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## Hybrid photocathode based on a Ni molecular catalyst and Sb<sub>2</sub>Se<sub>3</sub> for solar H<sub>2</sub> production†

 D. Alicia Garcia-Osorio,<sup>a</sup> Thomas P. Shalvey,<sup>a</sup> Liam Banerji,<sup>a</sup> Khezar Saeed,<sup>id ab</sup> Gaia Neri,<sup>‡a</sup> Laurie J. Phillips,<sup>a</sup> Oliver S. Hutter,<sup>id ac</sup> Carla Casadevall,<sup>id d</sup> Daniel Antón-García,<sup>id d</sup> Erwin Reisner,<sup>id d</sup> Jonathan D Major<sup>\*a</sup> and Alexander J Cowan<sup>id \*a</sup>

**We report a H<sub>2</sub> evolving hybrid photocathode based on Sb<sub>2</sub>Se<sub>3</sub> and a precious metal free molecular catalyst. Through the use of a high surface area TiO<sub>2</sub> scaffold, we successfully increased the Ni molecular catalyst loading from 7.08 ± 0.43 to 45.76 ± 0.81 nmol cm<sup>-2</sup>, achieving photocurrents of 1.3 mA cm<sup>-2</sup> at 0 V vs. RHE, which is 81-fold higher than the device without the TiO<sub>2</sub> mesoporous layer.**

Photoelectrodes for the production of solar fuels, for example by splitting water to generate H<sub>2</sub> and O<sub>2</sub>,<sup>1</sup> have the potential to play a key role in future energy systems. However, advances in both photoanodes for water oxidation<sup>2</sup> and photocathodes for hydrogen evolution (HER) are needed to improve the stability and to lower the cost for industrial scaling, since most long-lasting devices rely on precious metals.<sup>3–5</sup> Sb<sub>2</sub>Se<sub>3</sub> has recently gained interest from the photovoltaic (PV) community due to its near-direct band gap of 1.18 eV, a high absorption coefficient across the visible region,<sup>6</sup> and an unusual 1D nanoribbon structure that enables effective charge transport.<sup>7</sup> These properties, combined with improvements in material processability and the use of earth-abundant elements, have led to the suggestion that Sb<sub>2</sub>Se<sub>3</sub> could be a viable thin film PV material for use on a global scale.<sup>8</sup> Sb<sub>2</sub>Se<sub>3</sub> has also been studied as a photocathode for HER, the conduction band minimum at –0.5 V vs. RHE provides enough driving force for producing H<sub>2</sub>,<sup>9</sup> and its band gap (*E<sub>g</sub>*) is very close to the optimal calculated for the bottom electrode in dual absorber standalone device for water splitting.<sup>10</sup> Reported solar to hydrogen efficiencies, using state-of-the-art Sb<sub>2</sub>Se<sub>3</sub> photocathodes, have now exceeded 10%.<sup>11,12</sup> These photocathodes consist of a Sb<sub>2</sub>Se<sub>3</sub>/CdS buried

junction that is coated with a protective TiO<sub>2</sub> capping layer. The planar TiO<sub>2</sub> is then modified with a HER catalyst like Pt,<sup>13,14</sup> RuO<sub>2</sub>,<sup>12,15</sup> and MoS<sub>x</sub>.<sup>16</sup> Notably, even with state-of-the-art devices, reductive dissolution of TiO<sub>2</sub> caused by photoelectron accumulation can occur.<sup>11,13</sup> C<sub>60</sub> between TiO<sub>2</sub> and the H<sub>2</sub>-evolution catalyst can alleviate charge accumulation promoting the photoelectron transfer at the TiO<sub>2</sub>/Pt interface, but device stabilities are still low.<sup>11,13</sup> Therefore, a need still exists to identify new photoelectrode/catalysts systems that are able to keep up with the rate of photoelectron generation and to explore how the catalyst/TiO<sub>2</sub> interface can be modified to prevent the generation of high-electron densities. Earth abundant molecular electrocatalysts have not previously been explored on Sb<sub>2</sub>Se<sub>3</sub> photocathodes, even though they are an alternative to precious metal electrocatalysts and could potentially offer improved rates of charge transfer at the semiconductor/molecular catalyst interface.<sup>17,18</sup> Here, **NiP** with a [Ni(P<sub>2</sub><sup>R</sup>N<sub>2</sub><sup>R'</sup>)<sub>2</sub>]<sup>2+</sup> core (P<sub>2</sub><sup>R</sup>N<sub>2</sub><sup>R'</sup> = bis(1,5-R'-diphospha-3,7-R''-diazacyclooctane)), shown in Fig. 1b, was chosen as model molecular catalyst.<sup>19</sup> The **NiP** catalyst mimics the hydrogenase intramolecular proton transfer to the Ni centre through the pendant amine groups in the second coordination sphere.<sup>20</sup> Furthermore, it can be covalently anchored to TiO<sub>2</sub> by the phosphonic acid groups in the outer coordination sphere, Fig. 1b.<sup>21</sup>

