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# 1. Introduction

There is a growing interest in renewable and sustainable forms of energy. Hydrogen  $(H_2)$  is a promising candidate as it produces lots of energy and also burns cleanly. Besides steam reforming,1 electrolysis2 and photoelectrochemical splitting of water,3 it is also possible to produce H2 gas from degradation of organic pollutants in wastewater.4 Photocatalysts such as titanium dioxide (TiO<sub>2</sub>) can be added to the wastewater and upon illumination, the photogenerated electron-hole pairs or superoxides from the photocatalysts will break down the organic compounds present in the wastewater and produce H<sub>2</sub> gas at the same time. This makes photocatalytic wastewater treatment a dual functional process with additional recovery of energy from wastewater, hence reducing the overall cost of wastewater treatment. The general stoichiometry of photocatalytic degradation of organic compounds can be represented by the following equation.<sup>5</sup>

$$C_x H_y O_z + (2x - z) H_2 O \rightarrow x CO_2 + (2x + 0.5y - z) H_2$$
 (1)

This reaction involves decomposition and mineralization of organic compounds, water decomposition and hydrogen production.

# Hybrid organic PVDF-inorganic M-rGO-TiO<sub>2</sub> (M = Ag, Pt) nanocomposites for multifunctional volatile organic compound sensing and photocatalytic degradation-H<sub>2</sub> production<sup>+</sup>

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This work focused on the development of a hybrid organic–inorganic TiO<sub>2</sub> nanocomposite, which demonstrates the first ever report on harmful volatile organic compound (VOC) sensing and photocatalytic degradation–H<sub>2</sub> production. The sensing and photocatalytic properties are enhanced by the synergetic effects of well-structured TiO<sub>2</sub> nanotubes, metal nanoparticles and reduced graphene oxide loading for enhanced light absorption and charge-transfer kinetics. Hybridization of a functionalized TiO<sub>2</sub> nanocomposite with a polyvinylidene fluoride (PVDF) matrix induced strong cross-linking networks between the inorganic–organic components, which promote mechanical reinforcement-flexibility and highly porous asymmetric structures. The developed solution processable nanocomposite has immense potential to remedy the global environmental and energy issues by producing clean water/air and energy from organic compound waste.

 $TiO_2$  is an ideal candidate for this purpose because it is the most active natural semiconductor known for photoreactions,6,7 stable against photocorrosion, and has a bandgap with conduction band and valence band levels suitable for H<sub>2</sub> production.8 TiO2 nanotubes were chosen because of the higher surface area9,10 and better carrier transport properties attributed by its one-dimensional (1D) structure.<sup>11</sup> However, the performance is limited due to fast recombination rates and low absorption or inability to use the entire solar spectrum efficiently. There are several ways to prevent or diminish recombination,<sup>8</sup> one of which is to deposit reduced graphene oxide (rGO) and noble metal nanoparticles such as silver (Ag) and platinum (Pt) onto the surface of the nanotubes. The addition of rGO will act as an electron sink to reduce the recombination of the photogenerated electrons and holes,12 and this enhancement in the photocatalytic activity has also been reported in several papers.13-15 The presence of Ag or Pt acts as an electron scavenger, preventing recombination and facilitating the transfer of electrons for the reduction of H<sup>+</sup>.<sup>16,17</sup> Furthermore, the photocatalyst composite can be embedded in a polymer membrane such as PVDF with an asymmetric pore structure.18 In so doing, the photocatalyst can be applied to air and water filtration purposes and the photocatalyst can also be easily recovered and reused after reaction with organic compounds.19

The ability to sense the ppm level of harmful VOCs at room temperature offers immediate awareness and a response to harmful organic compounds by degradation has never been reported thus far. Hence, this work focused on the development and characterisation of a hybrid organic PVDF–inorganic TiO<sub>2</sub>

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nanocomposite with sensory and concurrent capabilities of degrading and producing  $H_2$  from harmful VOCs for improved air/water quality as well as generation of clean energy. Reduced graphene oxide (rGO) and metal nanoparticles (Ag and Pt) are added to the TiO<sub>2</sub> nanotubes to greatly enhance sensing and photocatalytic performance. Finally, immobilization of a TiO<sub>2</sub> nanocomposite within the PVDF matrix offers the benefits of combining the intrinsic physical and chemical characteristics of both the inorganic and organic components by conforming the asymmetric structure for promising high permeability and mechanical flexibility.

