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Photocatalytic H₂ production of composite one-dimensional TiO₂ nanostructures of different morphological structures and crystal phases with graphene

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One-dimensional TiO_2 nanostructures of different structural phases with graphene composites were employed as photocatalysts for photocatalytic H_2 production. Two strategies have been explored for enhancement of photocatalytic reactivity. The first is demonstrated through the use of one-dimensional nanostructures, which feature good vectorial electron transport due to decreased grain boundaries. The second strategy is to form a composite/network with two-dimensional reduced graphene oxide (RGO), which features visible light photosensitization and is an efficient charge transporter and separator. It is noted that other than structural design, it is crucial to attain anatase phase structures and superior interfacial contact between GO and TiO_2 nanostructures to enable optimal synergy between one-dimensional TiO_2 nanostructures and graphene for enhanced photocatalytic H_2 production performance. In this work, hydrothermal synthesis and an *in situ* solution-based photoreduction method are used owing to their scalability, low temperature, high yield and ease of temperature and reactant concentration control characteristics.

1. Introduction

Global energy consumption has increased dramatically over the years, driven by rising standards of living and a growing worldwide population. The increased demand for energy will require significant growth in energy generation capacity, secure energy sources, and zero carbon emissions motivations. Among the various alternative energy strategies, the production of chemical fuels by solar energy conversion has been considered as one of the major strategies for solving the global energy issues. Since the pioneering report by Fujishima and Honda¹ on photoelectrochemical water splitting on a TiO₂ electrode, photocatalytic processes have attracted immense research. This approach has shown promising results using solar energy for clean, low-cost, and environmentally friendly production of H₂. Other added advantages of H₂ as an energy carrier are being transportable as well as storable for an extended time. Among various oxide semiconductor photocatalysts, TiO₂ is still an important and promising semiconductor for H₂ production via water splitting owing to its exceptional properties, such as suitable band

alignments to water redox potentials, biological and chemical inertness, availability, environmental friendliness, low cost, and long-term stability against photo and chemical corrosion.² However, photocatalytic H₂ production efficiency using pristine TiO₂ is limited, mainly due to the rapid recombination rate of photogenerated carriers and light absorption in the UV region.³ Thus, numerous methods of noble metal loading, metal and non-metal ion doping, sensitization and adding of sacrificial reagents (electron donors or hole scavengers) have been proposed to improve the TiO₂ photocatalytic efficiency.⁴⁻¹²

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Graphene is an atomic sheet of sp²-bonded carbon atoms that are arranged into a honeycomb structure. It also has unique properties that are highly promising for photocatalysis applications. Firstly, it has high theoretical surface area of approximately 2600 m² g⁻¹, allowing it to be functionalized for attachment of nanostructured materials, serving as a twodimensional photocatalyst support.^{13,14} Secondly, it allows room temperature ballistic transport with electron mobility exceeding 15 000 cm² V⁻¹ s⁻¹, which makes an excellent electron sink.¹⁵ Thus, the combination of TiO₂ and graphene is a promising photocatalyst to simultaneously possess excellent adsorptivity, transparency, conductivity, and controllability. In particular, most of the work with graphene-metal oxide composites is related to the photocatalytic breakdown of organic compounds

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for waste remediation.^{16,17} Though some work on graphene– TiO_2 has been reported for photocatalytic H₂ production, most of the research was carried out using commercial Degussa P25 nanoparticles or TiO_2 nanoparticles.^{18–20} There is no exploration of the effects of one-dimensional TiO_2 nanostructures with graphene on photocatalytic H₂ production applications.

To the best of our knowledge, there is no reported work on the hydrothermal synthesis of tunable one-dimensional TiO_2 nanostructures composited with GO for photocatalytic H_2 production applications. Three methods of compositing TiO_2 nanostructures with GO, namely hydrothermal, one-pot hydrothermal and photoreduction, were studied. Notably, our work shows that there is a synergetic effect of having anatase phase nanostructures as well as an ideal structural morphology with superior interfacial contact to preserve high photocatalytic activity between the TiO_2 nanostructures and graphene. Thus, it is conceptually important to design and synthesize photocatalyst structures that can effectively facilitate the separation and transfer of the carriers for high H_2 evolution efficiency.