The complete device FTO/Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS/TiO<sub>2</sub>/TiO<sub>2</sub>-*meso*/NiP is shown in Fig. 1a. Sb<sub>2</sub>Se<sub>3</sub> (1.5 μm) was deposited on Au (70 nm) coated fluorine-doped SnO<sub>2</sub>-glass (FTO) by a two-step fast-cooling close space sublimation process, which generates a compact preferentially orientated nanoribbon crystal structure that facilitates rapid hole transfer to the Au contact.<sup>7,11,12</sup> Then, a thin sputtered CdS buffer layer (20 nm) was added which forms a Sb<sub>2</sub>Se<sub>3</sub> heterojunction with a negligible conduction band offset, thereby allowing efficient charge separation and electron transfer towards TiO<sub>2</sub> (Fig. 1c).<sup>6</sup> In this way, the onset potential and fill factor of the Sb<sub>2</sub>Se<sub>3</sub> photocathodes are improved despite the parasitic absorption of photons below λ < 500 nm in the CdS causing a decrease in the photocurrent.<sup>11,12</sup> After, TiO<sub>2</sub> (100 nm) was sputtered to provide a physical barrier preventing contact between the light absorber

<sup>a</sup> Stephenson Institute for Renewable Energy, University of Liverpool, L69 7ZF, UK.  
 E-mail: acowan@liverpool.ac.uk

<sup>b</sup> Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark

<sup>c</sup> Department of Mathematics, Physics and Electrical Engineering,

Northumbria University, NE1 8ST, UK

<sup>d</sup> Yusuf Hamied Department of Chemistry, University of Cambridge, CB2 1EW, UK

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‡ Current address: Enapter S.R.L, via di Lavoria 56/g, 56040 Pisa.





**Fig. 1** (a) Schematic diagram of  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  hybrid photocathode. (b) Chemical structure of **NiP** catalyst molecular catalyst, panel a and b are not drawn to scale. (c) Equilibrium band alignment diagram of  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2$  heterojunction based on VBM<sup>11</sup> and  $E_g$  measured separately for each layer (Fig. S2.1, ESI<sup>†</sup>), note that **NiP** redox couple is pH independent.<sup>21</sup>

and the electrolyte.<sup>22</sup> Full details of the synthetic procedures, the device characterisation and SEM images are provided in the ESI,<sup>†</sup> Fig. S2.1-3.

The molecular catalyst was first immobilized overnight onto the sputtered  $\text{TiO}_2$  (without the  $\text{TiO}_2\text{-meso}$ ) by soaking the photoelectrode in dry methanolic solution (0.5 mM **NiP**),<sup>19,23,24</sup> and from now on labelled as  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$ . It was removed from the soaking solution, thoroughly washed in methanol to remove the non-chemisorbed catalyst and dried under vacuum. **NiP** loadings were determined by stripping the catalyst off using NaOH and then quantified by UV-vis spectroscopy, as shown in Table S1 (ESI<sup>†</sup>). When **NiP** was attached to the sputtered  $\text{TiO}_2$  layer, a loading of  $7.08 \pm 0.43 \text{ nmol cm}^{-2}$  was achieved. All the photoelectrochemical tests were done under  $100 \text{ mW cm}^{-2}$  illumination (unless otherwise stated) and with  $\lambda > 340 \text{ nm}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  at pH 3. pH 3 was chosen due to past studies that showed **NiP** was most active at this pH.<sup>23,25</sup> Fig. 2 shows a photocurrent of only  $-16 \mu\text{A cm}^{-2}$  at 0 V vs. RHE, which exceeds only slightly the current in the absence of any catalyst ( $-3 \mu\text{A cm}^{-2}$  for  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2$ , Fig. S2.4, ESI<sup>†</sup>). The spikes in the light chopped Linear Sweep Voltammetry (LSV) of  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$  demonstrated that the photoelectrons are not being utilised at a fast-enough rate by the catalyst, instead recombination is dominating.<sup>26</sup>

The low photocurrent of the  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$  electrode is due to the low loading of **NiP** compared with previous devices.<sup>23,24</sup> A common approach to achieve higher catalyst loadings on a photoelectrode is to increase the available surface area for catalyst binding by using a mesoporous  $\text{TiO}_2$  layer



**Fig. 2** Chopped light LSV of the hybrid photocathodes  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$  (blue trace) and  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  (purple trace) at  $10 \text{ mV s}^{-1}$ . The  $\text{TiO}_2\text{-meso}$  enables a higher loading of the **NiP** catalysts and increased photocurrents. All experiments were carried out in 0.1 M  $\text{Na}_2\text{SO}_4$  pH 3 at  $100 \text{ mW cm}^{-2}$  and  $\lambda > 340 \text{ nm}$ .