### 2. Experimental methods

#### 2.1. Synthesis of Pt/Ag-rGO-TiO<sub>2</sub> nanocomposites

1 g of TiO<sub>2</sub> anatase powder was mixed with 20 ml of 10 M sodium hydroxide (NaOH) solution and stirred for 1 h. The mixture was heated at 130 °C for 10 h in a Teflon-lined autoclave. The precipitate was washed with 1 M hydrochloric acid (HCl) until the pH of the supernatant becomes 1 and then rinsed with deionized (DI) water until neutral pH. The powder was then annealed at 450 °C for 2 h. The graphene oxide (GO) was produced by the Hummer's method20 and dissolved in DI water to form a GO solution with a concentration of  $1 \text{ mg ml}^{-1}$ . The GO solution was then added to TiO<sub>2</sub> nanotubes in methanol and illuminated with a 300 W Xe lamp (Excelitas, PE300BFM, wavelength range 200 to 1100 nm) for 3 h under magnetic stirring to produce 10 wt% rGO-TiO2. Similarly, photoreduction of silver nitrate,  $AgNO_3$  (2 mg ml<sup>-1</sup>) and chloroplatinic acid,  $H_2PtCl_6$  (2 mg ml<sup>-1</sup>) to produce Ag and Pt nanoparticles was carried out under the similar illumination condition and duration. The PVDF powder and 1% Pt-rGO-TiO<sub>2</sub> composite were dissolved in 1-methyl-2-pyrrolidone at 40 °C with constant stirring (4 h) to obtain a homogeneous casting solution. The cast film was immersed into a water bath at room temperature to form a hybrid nanocomposite sheet based on the phase inversion process (PIP) induced by immersion precipitation.<sup>21</sup> The hybrid nanocomposite sheet was then soaked into DI water for 24 h to remove any remaining solvent completely.

#### 2.2. Materials characterisation

Various characterisation techniques were carried out on the samples. Scanning electron microscopy (SEM, JEOL FEG JSM 7001F) characterised the morphology of the synthesized products while the crystalline structure of the TiO<sub>2</sub> composites was analyzed by X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu-K $\alpha$  radiation at  $\lambda = 1.541$  Å) and transmission electron microscopy (TEM, Phillips FEG CM300). The elements present in the TiO<sub>2</sub> composites were analyzed by energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments). The optical absorbance of the photocatalysts was measured using a UV-VIS-NIR spectrophotometer (UV-vis, Shimadzu UV-3600).

#### 2.3. Sensing and photocatalytic measurements

Sensing measurements were carried out by cycling various concentrations of VOCs and clean dry air via mass flow

controllers. A sensor was placed in a sensing chamber and electrical leads from the sample were connected to a sourcemeter (Keithley 4200-SCS) via an electrical feed-through. The VOC vapor was created by bubbling nitrogen gas into the liquid VOC, and then channelling the vapor into the sensing chamber together with clean dry air. By varying the flow rate of VOC vapor and clean dry air into the sensing chamber via mass flow controllers, VOC vapor of various concentrations could be obtained. The photocatalytic reactions were performed in a quartz cylindrical reaction cell of volume 25 ml. 10 mg of photocatalyst is used for the photocatalytic studies. The reactor was purged with argon (Ar) gas for 10 min prior to illumination with a 300 W xenon arc lamp of intensity 100 mW cm<sup>-2</sup>. Gas samples were analysed using a gas chromatograph (Shimadzu GC2014). The photocatalytic reactions of 25 ml of 0.03 mM methyl orange (MO) aqueous solution was carried out based on 25 mg of the prepared TiO<sub>2</sub> composite under light irradiation with the same Xe arc lamp. The concentration of MO was determined using a UV-VIS-NIR spectrophotometer (UV-Vis, Shimadzu UV-3600) and the maximal absorbance peak value (at 462.5 nm) was noted to plot the amount of MO degraded and thus, determine the photodegradation activity of the composite.

