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1. Introduction

 TiO_2 films prepared at a low-temperature deposited on polymer substrates for flexible dye-sensitized solar cells (flexible DSSCs) usually suffer from a poor connection between the TiO_2 nanoparticles and the polymer because hightemperature annealing is the key process to ensure the effective connection between the nanoparticles and the substrate.^{1–3} Reduced graphene oxide (rGO), a new star material in recent years, has proved to be highly desirable for use as a two-dimensional catalyst support because it has a large theoretical surface area and excellent conductivity.^{4–7} Loading rGO onto low-temperature synthesized nanoTiO₂ particles may improve the photocatalytic performance⁸ of the film because rGO may act as an 'electron bridge' to promote the electron transfer between the TiO₂ particles and between the TiO₂ particles and the substrate.

But another problem needs to be solved first. Although the oxidized form of graphene (graphene oxide, GO)^{9,10} could remain stable in various solvents, the rGO, which was

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^cNew Energy Research Institute, CNOOC NEI Co. Ltd, Beijing, China † Electronic supplementary information (ESI) available: Photocatalytic performance measurements, gas-phase acetaldehyde decomposition method, Tyndall effect of nanoTiO₂ colloid, specific surface area of nanoTiO₂-rGO composites and UV-vis absorption spectrum of the nanoTiO₂-rGO films. See DOI: 10.1039/c3ra23095c

Low-temperature synthesis of stable nanoTiO₂–rGO composite colloids and their application in photoelectric films[†]

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It is found that low-temperature synthesized nanoTiO₂ particles and reduced graphene oxide (rGO) would make up for each other's shortcomings: on the one hand, negatively charged nanoTiO₂ particles could obviously enhance the dispersion of rGO. The nanoTiO₂–rGO colloid synthesized at a low temperature (95 °C) remained stable for at least 6 months; on the other hand, for the ultrathin and transparent nanoTiO₂–rGO films prepared using this stable colloid, rGO loading could enhance the connection of the nanoTiO₂ particles and the substrate and therefore effectively increase the photocurrent to 4.8 times more than the photocurrent generated by pure nanoTiO₂. The as-prepared transparent flexible film can be shaped into triangular calandrias which could make full use of the incident UV light, and thus increase the removal efficiency from the pass through of gas-phase acetaldehyde.

prepared by removing the hydrophilic oxygen functional groups from carbon planar GO sheets, would easily agglomerate and precipitate out. This strongly agglomerating characteristic becomes the biggest obstacle to the practical applications of rGO.

The stable composite colloid is important for industrial applications. The stability of the colloid will significantly improve manufacturing efficiency and cost efficiency in large scale industrial production of uniform films because it can be adapted to the spraying/printing/brushing film-forming technology.¹¹ Also, a stable colloid is particularly the key to making ultrathin and transparent films on flexible subtrates.^{12,13}

In the present paper, we present a simple method to prepare a stable nanoTiO₂-rGO colloid at a low temperature. The stable colloid could be deposited on conductive-plastic film substrates by various methods to make nanoTiO₂-rGO ultrathin and transparent films. In this system, the nanoTiO₂ and rGO will reduce the limitations of one another: On the one hand, the negatively charged nanoTiO₂ particles will obviously enhance the dispersion of rGO in solvent to obtain a stable nanoTiO₂-rGO colloid; whereas on the other hand, the rGO loading could in turn improve the connection of nanoTiO₂ particles and the connection of nanoparticles and the ITO-PET substrate (Scheme 1).