( $\text{TiO}_2\text{-meso}$ ). Typically, following deposition of a  $\text{TiO}_2$  nanoparticle-organic binder paste, thermal annealing is carried out in air ( $\sim 450 \text{ }^\circ\text{C}$ ) to remove the binder and sinter the  $\text{TiO}_2$  nanoparticles forming conductive pathways.<sup>26</sup>  $\text{Sb}_2\text{Se}_3$  is unstable at these temperatures in air,<sup>8</sup> therefore we modified a UV curing approach successfully developed by the Grätzel group for  $\text{CuO}_2/\text{AZO}/\text{TiO}_2$  photocathodes.<sup>27</sup> Following doctor blading of an anatase  $\text{TiO}_2$  paste (av. particle size 20 nm diameter) the sample was UV cured for 68 h using a 365 nm LED, Fig. S2.5 (ESI<sup>†</sup>). Note that the  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$  also included the sputtered 100 nm  $\text{TiO}_2$  layer since it was found to be essential during the UV curing to protect the  $\text{Sb}_2\text{Se}_3/\text{CdS}$ . The photocathode was then annealed at lower temperature ( $350 \text{ }^\circ\text{C}$ ) under  $\text{N}_2$  to improve the electrochemical properties of the  $\text{TiO}_2\text{-meso}$  layer (Fig. S2.6-7, ESI<sup>†</sup>) without hindering the light absorber capabilities (Fig. S2.9, ESI<sup>†</sup>). The  $\text{TiO}_2\text{-meso}$  was ca. 4–6  $\mu\text{m}$  thick determined by profilometry, the cross-sectional image and energy-dispersive X-ray spectroscopy (EDX) maps are shown Fig. 3a and Fig. S2.10 (ESI<sup>†</sup>), respectively. Neither the UV curing nor the  $\text{N}_2$  annealing alone resulted in a  $\text{TiO}_2\text{-meso}$  layer with electrical and mechanical features suitable for a molecular catalyst scaffold (Fig. S2.5 and S2.8, ESI<sup>†</sup>). The **NiP** immobilization on the  $\text{TiO}_2\text{-meso}$  device was carried out using the same experimental protocol as for the planar structure. The resultant  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  photocathode achieved an increased **NiP** loading ( $45.76 \pm 0.81 \text{ nmol cm}^{-2}$ ), in line with the literature.<sup>24</sup> Top view EDX mapping shows the catalyst is evenly distributed on the photocathode surface (Fig. S2.11, ESI<sup>†</sup>). X-Ray photoelectron spectroscopy (XPS) analysis of the **NiP** on the  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  electrode is shown in Fig. 3b–d. The energies of the Ni 2p (Fig. 3b, 1/2 at 872.1 eV and 3/4 at 854.6), P 2p (Fig. 3c, 132.6 eV) and N 1s (Fig. 3d, 399.6 eV) peaks are in good agreement with the **NiP** catalyst prior to immobilisation (all the XPS peak positions are shown in Table S2, ESI<sup>†</sup>).<sup>23–25</sup> The complete  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  photocathode achieves a photocurrent of  $-1.3 \text{ mA cm}^{-2}$  at 0 V vs. RHE with an onset potential of ca. +0.37 V vs. RHE (Fig. 2). The photocurrent for this electrode structure is amongst the highest reported for a **NiP** decorated photocathode, Table S3 (ESI<sup>†</sup>)





**Fig. 3** (a) Cross-sectional SEM image of  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ . (b–d) XPS spectra of **NiP** molecular catalyst (blue trace) after it is immobilized on  $\text{TiO}_2$  (pre-CPP, black trace), and after 5 h of CPP test at 0 V vs. NHE (post-CPP, red trace) with light intensity of  $100 \text{ mW cm}^{-2}$  and  $\lambda > 340 \text{ nm}$  in  $0.1 \text{ M Na}_2\text{SO}_4$  at pH 3. (b–d) XPS spectra showing Ni 2p, P 2p and N 1s regions respectively.