## 3. Results and discussion

Fig. 1a–c show SEM images of the as-synthesized  $TiO_2$  nanostructures, which are homogeneously precipitated in the growth solution. TEM structural characterisation was carried out on the  $TiO_2$  nanostructures (Fig. 1d). The  $TiO_2$  nanostructures possess a



**Fig. 1** (a–c) SEM images of  $TiO_2$  NTs of various magnifications. (d) TEM image of  $TiO_2$  NTs. SEM images of (e) 1% Ag–rGO–TiO<sub>2</sub> and (f) 1% Pt–rGO–TiO<sub>2</sub>.

hollow core and a rather uniform diameter of ~10 nm and a length of 0.1–1  $\mu$ m. Facile photoreduction was then carried out to form metal nanoparticles and reduced graphene oxide TiO<sub>2</sub> composites. Fig. 1e and f show the SEM images of the produced composites of 1 wt% Ag–rGO–TiO<sub>2</sub> and 1 wt% Pt–rGO–TiO<sub>2</sub>, respectively. However, the small diameter of the metal nanoparticles makes it challenging to identify them in the SEM images. In essence, photoreduction performed under xenon light irradiation will promote photogenerated holes in TiO<sub>2</sub> to react with the methanol molecules to form methoxy radicals, while the accumulated electrons interact with the GO sheets to reduce certain functional groups to yield rGO as depicted in eqn (2) and (3).<sup>22</sup>

$$\operatorname{TiO}_{2} + hv \rightarrow \operatorname{TiO}_{2}(h^{+} + e^{-}) \xrightarrow{\text{methanol}} \operatorname{TiO}_{2}(e) + \operatorname{CH}_{3}\operatorname{O} \bullet + \operatorname{H}^{+}$$
(2)

$$\text{TiO}_2(\text{e}^-) + \text{GO} \rightarrow \text{TiO}_2 + \text{rGO}$$
 (3)

A change in color from light brown to dark brown to black is evident with the reduction of GO (Fig. S1 in the ESI†) and partial restoration of the conjugated network in the carbon structure. The reduction of metal ions ( $Ag^+$  and  $Pt^{4+}$ ) into metal (Ag and Pt) nanoparticles takes place with a very similar reduction mechanism to that of GO reduction.<sup>23</sup>

The TEM images in Fig. 2 show the metal nanoparticles synthesized by the photoreduction method.24,25 The nanoparticles produced from a loading amount of 1% Pt (Fig. 2a and b) have a modal diameter range of 10-20 nm and this is illustrated by a histogram (inset of Fig. 2a) showing the distribution of nanoparticle sizes. The nanoparticles from 10% Pt were smaller with a modal diameter range of 3-4 nm (Fig. 2c and d). The 1% Ag nanoparticles (Fig. 2e and f) have a similar modal diameter range to that of 1% Pt (10-20 nm) and the nanoparticles from 10% Ag (Fig. 2g and h) were larger with a modal diameter range of 30-40 nm. The exact formation mechanism of the small 10% Pt nanoparticles is not clear and requires further investigation. However, a possible explanation is proposed here: the synthesis of photoreduced nanoparticles usually involves a two step process, *i.e.* nucleation followed by successive growth of the particles by reduction of the added bulk metal ions at the surface of the seeds (also know as autocatalytic growth of the nucleation centers).26 The 1% Pt, 1% Ag and 10% Ag nanoparticles seem to follow this mechanism but in the case of 10% Pt, the growth seems to stop after the nucleation stage. The high concentration of Pt ions resulted in a rapid formation of Pt seeds (nucleation stage), but the growth did not proceed onto the autocatalytic growth stage. This could be because all the available Pt ions were reduced to Pt seeds, hence no more Pt ions were available for the growth of these seeds. The high resolution TEM (HRTEM) images of the Pt and Ag nanoparticles are shown in Fig. 2b, d, f and h, respectively. The crystal lattice of the (111) planes of the Pt and Ag nanoparticles can be observed with a d-spacing of 2.2 Å27 and 2.4 Å, respectively.<sup>23</sup> This shows good crystallinity in the metal nanoparticles, indicating that highly crystalline metal nanoparticles can be produced by the photoreduction method.



**Fig. 2** TEM and HRTEM images of (a and b) 1% Pt nanoparticles, (c and d) 10% Pt nanoparticles, (e and f) 1% Ag nanoparticles and (g and h) 10% Ag nanoparticles. Insets of (a, c, e and g) show the histograms illustrating the size distribution of the nanoparticles.