2. Experimental details

2.1 Synthesis of GO and photocatalyst

GOs were synthesized through a chemical approach based on a modified Hummers method. Briefly, a small amount of graphite flakes (0.5 g) and NaNO₃ (0.5 g) were mixed together in a flask. Concentrated H₂SO₄ (23 ml) solution was added to the mixture and stirred in an ice bath. $KMnO_4$ (3 g) was slowly added to the reaction mixture to avoid overheating. The reaction mixture was then stirred at room temperature for 2 h. After that, 50 ml of distilled water was added slowly to increase the temperature to 90 °C. After another 30 min, 150 ml of distilled water was slowly added, followed by another slow addition of 5 ml of 30% H₂O₂ to stop the reaction. The GO solution was washed with 37% HCl/H2O solution with ratio 1:5 through centrifugation (10000 rpm for 30 min) three times to remove metal ions and the supernatant was decanted. The remaining solid material was then washed with DI water by using the same method to remove the remaining acid until the pH of the suspension was neutral.

0.34 g of TiO₂ anatase powder (Sigma-Aldrich, 99.8%) was mixed with an amount of 10 M of aqueous NaOH (Sigma-Aldrich, >98%). The alkaline solution functioned as a peptizing agent. 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 120 °C or 180 °C for 48 h to synthesize nanotubes (NT) and nanobelts (NB), respectively. After heating, the sample was left to cool down to room temperature in the oven. The precipitate was then mixed with 20 ml of 1 M HCl and stirred for 24 h. This process leached out the Na^+ via ion exchange with H^+ , which were present in the acidic wash solution. To prepare the one-pot hydrothermal synthesis, the experimental procedures mentioned earlier were repeated with the addition of GO (produced by Hummers method) with other growth precursors (TiO₂ powder and NaOH). As for the hydrothermal RGO-TiO₂ synthesis, the GO

suspension was mixed with TiO2 nanostructures and stirred for 1 h to get a homogenous suspension. The mixture was then placed in a Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 6 h to form the RGO-TiO₂ composite. As for the photoreduction method, GO was mixed with TiO₂ nanostructures and stirred for 1 h to get a homogenous mixture before it was exposed to illumination from a 300 W Xe lamp (Excelitas, PE300BFM) for 8 h while being constantly stirred. In the presence of light irradiation, the photogenerated holes in TiO₂ were reacted with methanol (CH₃OH) to form methoxy radicals. In the suspensions of GO and TiO₂, the accumulated electrons interacted with the GO sheets and reduce certain functional groups to yield RGO. Platinum (Pt) co-catalyst was loaded onto the photocatalyst using 2 mg ml^{-1} chloroplatinic acid, (H₂PtCl₆) under exposure of light irradiation for 8 h with constant stirring

2.2 Materials characterizations

Scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 6700F field-emission scanning electron microscope operating at 15 kV with a built-in energy dispersive X-ray (EDX) attachment (Oxford Instrument and Inca software). Transmission electron microscopy (TEM) characterization was carried out using (FETEM, JEOL JEM2010F). X-ray photoelectron spectroscopy (XPS), VG ESCALAB MK2 equipped with an Mg K α X-ray source was employed to study the elemental composition of the doped films. X-ray diffraction was carried out on a Philips X-ray diffractometer with Cu K α radiation ($\lambda = 1.541$ Å). Absorption spectra were obtained using a Shimadzu UV-3600 UV-vis spectrophotometer.

2.3 H₂ evolution measurements

30 mg of photocatalyst was used for 10 ml of reaction mixture contained in a quartz tube. The 10 ml reaction mixture consists of 10% methanol by volume and 90% tap water. The reaction mixture was purged with Ar gas for 15 min before carrying out reaction. The reaction mixture was illuminated with a 300 W Xe lamp (Excelitas, PE300BFM). 100 μ l of gas sample was drawn from the quartz tube using a syringe at about 30 min intervals to sample the gas composition using a gas chromatograph (Shimadzu, GC-2014AT).