2. Experimental

All reagents were analytical grade and used without any further purification. GO was synthesized by a modified Hummer's

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Scheme 1 On one hand, nanoTiO₂ could enhance the dispersion of rGO, which is important for the storage and utilization of rGO; on the other hand, the rGO loading could enhance the connection of nanoTiO₂ particles and obviously increases the photocurrent of the films deposited on an ITO-PET substrate.

method from natural graphite powder (99%, Sinopharm Chemical Reagent Co., Ltd.),¹⁴ while Ti(OBu)₄ (Sinopharm Chemical Reagent Co., Ltd.) was used as the TiO₂ precursor. Different amounts of GO suspensions were used as starting materials to prepare nanoTiO2-rGO composites with different GO concentrations. The samples were denoted A-F respectively as the concentration of GO was increased (see ESI †for details of GO concentration). After adding Ti(OBu)₄ and PrOH to the GO suspension (GO suspensions were adjusted to different pH values previously) and keeping the mixture under reflux conditions at 75 °C for 24 h, the nanoTiO2-GO composite colloid was obtained. Then hydrazine was added as reducing agent to reduce the GO to rGO. After stirring at 95 °C for 2 h and then ultrasonicating for 20 min, the homogeneous and stable nanoTiO2-rGO composite colloid was obtained.

The surface morphology was examined using a JEM-2100F high resolution-transmission electron microscope (HRTEM) operated at 200 kV with a point-to-point resolution of 0.19 nm. X-ray diffraction patterns (XRD) were measured on a Rigaku D/ Max-2200/PC X-ray diffractometer. Unpolarized micro-Raman mapping was performed on a Jobin Yvon LabRam HR800 UV micro-Raman spectrometer at room temperature. X-ray photo-electron spectroscopy (XPS) was examined using a PHI 5000C ESCA System (Perkin-Elmer). N₂-BET was determined using a Quantachrome Nova 1000 Surface Area Analyzer. UV-visible absorption spectra (UV-vis) were obtained using a SHIMADZU UV-2450 spectrophotometer. Zeta potential analysis was examined using a Nicomp380ZLS analyzer (PSS).

A CHI 660D Electrochemical Analyzer was used for photoelectrochemical performance measurements. Thin films deposited on ITO-PET substrates were fixed in a specially designed sample holder with a hole of 2 centimeters in diameter to let light in for measurements. A 350 W xenon lamp was used as a light source. The details of the photocatalytic performance measurements and gas-phase acetaldehyde decomposition are provided in the ESI.[†]



Fig. 1 (a) TEM images of GO, (b, c) nanoTiO₂ particles and (d) the nanoTiO₂-rGO composite.

3. Results and discussion

3.1 Morphological features

The morphology of the composites can be seen from the high resolution transmission electron microscopy (HRTEM) images. Fig. 1a shows the winkled and flexible GO layer. The nanoTiO₂ particles in the composites are spherical particles with an approximate diameter of 2–5 nm (Fig. 1b). The nanoTiO₂ particles are crystalline and the lattice arrangement can be clearly seen in the image (Fig. 1c). For the composite sample, the scattered nanoTiO₂ nanoparticles outside the rGO sheets in Fig. 1d indicate that the nanoTiO₂ are not tightly anchored on the rGO sheets.

3.2 Raman, XRD and XPS analysis

Raman spectroscopy can be used to study the ordered/ disordered crystal structures of carbonaceous materials. Fig. 2a shows the Raman spectra of the nanoTiO₂-GO composite (sample F) and the corresponding nanoTiO₂-rGO composite. Both of the composites present D and G bands at 1350 cm⁻¹ and 1605 cm⁻¹ respectively.^{15,16} Comparing the intensity ratios of the D and G bands (I_D/I_G), it can be observed that the I_D/I_G of the nanoTiO₂-rGO sample is smaller than that of nanoTiO₂-GO, which indicates lower defects and a higher degree of graphitization. The reduction of I_D/I_G suggests that the GO sheets are successfully reduced to rGO after the addition of the hydrazine reducing agent.

Fig. 2b shows the XRD patterns of the as-prepared nanoTiO₂, GO and the nanoTiO₂–GO composite. As the as-prepared nanoTiO₂ mainly exhibits characteristic diffraction peaks of anatase phases, the anatase phase is the major phase of the low-temperature synthesized nanoTiO₂ particles. The little peak around 31° , which is ascribed to the (121) planes of



Fig. 2 (a) Raman spectra of GO and the nanoTiO₂-rGO composite (sample F), (b) the XRD patterns of nanoTiO₂, GO and sample F, (c) the C 1s core-level XPS spectra of sample D and sample F.

the brookite phase, indicates that at such a low synthesis temperature, the transformation to the anatase phase is not complete. In the GO XRD pattern, a peak centered at $2\theta = 10.3^{\circ}$, which corresponds to the (002) inter-planar spacing of 0.86 nm, is shown. Consistent with the reported studies,¹⁷ no GO characteristic peaks but all the characteristic diffraction peaks of the nanoTiO₂ could be found in the nanoTiO₂–GO composite XRD pattern, which further indicted that nanoTiO₂ particles are successfully deposited on GO sheets during the drying process and hinder the restacking of GO sheets.

