shown in Fig. 5e. It is noted that both the NGH and NGH-Au have broad background peaks between 20 to 35°, which are due to the overlapped (002) graphene at 23.4° and anatase (101) TiO₂ at 25.4°. In comparison, the NGH-Au spectrum has addition diffraction peaks at 38.1°, 44.3° and 64.5° which correspond to the (111), (200) and (220) face-centered cubic Au nanoparticles (JCPDS 4-0783). Fig. 5f shows the optical absorption spectra of the pure TiO_2 nanorods, Au nanoparticle loaded TiO_2 nanorods and NGH samples taken at room temperature in the range of 200-800 nm. The absorbance in the visible light region is seen with the addition of Au nanoparticles. The visible absorption band at \sim 575 nm has been attributed to the surface plasmon band and arises from the collective oscillations of confined valence electrons.³⁰ The absorption wavelength and the shape of the surface plasmon band depends on many factors including the dielectric constant of the medium, nanoparticles geometrical shape and size, and coulombic charge of the nanoparticles amongst others.³¹ Similarly, the graphene composites display a broad background absorption in the visible-light region which is supported by the color change from white to grey. The addition of Au nanoparticles and graphene into the photocatalyst is observed to increase the light absorption intensity and range, which is beneficial for photocatalytic performance.

Proof-of-concept photocatalytic H_2 production based on the 3D NGH was carried out. As mentioned, the wide bandgap of TiO₂ (*ca.* 3.0–3.2 eV) limits photocatalytic H_2 production activities, due to the UV component of the solar spectrum accounting for less than 4%. One of the ways to enhance the photocatalytic performance of TiO₂ is to extend the light absorption to the visible region. There are two ways to go about it; band gap engineering *via* doping and sensitization. In this work, the latter approach was adopted, that is to sensitize



Fig. 5 (a–b) TEM images of NGH–Au. The Au nanoparticles (darker contrast) are fairly uniformly deposited on the TiO_2 nanorods. (c) High resolution TEM image shows lattice fringes of the Au nanoparticles, well matched to the (111) planes of Au. (d) Size distribution of Au nanoparticles 2.5–15 nm, mean diameter of ~10 nm. (e) XRD spectra of GH, NGH and NGH–Au. (f) Absorption spectra of TiO_2 nanorods, Au nanoparticle loaded TiO_2 nanorods and NGH–Au samples in the range of 200–800 nm.

the TiO₂ with graphene and the Au metal nanoparticles. Sensitization of TiO₂ with graphene and Au nanoparticles *via* surface modifications has the advantage over doping processes as it does not introduce any recombination centres to the crystal lattice. Besides that, graphene and noble metal nanoparticles are stable materials and are less susceptible to photodegradation during the catalytic reaction. The photocatalytic H₂ production activities of various samples were evaluated under xenon arc lamp (with and without cut-off filter, $\lambda = 420$ nm) irradiation in the presence of methanol as a hole scavenger.

Photocatalysis measurements of control samples, namely pure TiO₂ nanorods and 2D reduced graphene sheets-TiO₂ composite (2D RGO-TiO₂) and NGH with different wt% loading of Au nanoparticles under different light wavelength irradiations were carried out (Fig. 6a). Under UV-visible irradiation, the ${\rm TiO}_2$ nanorods and 2D ${\rm RGO-TiO}_2$ show \sim 156 and 51 µmol h⁻¹ g⁻¹ of H₂ being produced respectively. 2D RGO-TiO₂ experiences light shielding of TiO₂ by graphene resulting in low H₂ production due to the incorporation of TiO₂ nanorods between tightly packed/stacked 2D graphene sheets. In contrast, by incorporating TiO2 nanorods into a 3D graphene with interconnected network pores, the photocatalytic activity is observed to increase to $\sim 167-242 \ \mu mol \ h^{-1}$ g^{-1} . The H₂ production increases with the Au nanoparticles loading up to 8 wt%. Furthermore, the photoresponse of the pure TiO₂ nanorods, 2D RGO-TiO₂, NGH and NGH-Au were studied under visible light irradiation. Under visible irradiation, the production of H₂ increased with 2D RGO-TiO₂, NGH

and NGH–Au (8 wt% loading) samples as such photocatalytic reactivities under visible light are much more efficient than the TiO_2 nanorods.