provides the state-of-the-art hybrid photocathodes for  $\text{H}_2$  production. **NiP** has been previously used with a  $\text{Si}/\text{TiO}_2\text{-meso}$  photocathode to achieve a photocurrent of  $-0.3 \text{ mA cm}^{-2}$  at 0 V vs. RHE<sup>24</sup> and  $-0.6 \text{ mA cm}^{-2}$  at 0 V vs. RHE for a  $\text{La}_5\text{Ti}_2\text{Cu}_{0.9}\text{Ag}_{0.1}\text{S}_5\text{O}_7/\text{TiO}_2$  photocathode.<sup>23</sup> A control experiment without the catalyst ( $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$ , Fig. S2.4, ESI<sup>†</sup>) demonstrates the importance of the **NiP** catalyst, it showed a photocurrent of only  $-0.12 \text{ mA cm}^{-2}$  at 0 V vs. RHE. Incident photon to current efficiency (IPCE, Fig. S2.12, ESI<sup>†</sup>) demonstrates the device is active at wavelengths up to 900 nm (at 0 V vs. RHE), in-line with the  $E_g$  of  $\text{Sb}_2\text{Se}_3$ .<sup>6,7</sup>

Controlled potential photoelectrolysis (CPP) carried out at 0 V vs. RHE assessed the stability of the  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  electrode, results shown in Fig. 4. The  $\text{H}_2$  faradaic efficiency after 1 h was  $77.5 \pm 9.1\%$ , giving a  $\text{TON}_{\text{NiP}}$  of  $12.8 \pm 2.8$ . However, the photocurrent decreased significantly in the first hour reaching  $-40 \mu\text{A cm}^{-2}$  and by 5 hours, it decreased to only  $-15 \mu\text{A cm}^{-2}$  (Fig. S2.13, ESI<sup>†</sup>). The loss of photoactivity of **NiP** photoelectrodes has previously been attributed to the hydrolysis of the phosphonic anchoring group from the  $\text{TiO}_2$ .<sup>23,24</sup> XPS analysis of the hybrid photocathode post CPP shows the loss of the  $\text{Ni}^{2+}$  bands (red trace, Fig. 3b). However, it is clear that both the N 1s and P 2p signals are still present, although significantly shifted. A broadening of the N 1s band has previously been assigned to protonation of the amine in the acidic electrolyte<sup>23</sup> and the shifting of the P band is due to the loss of the metal centre.<sup>28</sup> The XPS results suggest the phosphonate linkage has been retained but the Ni is no longer coordinated to the ligand, in-line with the stability of the phosphonate linkage at pH < 7.<sup>29</sup> Past studies have shown that **NiP** degradation occurs on photocathodes but with a slower decay rate.<sup>23,24</sup>



**Fig. 4** CPP at 0 V vs. RHE of the hybrid photocathodes  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$  (a) and  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  (b) in  $0.1 \text{ M Na}_2\text{SO}_4$  pH 3 at  $100 \text{ mW cm}^{-2}$  and  $\lambda > 340 \text{ nm}$ .

To explore the mechanism of the hybrid photocathode decay here, we examined the  $\text{TiO}_2\text{-meso}/\text{NiP}$  interface (without  $\text{Sb}_2\text{Se}_3/\text{CdS}$ ). CPE at  $-0.24 \text{ V vs. RHE}$  (Fig. S2.7b, ESI<sup>†</sup>), shows that following an initial drop in the current in the first 600 s, the electrode maintains a stable current of  $-0.24 \text{ mA cm}^{-2}$  for 1 h suggesting that the  $\text{TiO}_2\text{-meso}/\text{NiP}$  interface is stable at this potential and capable of dealing with low current density. However, the current spikes observed with  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$  when the light is turned off in Fig. 2 are typical features of electron accumulation in the  $\text{TiO}_2$ , suggesting that the **NiP** catalyst was unable to turnover at the rate of photoelectron generation under  $100 \text{ mW cm}^{-2}$  illumination. Based on the concentration of immobilised **NiP** ( $45.76 \pm 0.81 \text{ nmol cm}^{-2}$ ), and the highest reported turnover frequency of **NiP** ( $460 \pm 5 \text{ h}^{-1}$ ),<sup>21</sup> we calculate that the **NiP** on the surface could support a photocurrent of  $-1.15 \text{ mA cm}^{-2}$ . This magnitude of photocurrent is achieved briefly in the LSV, but CPP shows the photocurrent decreases rapidly as the **NiP** catalyst degrades. To assess the photoelectron generation of  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$ , we used Pt as co-catalyst (see ESI<sup>†</sup> for synthetic details, Fig. S2.14). The  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{Pt}$  electrode achieved a stable photocurrent of  $-3 \text{ mA cm}^{-2}$  at 0 V vs. RHE for 5 hours. It is clear that the rate of photoelectron generation at the  $\text{Sb}_2\text{Se}_3/\text{CdS}$  interface greatly exceeds the maximum current density that **NiP** can sustain. The catalytic mechanism of **NiP** is shown in Fig. S2.15 (ESI<sup>†</sup>),<sup>20</sup>  $\text{H}_2$  production occurs following the  $\text{Ni}^{\text{III/I}}$  reduction. Further reduction from  $\text{Ni}^{\text{I}}$  to  $\text{Ni}^0$  can also potentially occur deactivating the catalyst if the rate of photoelectron generation is too high.<sup>30</sup> To explore if limiting the photoelectron generation on the  $\text{Sb}_2\text{Se}_3$  would be beneficial, experiments at  $20 \text{ mW cm}^{-2}$  (Fig. S2.16 and S17, ESI<sup>†</sup>) were carried out. Notably, only a small decrease in photocurrent was observed from  $1.30$  to  $0.81 \text{ mA cm}^{-2}$  at 0 V vs. RHE, and 20% of photocurrent was retained after 1800 s compared with the 11% at  $100 \text{ mW cm}^{-2}$ .