3. Results and discussion

Hydrothermal treatment of TiO_2 powder in a strong alkaline solution was used to transform the anatase nanoparticles (Fig. 1a and b) into one-dimensional NTs and NBs at different synthesis temperatures. Fig. 1c and d show the produced NBs, which are well-dispersed and have diameters of 30–300 nm and lengths of 5–20 µm. The NBs appear to be thin, as such they are electron translucent. Fig. 1e and f show the as-prepared NTs, which are highly uniform and have diameters of 7–15 nm and lengths of 0.5–1 µm. Under the hydrothermal alkaline conditions, Na⁺ ions intercalate into the anatase crystal structure resulting in delamination and formation of a layered structure.²¹ The rolling up of the multiple layer of delaminated



Fig. 1 SEM images of (a–b) TiO₂ nanoparticles used as precursor and the corresponding (c–d) NB and (e–f) NT produced by the hydrothermal synthesis.

anatase sheets leads to the formation of NT. The delaminated anatase sheet tends to roll up due to energetic factors, such as reduction of surface energy and dangling bonds by closing up to form a tubular structure.²¹ In the case of the NBs, it has been proposed that at a higher synthesis temperature, dissolutioncrystallization occurs in an alkaline-hydrothermal process.²² Anatase TiO₂ nanoparticles dissolve and Ti-O-Ti bonds are broken to form a six-coordinated complex, $[Ti(OH)_6]^{2-}$. The $[Ti(OH)_6]^{2-}$ complex is unstable and tends to combine *via* oxolation/olation to initiate nucleation and growth of NB.22 The NB is composed of layers of [TiO₆] octahedra with Na⁺ located between the layers to form one-dimensional Na₂Ti₃O₇ NB. After leaching in 1 M HCl, the H⁺ can replace the Na⁺ between the layers to form H₂Ti₃O₇ NBs. Anatase TiO₂ NBs can then be obtained by dehydrating H₂Ti₃O₇ NBs at a higher temperature.²² The reason for disparity in the formation mechanisms of NTs and NBs is probably due to the difference in synthesis temperature. At a higher synthesis temperature of 180 °C, transformation of Ti-O bonds into $[Ti(OH)_6]^{2-}$ occurs while at lower temperature of 120 °C, breaking of chemical bonds is not possible, resulting in the delamination of anatase sheets.

Fig. 2 shows the XRD spectra of anatase nanoparticles (reference), NBs and NTs as-prepared and annealed at 300 $^{\circ}$ C and 450 $^{\circ}$ C. The diffraction peaks of NBs annealed at 300–450 $^{\circ}$ C are attributed to hydrogen titanate, H₂Ti₄O₉ (PDF No. 00-036-0655, ICDD). The crystallinity of the NBs samples improve with annealing. However, it is noted that in our work, the NBs do not transform into the anatase phase upon annealing at a higher temperature. On the other hand, the diffraction peaks





Fig. 2 XRD spectra showing as-prepared NTs and NBs and samples annealed at 300 °C and 450 °C produced by the hydrothermal synthesis. TiO₂ anatase powder acts as a reference.

of NTs indicate anatase phase. It is observed that the crystallinity improves with annealing temperature. Triplet and doublet peaks seen in the anatase powder reference appear as a single broad peak in the NTs samples due to size-induced peak broadening of NTs. It is noted that attaining the anatase crystal structure is ideal since it is known to be the most active TiO_2 phase for photocatalytic reactivity.²³