The crystal structures of TiO<sub>2</sub> nanotubes and its composites were also investigated by XRD and the diffraction patterns are shown in Fig. 3a. The peaks in the pristine TiO<sub>2</sub> nanotube spectrum at 25.45, 38.05, 48.25, 54.15, 55.15, 62.95, 68.95, 70.45 and 75.55° can be indexed to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of the anatase phase of TiO<sub>2</sub> (JCPDS file no. 21-1272), respectively. The (103) peak observed at 27.95° is due to the TiO<sub>2</sub> nanotubes which is akin to that of a rolled up delaminated anatase sheet.<sup>28</sup> These peaks are also present in the rGO–TiO<sub>2</sub>, 1% Ag–rGO–TiO<sub>2</sub> and 1% Pt–rGO– TiO<sub>2</sub> composites. No GO peaks were observed indicating that all GO have been reduced during the photoreduction process. The rGO peak is not visible because it overlaps with the (101) peak of anatase TiO<sub>2</sub>.<sup>14</sup> No peaks from Pt were also observed, which may



**Fig. 3** (a) XRD spectra of TiO<sub>2</sub>, rGO–TiO<sub>2</sub>, 1% Ag–rGO–TiO<sub>2</sub> and 1% Pt–rGO–TiO<sub>2</sub> composites. (b) EDX spectra of 1% Ag–rGO–TiO<sub>2</sub> and 1% Pt–rGO–TiO<sub>2</sub> composites.

be due to that the small amounts of Pt loaded onto the catalysts were too small to be detected. The main diffraction peak of Ag (38.1°) is irresolvable because it closely overlaps the (004) peak of anatase  $\text{TiO}_2$ .<sup>29</sup> However, two peaks located at 32.5° and 46.5° were observed in 1% Ag-rGO-TiO<sub>2</sub>. These two peaks can be attributed to the (111) plane of Ag<sub>2</sub>O<sup>30</sup> and the (200) plane of face-centre cubic silver.<sup>31</sup>

EDX was also carried out to determine whether the metal nanoparticles were successfully loaded onto the TiO<sub>2</sub> nanotubes during the photoreduction process. The EDX spectra in Fig. 3b show that Ag and Pt were detected from the 1% Ag-rGO-TiO<sub>2</sub> and 1% Pt-rGO-TiO<sub>2</sub> composites, indicating that metal nanoparticles were successfully deposited. Prominent peaks of Ti  $L\alpha_{1,2}$  at 0.45 keV, Ti  $K\alpha_{1,2}$  at 4.51 keV and Ti  $K\beta_{1,3}$ at 4.93 eV due to the TiO<sub>2</sub> nanotubes were clearly observed in the spectra. Several peaks related to the Ag nanoparticles were also detected: Ag L<sub>1</sub> at 2.63 keV, Ag L $\alpha_1$  at 2.98 keV and Ag L $\beta_1$  at 3.15 keV. The Pt peak at 2.05 keV ascribed to the M $\alpha_1$  transition was also detected from the Pt nanoparticles deposited on the composite. This shows that photoreduction is a reliable method to deposit metal nanoparticles onto the TiO<sub>2</sub> nanotubes.

To demonstrate the sensing capability of the composite material, the 1 wt% Pt-rGO-TiO<sub>2</sub> composite was exposed to various concentrations of VOC vapor and the dynamic resistance-time measurement is shown in Fig. 4. The resistance of the composite sensor is observed to increase in VOC ambient and decrease in air ambient. This p-type semiconducting behavior agrees with the results reported for reduced graphene prepared by chemically reduced GO when exposed to the ambient environment.<sup>32</sup> The p-type characteristics have been attributed to the polarization of adsorbed molecules (*e.g.* water

and  $O_2$ ) and/or defects introduced to the graphene sheets during the preparation or reduction process.<sup>33</sup> The effect of VOC vapor concentration on the sensor response was investigated where vapors of various concentrations were flowed over the sensor at room temperature. Fig. 4a–c show that the composite is capable of sensing different concentrations of ethanol, methanol and isopropanol, respectively. It is worth noting that operating the composite sensor at room temperature will not result in adverse sensing instability since it is known that a high operating sensing temperature can cause an electrical drift due to structural changes such as grain coalescence, porosity modification or grain-boundary formation.