Past studies using precious metal HER catalysts like Pt on planar  $\text{TiO}_2$  coated  $\text{Sb}_2\text{Se}_3$  photocathodes have noted that



dissolution of TiO<sub>2</sub> can also occur due to photoelectron accumulation.<sup>11,13</sup> The SEM images post-CPP Sb<sub>2</sub>Se<sub>3</sub>/CdS/TiO<sub>2</sub>-*meso*/NiP electrodes (tested at 100 mW cm<sup>-2</sup>) did not show significant change in the morphology of the device (Fig. S2.18, ESI†) despite the demonstration of electron accumulation in the device. XRD analysis of a post-CPP sample only showed the typical peaks of Sb<sub>2</sub>Se<sub>3</sub> and TiO<sub>2</sub> (Fig. S2.19, ESI†) and no indication of Sb<sub>2</sub>O<sub>3</sub> formation, which has been associated with the deactivation of the Sb<sub>2</sub>Se<sub>3</sub> photoelectrodes (Fig. S2.20, ESI†).<sup>12,13</sup> However experiments where Sb<sub>2</sub>Se<sub>3</sub>/CdS/TiO<sub>2</sub>-*meso*/NiP underwent (i) LSV and CPP at 0 V vs. RHE for 1 h, (ii) removal of any remaining NiP by NaOH stripping, and (iii) Pt addition and photoelectrochemical testing showed evidence of partial failure of the sputtered TiO<sub>2</sub> layer due to photoelectron accumulation. Significantly higher dark currents (< -5 mA cm<sup>-2</sup>, Fig. S2.21, ESI†) and decreased photocurrents were measured compared to a pristine platinized photoelectrode, reinforcing the importance of preventing photoelectron accumulation in the Sb<sub>2</sub>Se<sub>3</sub>/CdS/TiO<sub>2</sub>-*meso*/NiP photocathode.

Emergent chalcogenide semiconductors such as Sb<sub>2</sub>Se<sub>3</sub> are promising photocathodes due to their ability to achieve a high rate of photoelectron generation but they suffer from thermal instability limiting processing opportunities. Furthermore, Sb<sub>2</sub>Se<sub>3</sub> interfaces need to be protected by metal oxide capping layers where corrosion could occur due to photoelectron accumulation. To prevent electron accumulation research has focused on the use of these absorbers with precious metal HER catalysts. Here we present an alternative approach using a Sb<sub>2</sub>Se<sub>3</sub>/CdS/TiO<sub>2</sub>-*meso* photocathode. The high surface area TiO<sub>2</sub> support, prepared by a UV and low temperature N<sub>2</sub> annealing process that is compatible with Sb<sub>2</sub>Se<sub>3</sub>, enables a high loading of an earth abundant molecular HER catalyst, NiP. An 81-fold increase in the photocurrent was achieved when compared to a similar device without the mesoporous TiO<sub>2</sub>. Despite the high catalyst loading, stability and activity under 100 mW cm<sup>-2</sup> is still limited by the turnover frequency of the HER catalyst. However, initial experiments under low light intensities indicate that improved stability is achievable with further advances in the catalytic turnover frequency.

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## Conflicts of interest

There are no conflicts to declare.

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