Three different processing methods employing hydrothermal, one-pot hydrothermal and photoreduction were carried out to form RGO-TiO₂ nanostructured composites of 10% GO loading. Fig. 3a and b show the composites of RGO-NB and RGO-NT produced by hydrothermal treatment, respectively. The composites RGO-NB are observed to partially transform into nanocrystals of diameter approximately 30 to 100 nm, somewhat interconnected, whilst the RGO-NT are mostly transformed into nanoparticles. The different extent of the structural collapse is probably due to the size effect of the NBs and NTs. Larger dimension NBs result in partial structural disintegration while the smaller NTs show complete granule structure collapse into nanoparticles. Hence, a one-pot hydrothermal synthesis is devised where the synthesis of nanostructures together with the loading and reduction of GO were carried in one processing step. From Fig. 3c and d, it can be observed that the NBs remain intact as there is no observable structural transformation. In addition, we are not able to differentiate the NBs from the GO since they have similar two-dimensional structures. There is an insignificant difference between the NBs sample before and after compositing with 10% GO, the NBs with GO composite seem to display some extent of alignment. It is believed that the GO sheets act as scaffolds for the micro/macroscopic ordering of NBs. Fig. 3e and f show RGO-NT, which exhibit multilayer folding of NTs. Similarly, the GO sheets serve as scaffolds for NTs to adhere to and are collectively stacked due to capillary and Van der Waals forces induced during the mixing and drying processes. The apparent morphological differences between RGO-NB and RGO-NT composites produced by the one-pot hydrothermal method are likely due to the larger NB compared to the NT,



Fig. 3 SEM images of GO composited with TiO_2 (a) NBs and (b) NTs *via* hydrothermal; (c–d) NBs and (e–f) NTs *via* one-pot hydrothermal and (g–h) NTs *via* photoreduction.

which made them stiffer to conform to multilayer foldings. Fig. 3g and h show a RGO-NT composite prepared under steady state UV-Vis irradiation with continuous stirring. It can be observed that the composite attained layered structures of RGO sheets with NT integrated between them. An obvious and distinct colour change from brown to dark grey solution (not shown here) is observed after the photoreduction process. The color change proves the success of GO photoreduction due to the partial restoration of the π network within the carbon structure.^{11,12} The reasons that contribute to the realization of GO reduction and formation of a layered composite is that the light irradiation with constant mechanical stirring promotes good dispersion of GO amongst the TiO₂ NTs. With a well-dispersed composite, the high affinity hydroxyl groups at the surfaces of TiO₂ NTs are sufficiently exposed to carboxylic acid functional groups. This in turn enables intimate integration and compositing of the GO sheet and TiO₂ NTs. It is expected that, in this case, the excellent conductivity of RGO can be fully utilized to improve photocatalytic activity.

TEM structural characterizations were carried out on RGO-NB and RGO-NT composite samples. Fig. 4a shows the one-pot

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Fig. 4 TEM images of RGO–TiO₂ composites produced by various processing methods (a) nanobelts (NB) by one-pot hydrothermal (inset: RGO-NB composite) (b) HRTEM of the layered polycrystalline NB (c) nanotubes (NT) by one-pot hydrothermal and (d) NT by photoreduction. (The arrows indicate the GO sheets).

hydrothermal prepared composite sample with NB of widths 50–400 nm and lengths 5–10 μ m. Fig. 4a inset shows the RGO-NB composite, at higher resolution (Fig. 4b) the NB is observed to possess a defective polycrystalline layered structure. Fig. 4c shows one-pot hydrothermal produced RGO-NTs, which shows GO sheets with randomly oriented NTs. The NTs possess a rather uniform diameter of ~10 nm and lengths of 0.1–1 μ m. Fig. 4d shows RGO-NT produced by a photoreduction method where a good dispersion of GO sheets throughout the matrix of TiO₂ NTs are observed and evidently the NTs are homogeneously adhered on GO sheets. Hence from the SEM and TEM analyses, the processing methods for compositing GO with TiO₂ nanostructures have substantial effects on the morphological features of the resulting photocatalyst.

XRD spectra (Fig. 5a) were obtained on one-pot hydrothermal and photoreduction composites to ensure the preservation of crystallinity. No typical diffraction peaks of GO or RGO are observed in any of the composite samples due to their low concentrations. The XRD spectra are similar to that of pristine NBs and NTs obtained in Fig. 2. Hence, RGO compositing methods do not have adverse effects on the crystallinity and structural phase of the NB and NT. Fig. 5b shows chemical composition studies of C1s for GO and RGO-NT composites prepared by one-pot hydrothermal and photoreduction methods. The main C1s peak located at 284.6 eV is assigned to elemental carbon (C-C). The sharp peak located at 285.6 eV for the composite samples is attributed to defect-containing sp²-hybridized carbons.²⁴ After compositing with TiO₂ nanostructures, the peak at 286.8 eV for the C-O group of GO vanishes.²⁵ The significant reduction of the concentration of oxygen containing bonds in the composite samples suggests an effective chemical reduction of the GO.²³ However, it is noted that the C=O bonds at 287.5 eV of the photoreduction composite has decreased while those of the one-pot hydrothermal composite have increased slightly