Various composites were tested for their photocatalytic activity in producing H2 from the decomposition/degradation of VOCs. In Fig. 5a, four types of catalysts namely TiO<sub>2</sub>, rGO-TiO<sub>2</sub>, 1 wt% Ag-TiO<sub>2</sub> and 1 wt% Ag-rGO-TiO<sub>2</sub> were tested for H<sub>2</sub> production from ethanol. 1 wt% Ag-rGO-TiO2 was chosen as a representative composite to study the degree of enhancement that rGO and metal nanoparticles can bring to the TiO<sub>2</sub> nanotubes. The type of composite with the best photocatalytic performance will be elucidated in subsequent experiments. The TiO<sub>2</sub> and rGO-TiO<sub>2</sub> were producing  $\sim$ 90 and 150 µmol g<sup>-1</sup> h<sup>-1</sup> of H<sub>2</sub>, respectively. After the addition of 1 wt% Ag to TiO<sub>2</sub>, the photocatalytic H<sub>2</sub> production was markedly improved to 810  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> and this number increased to 1108  $\mu$ mol g<sup>-1</sup>  $h^{-1}$  when 1 wt% Ag was added to the rGO-TiO<sub>2</sub> composite, making it  $\sim$ 7–12 times more effective than TiO<sub>2</sub> and rGO–TiO<sub>2</sub>. The Fermi level of Ag is lower than the conduction band of TiO<sub>2</sub>,<sup>34</sup> thus the photo-excited electrons will be transferred from the conduction band of  $TiO_2$  to the Ag nanoparticles, while the photo-generated valence band holes remain on the photocatalyst. The accumulated electrons will then reduce the H<sup>+</sup> ions to produce  $H_2$  gas, while the holes on the photocatalysts will be



**Fig. 4** Resistance–time gas sensing measurements of 1% Pt–rGO–TiO<sub>2</sub> in the presence of (a) ethanol, (b) methanol and (c) isopropanol vapor of concentrations 250–1000 ppm.



**Fig. 5** H<sub>2</sub> production from (a) ethanol using TiO<sub>2</sub>, rGO–TiO<sub>2</sub>, 1% Ag–TiO<sub>2</sub> and 1% Ag–rGO–TiO<sub>2</sub>; and from various organic compounds using 1% Ag–rGO–TiO<sub>2</sub>. (b) H<sub>2</sub> production from ethanol, methanol, and isopropanol over various TiO<sub>2</sub> composites. (c) UV-Vis absorbance spectra of TiO<sub>2</sub> NTs and the various TiO<sub>2</sub> composites.

involved in the oxidation of ethanol. In this way, the Ag nanoparticles help to reduce electron-hole recombination, leading to higher photocatalytic activity of the TiO<sub>2</sub> composite. The 1% Ag-rGO-TiO<sub>2</sub> was then further tested with several other organic compounds namely methanol, isopropanol, formaldehyde and acetone to study its effectiveness in producing H<sub>2</sub> by photocatalytic degradation of various types of organic compounds (Fig. 5a). The evolution of H<sub>2</sub> is relatively higher for ethanol and methanol followed by isopropanol, formaldehyde and acetone of less than ~100 µmol g<sup>-1</sup> h<sup>-1</sup>. The disparity in H<sub>2</sub> production performance can be attributed to the molecular structure of the organic compounds.<sup>35</sup>

A variety of composites were also produced by loading 1 wt% and 10 wt% of Ag and Pt nanoparticles on  $rGO-TiO_2$  and subsequently testing them for  $H_2$  production in ethanol,

