

Tailoring the Interfacial Interactions of van der Waals 1T-MoS₂/C₆₀ Heterostructures for High-Performance Hydrogen Evolution Reaction Electrocatalysis

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ABSTRACT: Fullerene-based low-dimensional (LD) heterostructures have emerged as excellent energy conversion materials. We constructed van der Waals 1T-MoS₂/C₆₀ 0D-2D heterostructures via a one-pot synthetic approach for catalytic hydrogen generation. The interfacial 1T-MoS₂-C₆₀ and C₆₀-C₆₀ interactions as well as their electrocatalytic properties were finely controlled by varying the weight percentages of the fullerenes. 1T-MoS₂ platforms provided a novel template for the formation of C₆₀ nanosheets (NSs) within a very narrow fullerene concentration range. The heterostructure domains of 1T-MoS₂ and C₆₀ NSs exhibited excellent hydrogen evolution reaction (HER) performances, with one of the lowest onset potentials and ΔG_{H^*} values for LD non-precious nanomaterials reported to date.

In the past decade, hydrogen has become a significant competitor as a stable and non-carbon energy source in the renewable energy grid.^{1,2} The conventional methods of hydrogen production are still very far from reaching the standards for energy sustainability. Thus, the development of green and clean technologies to boost the hydrogen economy is of paramount importance. In this direction, water splitting processes represent a sustainable approach to obtaining hydrogen, which has triggered the development of advanced electrolyzer technologies using different types of catalytic materials.³ Noble metals catalyze the electrochemical generation of hydrogen at ultralow overpotential values,⁴ but their high prices and scarcity are important drawbacks. Therefore, the discovery of Earth-abundant hydrogen evolution reaction (HER) catalysts with very low overpotentials is highly desirable.^{5,6}

Molybdenum disulfide (MoS₂) has been widely investigated as a promising electrocatalyst for HER.^{7,8} It has been theoretically and experimentally confirmed that the sulfur edge domains of 2H-MoS₂ nanosheets (NSs) exhibit high catalytic activities towards hydrogen electrocatalysis, while the basal planes remain largely inactive.^{9,10} Efforts to maximize the number of catalytically active sites vary from the addition of thiomolybdate nanoclusters, an artificial sub-monolayer of edge sulfur atoms, to the MoS₂ network¹¹ and the creation of S-vacancies in the basal planes,¹² to the conversion of the semiconductor 2H phase into metallic 1T phase MoS₂ NSs.^{13,14} Despite all these breakthroughs, the activation and optimization of the HER electrocatalytic activity on MoS₂ nanostructures via their hybridization with low-dimensional (LD) materials has been scarcely investigated.¹⁵ Buckminsterfullerenes constitute promising candidates to form electrocatalytic MoS₂/C₆₀ heterostructures due to their ability to

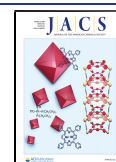
induce intermolecular charge transfer processes, thus creating highly active interfacial catalytic active sites.¹⁶

In this work, we have drastically improved the electrocatalytic HER properties of van der Waals (vdW) 1T-MoS₂/C₆₀ heterostructures by the formation of well-organized arrays of C₆₀ molecules in a very narrow fullerene concentration range. The catalytic performances of the 1T-MoS₂/C₆₀ were nicely tailored by varying the fullerene weight percentages. We have also prepared 2H-MoS₂/C₆₀ materials to compare the effect of the MoS₂ phase on the electrocatalytic performance. The modulation of the MoS₂-C₆₀ and C₆₀-C₆₀ interactions at specific ratios seems to be the driving force to form highly active HER catalysts that yielded an optimal $\Delta G_H = -0.03$ eV value, which allowed us to achieve one of the lowest onset overpotential values among LD non-precious HER nanomaterials. This is the first time, to the best of our knowledge, that the structure/catalytic function relationship of fullerene-based LD nanomaterials is reported using a framework of experimental and theoretical techniques.