Fig. 5 (a) XRD spectra of RGO–TiO₂ composites (NT and NB) produced by the one-pot hydrothermal (OPH) and photoreduction (PR) method with anatase TiO₂ as a reference sample. (b) XPS C1s spectra of GO, RGO-NT composite produced by OPH and PR.

compared to the GO reference sample. Thus, the results suggest that the one-pot hydrothermal method may be less effective in the reduction of the GO sheet. Furthermore, a desirable reduction of oxygen-containing species and restoration of the conducting π -electron network is visually observable for the photoreduction method, as seen from the color change of the suspension from brown to dark gray.

The range of light absorption plays an important role in the photocatalytic performance. Extending light absorption from UV to visible light range will allow more efficient utilization of the solar spectrum. As can be seen, the addition of GO increases light absorption intensity in the visible light regions, as compared to the pristine P25, NTs and NBs (Fig. 6a). Therefore, compositing GO with TiO₂ nanostructures effectively promotes visible light absorption, which can be attributed to electronic interactions or chemical bonding between GO and TiO₂ nanostructures. Fig. 6b shows the rates of H₂ evolution compared between different structures; nanoparticles, NBs and NTs as well as different reduction/compositing methods: one-pot hydrothermal and photoreduction. The pristine NTs annealed at 450 $^\circ C$ showed higher photocatalytic activity than P25 and pristine NBs. Thus, for the same structural anatase phase, the onedimensional nanotubular structure has a higher catalytic reactivity than P25 nanoparticles. One-dimensional nanostructures



Fig. 6 (a) UV-Vis absorption spectra and (b) H_2 evolution of various nanostructures and composites prepared by one-pot hydrothermal (OPH) and photoreduction (PR) methods.

have proven to facilitate electron transport unlike the nanoparticles, electron transport is not limited by slow trap-limited diffusion processes.²⁶ We also noted that the NB samples consistently show poor H₂ production performance. A few possible reasons have been put forth. Firstly, NB does not have an anatase TiO_2 phase according to the XRD spectra (Fig. 5a). Secondly, it has a highly defective polycrystalline layered structure (high resolution TEM results) and finally it has a relatively low surface area due to its large dimensions. Thus, subsequent work was focused on the optimization of the RGO-NT composite for enhanced photocatalytic activity. The RGO-NT composites prepared by the photoreduction method shows the highest photocatalytic activity. Both XPS and H₂ evolution results show that photoreduction is a more effective method to prepare a well-dispersed and good interfacial RGO-TiO₂ composite compared to the one-pot hydrothermal method. From the XPS studies, the one-pot hydrothermal method is not as effective for GO reduction, thus greatly hampering the capability for facilitating separation and transfer of charge carriers. Though the earlier UV-Vis spectroscopy studies suggest an extended light absorption for all the GO composites, it seems that an increased visible absorption is not always accompanied by an enhancement of photocatalytic activity.

The Brunauer–Emmmett–Teller (BET) specific surface area and porous structure characteristics of various samples were



determined using nitrogen isothermal adsorption. Fig. 7a–d show nitrogen adsorption/desorption isotherms of the TiO_2 nanoparticles (P25), TiO_2 NT, RGO-NT loaded with 1 and 10%, respectively. Their corresponding specific surface areas are 48.7, 111.6, 145.7 and 334.7 m² g⁻¹, respectively. The surface areas were increased significantly with the formation of nanotubes and the addition of graphene. It is believed that the large specific surface area facilitates better access and diffusion of liquid and gaseous reactants, which is beneficial for photocatalytic reactivity.