XPS analysis was utilized to investigate the chemical state variations of nanoTiO2-rGO composites prepared using different concentration GO suspensions as the starting materials. Fig. 2c shows XPS spectra for the C1 score level of sample D and sample F. The morphology and distribution of the peaks are almost the same. The C1s region is composed of two contributions. The main contribution is the peak at a binding energy of 285.0 eV, which is attributed to the C-C, C=C and C-H bonds.¹⁸⁻²⁰ The other contribution is assigned to the C-O bonds. The peaks at 286.0, 287.7 and 289.2 eV were assigned to the C-OH, C=O and O=C-OH functional groups respectively. Slight differences in intensity exist among these C-O peaks between sample D and sample F; this may due to the reducing effect of the reducing agent on different types of oxygen-containing functional groups of graphene oxide being not fully controllable. Meanwhile, the peak at 281.9 eV, which would indicate the C-Ti bonds, was not observed in the spectra.18,19,21 C-C and C-O bonds existing without the existence of C-Ti bonds indicates that the nanoTiO2 was deposited on the surface of the rGO without the formation of chemical bonds. The chemical bonds, which are usually formed between the TiO₂ and graphene after high temperature annealing²²⁻²⁴ cannot form in the low temperature synthetic environment used in our research. Due to the non-formation of this tight connection, the nanoTiO₂ particles can remain suspended in the sol and their surface charges promote the dispersion of rGO.

3.3 Dispersion enhancement

The zeta potentials, widely used for the quantification of the magnitude of the electrical charge at the double layer in colloidal systems, could be used as indicators for colloidal stability. Colloids with a high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. The pH and solvent type has a great influence on the zeta potentials.²⁵ Because the rGO would aggregate very quickly in the pH < 9 solvent, in contrast to the other samples, the zeta potential measurement of rGO began from pH = 9.

Fig. 3a shows the zeta potentials of nanoTiO₂, GO, rGO and nanoTiO₂-rGO (sample F) with different pH values. While the GO colloid could stay stable at different pH values, after reduction, the stability of rGO greatly decreases owing to the removal of the hydrophilic oxygen-containing functional groups from the carbon plane. The addition of nanoTiO₂ could obviously increase the stability of the colloid which may result from the repulsion provided by the negatively charged nanoTiO₂ particles. The nanoTiO₂-rGO composite colloid (sample F, pH = 10) stays stable for more than three months, which is much more stable than the rGO colloid which would aggregate after only one day (Fig. 3b). The difference of the colloid stability could also be seen in the photograph of the films which were prepared from membrane filter. The film prepared from stable nanoTiO2-rGO composite colloid is smoother and more even than the film prepared from the rGO colloid (Fig. 3c).

The effect of rGO concentration on the stability of the nanoTiO₂-rGO composites is shown in Fig. 3d. This suggests that the stability of the composite samples would decrease with an increased loading of rGO. At pH = 9, the composites with less rGO loading (samples A, B, C and D) could stay stable for more than one year, while for samples E and F, a certain amount of precipitation will gradually appear after 12 months. But the agglomeration of sample E and F is not as irreversible as that of rGO. Simple shaking or sonication could quickly recover the dispersed state of this colloid (Fig. 3f).

Stable composite colloids can be obtained only through the condensation reflux of the GO and the precursor of nanoTiO₂ together. If the nanoTiO₂ and GO colloid were prepared separately and then mixed together, the stability of the colloid would immediately be destroyed (see Fig. S4, ESI[†]).