vdW MoS₂/C₆₀ heterostructures were synthesized using a one-pot strategy (Figure 1a) to accomplish the non-covalent functionalization with different C₆₀ weight contents (from 5% to 95%) onto 1T- and 2H-MoS₂ NSs (see the Supporting Information for synthetic details and Figure S1). The resulting 1T-MoS₂/C₆₀ heterostructures were characterized by a multi-

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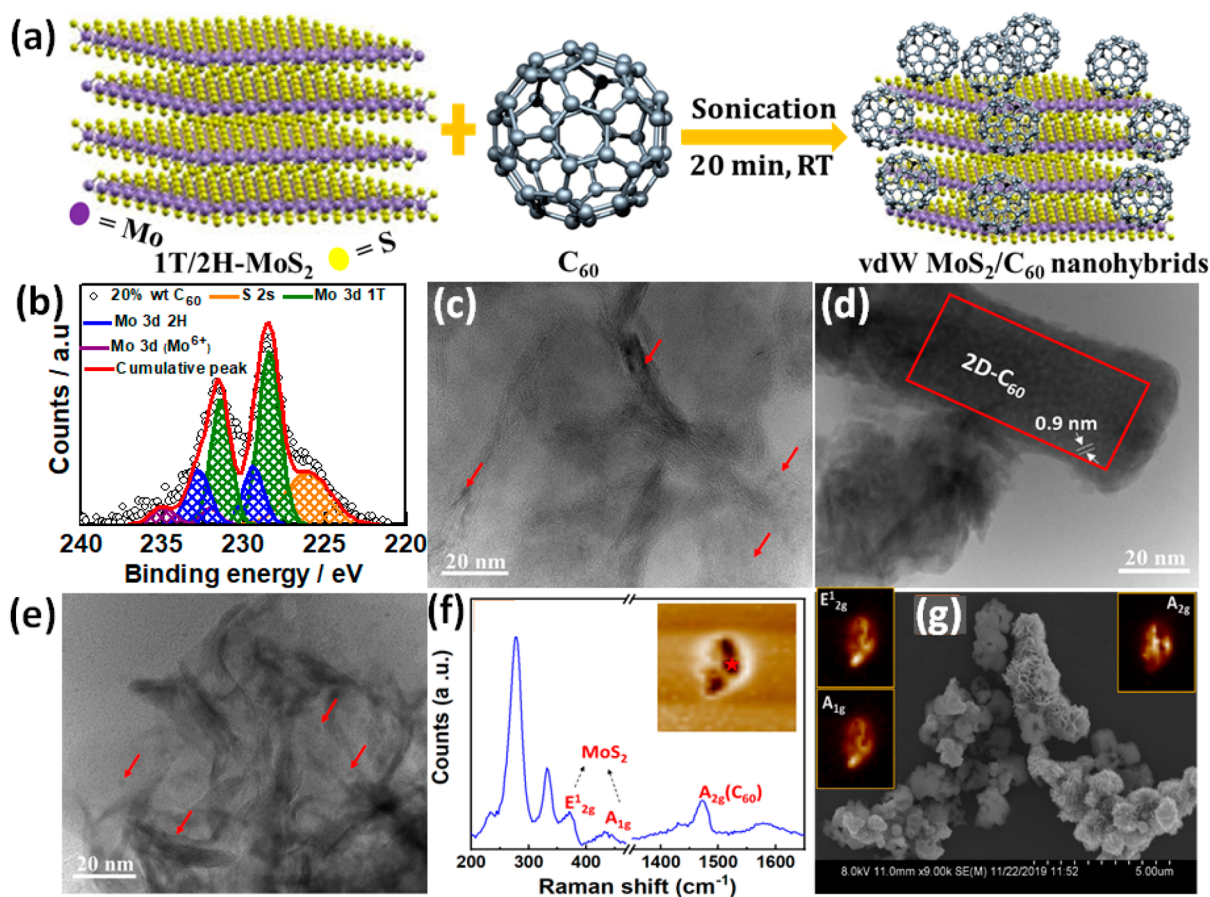