The RGO-NT composites with different GO wt% loadings were prepared using the photoreduction method. Fig. 8a displays the absorbance spectra of the various RGO-NT composites. The pure TiO₂ sample absorbs only at a wavelength of less than 400 nm. With the addition of GO, an extended light absorption towards the visible light region was observed. The composites allow better utilization of the solar spectrum, which consists predominantly of visible irradiation. However, it is observed that the UV light absorption was compromised with the increase in GO wt% loading. Furthermore, photocatalytic H₂ production measurements (Fig. 8b) show enhancement with increase GO loading up to ~5 wt% before the H_2 production starts to decrease. Excessive GO content in the composite may effectively block TiO2 NTs from UV light irradiation, which may correlate with the decrease in UV light intensities, as seen from the absorbance spectra (Fig. 8a). Generally, all the composite photocatalysts show improvement in H₂ generation over P25 nanoparticles except for the sample with 20 wt% loading. When loaded with a suitable amount of GO, we can observe a synergistic effect between the superior electron conductivity of one-dimensional NT and RGO, which can suppress the recombination of photogenerated electron-hole pairs. Moreover, the formation of chemically well-bonded composites

promotes extended photosensitization of TiO₂ NTs.²⁷ In addition, the effect of Pt loaded composite on the photocatalytic reactivity was also investigated (Fig. 8c). Pt loading was kept at 1% since it is observed that excessive Pt-loading causes agglomeration, which may shield the photosensitive TiO_2 and graphene surfaces. The increased H_2 evolution rate with Pt-loading is observed for P25 and all composite samples. The H₂ production rates with Pt co-catalyst composite samples increased by 6 to 12 times over the ones without Pt loading. This can be explained by the formation of a Schottky barrier at the metal/TiO₂ interface, which favors capturing of conductionband electrons from the photocatalyst, thereby decreasing the possibility of electron-hole recombination. In addition, Pt co-catalysts advocate easy migration of electrons to react with water, thereby decreasing the activation energy needed for the reduction of water.28,29

Based on the obtained results, the possible mechanism of observed photocatalytic activity is proposed (Fig. 9). In the absence of RGO, photogenerated electrons from the valence band (VB) and conduction band (CB) will quickly recombine and leaving only a small fraction of electrons and holes taking part in the photocatalytic reaction. However, with the composite RGO-TiO₂ NTs, the photogenerated electrons in the CB of TiO₂ favor the transfer of electrons to graphene sheets due to slightly lower potential (-0.08 eV vs. SHE, pH = 0) than the CB level (about -0.24 eV) of TiO₂ anatase. Other attributes of graphene *i.e.* its high mobility and conductivity properties, also contribute to the reduction of photoinduced electron and hole recombination. Subsequently, the excited electrons are transferred to the active sites at RGO where H₂ is produced via the reduction of water molecules or protons. Furthermore, this synergistic composite photocatalyst also tackles the issue of spontaneous backward reaction in the

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Fig. 8 (a) UV-Vis absorption spectra of various wt% GO loadings. H₂ evolution of (b) various GO loading composites ranging from 1% to 20% and (c) 1% Pt co-catalyst loaded composites with suspended photocatalysts under xenon-lamp irradiation.

RGO-NT

RGO-NT



Pt

RGO-NT

Fig. 9 A schematic of the RGO-NTs composite with the proposed mechanism of enhanced synergistic photocatalytic activity.

photocatalytic suspension system by separating the $\rm H_2$ and $\rm O_2$ evolution sites.

RGO-NT

RGO-NT

4. Conclusions

RGO-NT

We have achieved a synergistic design of a RGO–TiO₂ 1D nanostructure composite for enhanced photocatalytic H₂ production. Our studies show a nanotubular structure prepared by photoreduction compositing method is the best compared to hydrothermal and one-pot hydrothermal methods. Chemical and structural analyses show that highly reduced GO and TiO₂ with anatase phase exhibit high photocatalytic activity which correlates to the enhanced H₂ evolutions. Highly reduced GO was demonstrated to be an effective photosensitizer and charge conductor/transporter to enhance the photocatalytic H_2 production. Lastly, the RGO content of the composite and the addition of Pt co-catalyst have a significant influence on the photocatalytic performance. The synergistic effect can be achieved under an optimal amount of 2.5 wt% RGO content and 1 wt% Pt co-catalyst loading, which gives a 12 times enhancement of H_2 production compared to P25.

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