Fig. 3 (a) The zeta potential of nanoTiO₂, GO, rGO and sample F colloids at different pH values. (b) The optical photograph of nanoTiO₂, GO, rGO and sample F colloids, the rGO was unstable and tended to aggregate after one day while the nanoTiO₂–rGO composite (with the same rGO amount as the rGO suspension) could be stable for months. (c) The films prepared from the rGO suspension and nanoTiO₂–rGO composite colloid. (d) The effect of rGO loading amount on the zeta potential of nanoTiO₂–rGO composite colloids. (e) The optical photograph of the nanoTiO₂–rGO composite colloids with different rGO loading amounts (the concentration of nanoTiO₂ in all the samples is the same while the rGO concentration increases from sample A to F). (f) The aggregation of sample E and sample F is reversible and the colloid would return to a homogeneous state after simple shaking or sonication.

3.4 Photoelectrochemical performance of the films

NanoTiO₂-rGO films on PET substrates were prepared by various methods using stable composite colloids. Fig. 4a and 4b show the nanoTiO₂-rGO film prepared using scotch-tape and spraying methods. It is worth noting that the stable colloids are also compatible with the popular screen printing technique. In the scotch-tape method, the composite colloid was spread onto ITO-PET substrates with the aid of micro pipette tip and scotch tape. After being dried at room-temperature for about 24 h, the homogeneous and compact films were obtained. The film would not be erased off the

substrate even after rubbing it vigorously. In the spraying method, we use a spray gun combined with thermal-curing for coating films on PET substrates. The role of the rGO in the photoelectrochemical performances of the nanoTiO₂-rGO composite films was examined. A series of films deposited on ITO-PET with same amount of nanoTiO₂ and different amounts of rGO were prepared using the scotch-tape method. We employed as-made films as photoanodes in the photoelectrochemical cell, Pt as the counter electrode and Na₂SO₄ as the electrolyte to study the photocurrent generation of the nanoTiO₂-rGO films. Fig. 4c shows the photocurrent action



Fig. 4 (a) Optical photographs and optical properties of $nanoTiO_2$ -rGO films deposited on ITO-PET substrates using the scotch-tape method and (b) the spraying method. (c) Transient photocurrents of $nanoTiO_2$ and $nanoTiO_2$ -rGO composite films deposited on ITO-PET under the full light spectrum of a 350 W xenon lamp and without bias introduced to the system. (d) An illustration of the $nanoTiO_2$ -rGO film and the $nanoTiO_2$ film; the rGO acts as an "electron bridge" to improve the connection between the $nanoTiO_2$ particles and the substrate.

Table 1 The photosensitivity (l_{photo}/l_{dark}) of nanoTiO₂ and nanoTiO₂-rGO composite films deposited on ITO-PET under the full light spectrum of a 350 W xenon lamp and without bias introduced to the system

	А	В	С	D	Е	F	nanoTiO ₂
$I_{\rm photo}$ (μ A)	0.395	1.057	0.930	0.513	0.324	0.027	0.222
I_{dark} (μ A) $I_{\text{photo}}/I_{\text{dark}}$	7.75	26.43	10.81	8.27	0.042 7.71	13.50	2.31

spectra of the nanoTiO₂-rGO films with different rGO loading amounts with no anodic bias introduced into the system. We can see from the spectra that the transient photocurrent generated from the TiO₂ film is about 0.22 µA. The intensity of the photocurrent generated from the films greatly changed as the amount of rGO changed. For sample B, the transient photocurrent significantly increased to about 1.06 µA, which is about 4.8 times the photocurrent generated from nanoTiO₂ film. The intensity of photocurrent depends on the amount and mobility of photogenerated charge carriers, while the same amount of nanoTiO₂ generated same amount of photoelectrons and photoholes in all of the films, the increasing photocurrent is attributed to either a reduction in the chance of electron-hole recombination or an increased carrier mobility. Because the work function of graphene is in the range of 4.42-4.5 eV, the electrons generated on the nanoTiO₂ surface under UV irradiation will transfer to the rGO.^{26,27} The transfer of electrons from TiO₂ to rGO may not only be conducive to the separation of photogenerated electrons and holes, but will also have benefits for the transfer speed because graphene has remarkably high electron mobility at room temperature. Futhermore, instead of transferring from nanoTiO₂ to nanoTiO₂, the electrons generated on the upper layer of the nanoTiO₂ would transfer from the nanoTiO₂ to the rGO and then to the substrate. Thus as an "electronic bridge", the rGO improves the connection between nanoTiO₂ and the substrate. Although adding rGO could obviously increase the photocurrent, overloading with rGO is not conducive to photocurrent generation. The intensity of photocurrent decreased when the rGO loading amount was increased. This may be because higher loading of rGO will darken the color of the films, thus hindering the light absorption of the TiO_2 .