methanol and isopropanol (Fig. 5b). Similarly, it was also noted that all the catalysts produced the most H<sub>2</sub> with ethanol, followed by methanol and the least from isopropanol. The Pt-loaded composites generally performed better than the Ag-loaded composites in terms of H<sub>2</sub> production. The 10% Pt-rGO-TiO2 was the best performing composite among the four types of catalysts and it consistently produced the highest amount of H<sub>2</sub> in all three types of organic compounds of  $\sim 2360$ , 2144 and 1159  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> from ethanol, methanol and isopropanol, respectively. The difference in the photocatalytic performance between the two types of metal nanoparticles can be explained by their work function values ( $\Phi$ ). A higher Schottky barrier36,37 will increase the efficiency of photogenerated electron transferring and trapping by the metal nanoparticles, leading to enhanced H<sub>2</sub> production. The work function of Ag is 4.74 eV and that of Pt is 5.93 eV,<sup>38</sup> while the work function of TiO<sub>2</sub> reported in the literature is 4.6-4.7 eV.39 Pt has a larger work function than Ag, and hence forms a higher Schottky barrier than that of Ag, which explains the overall photocatalytic performance improvement of Pt over Ag. The photoactivity of 10% Pt-rGO-TiO<sub>2</sub> was better than that of 1% Pt-rGO-TiO2 because the Pt nanoparticles in 10% Pt-rGO-TiO<sub>2</sub> were smaller than the ones in 1% Pt-rGO-TiO<sub>2</sub>, thus creating a larger surface area for reaction with the VOCs. This was also the case for Ag-rGO-TiO<sub>2</sub> composites, where the Ag nanoparticles in 1% Ag-rGO-TiO<sub>2</sub> were smaller than the ones in 10% Ag-rGO-TiO<sub>2</sub>, thus resulting in higher photoactivity in the 1% Ag-rGO-TiO<sub>2</sub> composite.

UV-vis absorption measurements of the pristine  $TiO_2$  NTs and composites were carried out and the absorbance spectra are shown in Fig. 5c. The strong absorptions below a wavelength of 340 nm were observed in all the samples associated with the optical band gap of  $TiO_2$ . It was noted that the absorbance intensity of pristine  $TiO_2$  NTs is the lowest and the intensity increased with the addition of graphene. The absorbance intensity increased further with the loading of metal nanoparticles. The absorbance of 10% Pt-rGO-TiO<sub>2</sub> is the highest among the four composites. The addition of a metal and graphene to  $TiO_2$  exhibits a broader photon absorption spectrum, which extends into the visible-light region, hence beneficial for photocatalytic performance.

Subsequently, hybrid organic-inorganic hybrid PVDF-TiO<sub>2</sub> composite films were fabricated by adding the pre-prepared inorganic composites into the organic PVDF casting solution. During the coagulation process, polymerization allows integration of TiO<sub>2</sub> composites with the PVDF chains, which enhances the mechanical integrity of the cast film. The fabrication of a hybrid organic-inorganic film is simple, scalable and economical. Excellent material compatibility is established as there were no observable evidence of particle agglomeration and cracking. Castings of the organic-inorganic solution were carried out on glass or scaffold (i.e. air filter mesh) to yield a freestanding or supported film (Fig. 6a and inset). Different ways of flexing the hybrid organic-inorganic film show no delamination and tearing of the hybrid film. The PVDF polymer has induced strong cross-linking networks between the inorganic-organic components within the hybrid composite, hence overcoming the conventional brittleness issue of an inorganic composite. Other



**Fig. 6** (a) A digital photograph showing bending of the hybrid organic–inorganic film. Insets show flexing of the hybrid film in another direction and a freestanding hybrid film. SEM images showing (b) top and cross-sectional views at (c) low and (d) high magnifications of the hybrid PVDF–TiO<sub>2</sub> film.

than establishing higher mechanical reinforcement for the composite, immobilizing an inorganic composite within the organic PVDF framework offers filtration functionality and easy recovery/recycling of the nanocomposites for multiple photocatalytic reactions. Fig. 6b shows the SEM top view of the hybrid film, which possesses a porous surface (pore diameter of ~200– 500 nm). From the cross-sectional image of the hybrid film shown in Fig. 6c, it can be seen that an asymmetric structure has been formed and a morphological transition from a finger-like at the skin depth to a sponge-like structure at the sublayer is observed. The benefits of attaining an asymmetric pore structure are high permeability and low in-depth fouling of the film.<sup>40</sup> Furthermore, a high resolution SEM image (Fig. 6d) at the sponge-like area proves that the inorganic composite do not aggregate and are uniformly dispersed within the hybrid matrix.