As illustrated in Fig. 6b, upon visible light irradiation, electrons from the Au nanoparticles are injected into the TiO₂ conduction band leading to the generation of holes in the Au nanoparticles and electrons in the TiO₂ conduction band. The holes are quenched by sacrificial electron donors. The electron injection from Au to TiO₂ is based on LSPR excitation³² which has been demonstrated and proven in other Au/TiO2 work as well as other material systems, Au/ZnO and Ag/TiO2.33-37 Essentially, the incident photons are absorbed by ~ 10 nm Au nanoparticles through LSPR excitation which effectively injects electrons from the Au nanoparticles into the conduction band of TiO₂. One possible explanation is that the intense optical near-field collective oscillation of electrons on the SPR excitation leads to interband excitation from the d bands to the sp conduction band.³⁴ This promotes electrons transfer from Au to TiO₂ after overcoming the Schottky barrier at their interface and results in charge separation in the Au/TiO2 photocatalyst.³⁴ In addition, upon UV-vis irradiation, TiO₂ absorbs photons of energy greater than the band gap which generates electron-hole pairs. All the excited electrons are in turn transferred from the TiO2 conduction band to the graphene active sites to produce protons in the solution to generate H₂. This is highly anticipated since the potential of RGO is lower than the conduction band of anatase TiO₂, thus all photoinduced electrons can be transferred to the graphene leading to effective electron-hole separation. The graphene

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Fig. 6 Photocatalytic H₂ production studies of the various samples. (a) H₂ production of the control samples (pure TiO₂ nanorods and 2D RGO–TiO₂ composite) and NGH with different wt% loading of Au nanoparticles under different light wavelength irradiations. (b) Proposed photocatalytic mechanism of the NGH–Au under ultraviolet and visible light irradiation.

network acts as an effective charge separator so it facilitates interfacial charge transfer along the graphene sheets which can be derived from EIS results (to be discussed later).

Another study on H₂ adsorption in the various samples; pure TiO₂, 2D RGO-TiO₂ and 3D NGH were carried out. The samples were irradiated with a xenon lamp for 2 h before removing them from the lamp. This is followed by mechanical agitation in a conventional ultrasonic bath for 90 min while H_2 that was trapped and released was intermittently measured at 30, 60 and 90 min as shown in Fig. S1, ESI.† It is noted that the pure TiO_2 and 2D RGO-TiO_2 show lower H_2 content as compared to the 3D NGH. Forming a 3D interconnected framework (hydrogel) creates desirable pores which facilitate the adsorption of H₂. Furthermore, a pressure-composition isotherm of NGH at room temperature and a pressure range of 0 to 100 atm was carried out to affirm H₂ adsorption of the NGH (Fig. S2, ESI[†]). It is postulated that after the initial 2 h of light irradiation some of the H₂ molecules diffuse through the aqueous phase and emerge as a gas as measured in Fig. 6a; the remaining H₂ is trapped within the NGH. Hence during the

mechanical agitation, the graphene sheets are buckled to release the trapped H_2 gas within the pores as well as between the interlayered graphene sheets. It has been theoretically predicted that graphene sheets exhibits fast kinetic (quick H_2 uptake and release) characteristics and that buckling of graphene sheets can easily release trapped H_2 .³⁸

The Nyquist plots of the NGH and TiO₂ nanorods films are shown in Fig. 7a and b. $R_{\rm ct}$ of NGH is ~3.51 k Ω , which is smaller than for the TiO₂ nanorods ~11.82 k Ω , indicating a better electron conductivity between the NGH electrode and electrolyte.³⁹ Furthermore, the time constant can be determined using the following relation:

$$\tau_n = R_{\rm ct} \times C_{\rm p}$$

where τ_n relates to electron lifetime, C_{μ} is the chemical capacitance and R_{ct} is the charge transfer resistance between the electrodes and the electrolyte interface. The NGH electrode shows a higher τ_n of 2.06 s as compared to the TiO₂ nanorods (0.11 s) which implies a longer electron lifetime. Also, the characteristic frequency peaks



Fig. 7 Electrochemical impedance spectra of TiO₂ nanorods and NGH. (a–b) Nyquist and (c) Bode phase plots. The equivalent circuit is shown in the inset of (a).

on the Bode phase plots show the peak for the TiO_2 nanorods is at a higher frequency than the NGH (Fig. 7c). The characteristic frequency peaks are inversely related to the electron lifetime, which suggests that the electrons take a longer time to recombine in the NGH film as compared to the TiO_2 nanorods film.

Conclusions

We have demonstrated a facile solution processable method of using VC as reducing agent for the synthesis of a 3D NGH. By forming a 3D framework of NGH, we are able to create desirable pores that facilitate water absorption, an open structure for the integration of functional TiO_2 nanorods and Au nanoparticles for charge generation and collection *via* interconnected highly conductive electrical pathways. Moreover, sensitization of the TiO_2 nanorods with Au nanoparticles and graphene, has allowed us to extend the utilization of the solar spectrum beyond the UV wavelength. This is important since photocatalytic materials with a visible light response are required for efficient solar energy utilization. For the first time, we show that NGH is a promising selfcontained media for H_2 production and adsorption.

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