Photosensitivity is defined as the ratio of the current under photo-illumination to that in the dark state $(I_{\text{photo}}/I_{\text{dark}})$.^{28,29} From Table 1 we can find that rGO can effectively increase the photocurrent without obviously increasing the intensity of the dark current, thus greatly increasing the photosensitivity.

3.5 Photocatalytic performance of the films

It is not convenient to use a powder catalyst to remove air pollutants because it can easily be blown away and the recycling is inconvenient. In order to resolve this problem, in a lot of research the catalyst is coated on the walls of a ceramic honeycomb to carry out the air pollution removal process. But the incident light will obviously be attenuated in the ceramic honeycomb which would obviously decrease the catalytic efficiency. In our research, the as-prepared flexible film can be shaped into triangular tubes, and then be tied up to form a cellular structure (Fig. 5a). It can be seen from the opposite end of the tubes (tube length = 40 mm) that the incident light intensity loss was much less obvious than in the traditional ceramic honeycomb and thereby this structure allows more effective use of the incident ultraviolet light (Fig. 5b). The cellular pipelines were used as flow-through photocatalytic tunnel to examine the photocatalytic decomposition of the gas-phase of acetaldehyde (Fig. 5c). The gas-phase acetaldehyde entered from one side of the cellular pipelines with a fuel exiting from the other. The acetaldehyde decomposition rate and the CO_2 evolution were recorded in these experiments.

Fig. 5d shows the results of the one-pass gas-phase acetaldehyde photocatalysis decomposition performance of the cellular pipelines and the P25 powder. The quantity of the P25 powder was the same as the nano TiO_2 -rGO content in the films. Although the CO₂ conversion is almost the same, the



Fig. 5 (a) A photograph of the cellular structure made from combined nanoTiO₂–rGO (sample B) film pipelines. (b) The incident light seen from the opposite side of the 40 mm length transparent tubes. (c) The scheme of the flow-through the photocatalytic tunnels to achieve the photocatalytic decomposition of the gas-phase acetaldehyde. (d) One-pass photocatalytic decomposition of acetaldehyde and CO_2 selective conversion using the cellular structure made from combined nanoTiO₂–rGO (sample B) film calandrias, P25 powder and nanoTiO₂ powder. The tests used a 500 W xenon lamp and 0.3 g catalyst.

acetaldehyde deposition obviously increased from the 35.9% of P25 to 63.3%.

4. Conclusions

In summary, we found that the nanoTiO₂ and rGO will help overcome the shortcomings of one another. Negatively charged nanoTiO₂ particles will obviously enhance the dispersion of rGO in solvents and rGO will effectively improve the poor connection between low-temperature synthesized nanoTiO₂ particles and the substrate when it was deposited on the substrate to make a photoelectric film.

The stable nanoTiO₂-rGO colloid was successfully synthesized at a low temperature (95 °C). The colloid could be stable for at least 6 months and adapted for the spraying/printing/ brushing film-forming technology in industry. Ultrathin and transparent nanoTiO₂-rGO films on ITO-PET were also fabricated using this stable colloid. Adding the proper quantity of rGO could effectively increase the photocurrent to 4.8 times that of the photocurrent generated by pure nanoTiO₂. The asprepared transparent flexible film can be shaped into triangular calandrias to make full use of the incident UV light, and thus increase the removal efficiency from the pass through of gas-phase acetaldehyde.

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