Fig. 7a shows the H<sub>2</sub> evolution of the hybrid film from liquid phase ethanol, methanol and isopropanol VOCs. The catalysis conditions are the same as that described in Section 2.3, except that a hybrid film was suspended in the reaction cell instead of using powdered photocatalysts. Despite the inorganic nanocomposites being embedded in the hybrid matrix, H<sub>2</sub> production based on degradation of VOCs in the presence of light irradiation still takes place. However, the amount of H<sub>2</sub> produced from methanol, ethanol and isopropanol are  $\sim$ 835, 518 and 214  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, respectively as such the H<sub>2</sub> evolution from the hybrid film is  $\sim$ 2–3 times less than that from the nanocomposite suspension. One possible reason could be that the total surface area of the TiO<sub>2</sub> composite embedded in the hybrid film that is exposed to light irradiation is less than that of the powder suspension. The hybrid film was also exposed to ethanol vapour (instead of the liquid phase) of various concentrations (15 000, 1000 and 500 ppm) to evolve 272, 50 and 11  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of H<sub>2</sub>, respectively (Fig. 7b). The amount of H<sub>2</sub> produced was observed to decrease with the initial concentration of ethanol vapour. This is evident that the hybrid film is



**Fig. 7** H<sub>2</sub> production from (a) liquid phase VOCs and (b) ethanol vapor of various concentrations over the hybrid PVDF–TiO<sub>2</sub> composite film. (c) Degradation kinetics and pseudo-first order kinetics (inset) of a time evolution MO photodegradation study in the absence and presence of various photocatalysts. (d) A digital photograph illustrating time evolution MO photodegradation using 1% Pt–rGO–TiO<sub>2</sub>.

also capable of decomposing/degrading gaseous other than liquid VOCs to produce  $H_2$ .

Finally, degradation kinetics of MO, a common textile pollutant was measured *via* the change in their concentration, which was calculated from the absorbance peaks. Fig. 7c shows the time profiles of the decrease in MO concentration in the absence and in the presence of different composites. A control experiment was carried out to show that photodegradation is not apparent without the use of a nanocomposite photocatalyst. Also, photocatalytic degradation capabilities of commercial TiO<sub>2</sub> nanoparticles (P25 and anatase powder) were tested and shown to degrade the MO molecules after 150–180 min of UV-Vis irradiation. In contrast, Pt and Ag composites show

Photocatalysts	Kinetic constants, $k (\min^{-1})$	Correlation coefficient, <i>R</i> <sup>2</sup>
P25	0.023	0.9773
Anatase TiO <sub>2</sub>	0.0234	0.9605
1% Ag	0.0268	0.9303
1% Pt	0.0362	0.9489

appreciable photocatalytic activity under UV-Vis irradiation and were able to fully degrade the MO dye after 120 min. A digital photograph illustrating the time evolution photodegradation study using 1% Pt-rGO-TiO<sub>2</sub> is shown in Fig. 7d. In Fig. 7c, inset shows the pseudo-first order kinetics of the MO degradation of the various photocatalysts. The efficiency of MO photodegradation by the composite was determined quantitatively using the pseudo-first order model<sup>41</sup> as follows:

$$\ln(C_0/C_t) = kt \tag{4}$$

where  $C_0$  and  $C_t$  are the concentrations of dye at time 0 and t, respectively and k is the pseudo-first order rate constant.

The pseudo-first order rate constants, k, of the various photocatalysts are shown in Table 1. The constants k of the Pt and Ag based composite photocatalysts are 0.362 and 0.268 min<sup>-1</sup> respectively. The results clearly demonstrate that the composites exhibit enhanced photodegradation over conventional TiO<sub>2</sub> powder.

# 4. Conclusions

We have demonstrated a hybrid organic–inorganic film which has the capability of sensing at room temperature as well as photocatalytic oxidation with effective  $H_2$  production and degradation of VOCs in air/water. The hybrid film has the potential of offering low cost technology due to solution processability as well as low maintenance and longer lifetime due to their inherent TiO<sub>2</sub>/Ag self-cleaning properties, asymmetric structures and superior mechanical integrity characteristics. The ability to cast the hybrid composite onto a free-standing film or onto a filter mesh makes it highly promising for various membrane technologies *e.g.* heating, ventilation, air conditioning (HVAC) and air/water filtration systems.

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