Figure 1. (a) Schematic representation of the synthesis of the MoS₂/C₆₀ heterostructure. (b) Mo 3d and S 2s XPS bands of the 1T-MoS₂/20 wt% C₆₀ heterostructure. HRTEM images of (c) 1T-MoS₂/5 wt% C₆₀, (d) 1T-MoS₂/20 wt% C₆₀, and (e) 1T-MoS₂/80 wt% C₆₀. (f) Representative Raman spectrum of a MoS₂ and C₆₀ heterostructure sample. The inset shows the 2D spectrum of the sample region from which the Raman spectrum image is recorded. (g) SEM image of the same sample region shown in the inset of (f). The insets show the 2D maps of the corresponding E_{12g}, A_{1g}, and A_{2g} modes of the MoS₂ and C₆₀ regions.

technique approach. Raman spectroscopy revealed that the typical pinch-mode band of C₆₀ at ca. 1480 cm⁻¹ as well as the two characteristic in-plane (E_{12g}) and out-of-plane (A_{1g}) Raman bands of MoS₂ nanosheets were shifted in the heterostructures (Figure S2), suggesting pronounced interfacial interactions between C₆₀ and MoS₂ layers.¹⁷ High-resolution spectra from the X-ray photoelectron spectroscopy (XPS) analysis of the Mo 3d region revealed that 1T is the main phase of the MoS₂ in the heterostructures (Figure 1b, Figure S3). The Mo 3d spectra showed features corresponding to the 3d_{5/2} and 3d_{3/2} contributions of 1T-MoS₂, located at 228 and 231.2 eV, respectively.¹⁸ High-resolution transmission electron microscopy (HRTEM) displayed unique morphological features for the materials formed from 20 wt% of C₆₀. Fullerenes adopted cluster-like or well-dispersed distributions in mostly all the MoS₂/C₆₀ ratios explored (Figure 1c,e), while they formed well-ordered 2D arrays at a specific C₆₀ weight content around 20% (Figure 1d). These findings suggest that the 1T-MoS₂ nanosheets act as templates for the nucleation and subsequent growth of fullerene 2D NSs at 20 wt% of fullerenes. The unique growth of C₆₀ NSs on 1T-MoS₂ surfaces is linked to the modulation, at specific ratios, of the MoS₂-C₆₀ and C₆₀-C₆₀ interfacial interactions, which minimize the aggregation of fullerenes, thus optimizing their two-dimensional growth to a self-assembly process on the top of the 1T-MoS₂ surfaces.¹⁹ Scanning electron microscopy (SEM) and

energy-dispersive spectroscopy (EDS) measurements have confirmed the presence of two different domains in the 20 wt% C₆₀ heterostructures (Figure S4). They are composed of C₆₀ NSs and 2D-2D 1T-MoS₂/C₆₀ NSs. The last ones most likely form MoS₂/C₆₀ NS/MoS₂ sandwich-like frameworks. This was further verified using Raman mapping experiments, which were employed to probe the vibrational modes of the different domains in the 1T-MoS₂/C₆₀ structures. A two-dimensional (2D) Raman spectrum map was recorded from a sample region that was imaged using SEM by excitation at 532 nm (Figure 1f,g). Figure 1f shows a representative Raman spectrum corresponding to the region marked in the 2D spectrum (inset). The peaks at 380 and 405 cm⁻¹ correspond to E_{12g} and A_{1g} vibrational modes of MoS₂, whereas the peak at 1460 cm⁻¹ corresponds to the A_{2g} mode or pentagonal pinch mode of C₆₀. Further, we reconstructed 2D Raman maps of E_{12g}, A_{1g} of MoS₂ and A_{2g} of C₆₀ (see Figure 1g). These images show that the A_{2g} peak intensity of C₆₀ is higher in the area where we observed C₆₀ nanosheet-like features using SEM, and the E_{12g} and A_{1g} modes of MoS₂ show higher intensities in the other parts of the heterostructure region, which correspond to the 2D-2D 1T-MoS₂/C₆₀ NS domains.

To investigate the effects of the C₆₀ adsorption patterns on the HER electrocatalytic behavior of our 1T-MoS₂/C₆₀ nanomaterials, we carried out linear sweep voltammetry (LSV) measurements in 0.5 M H₂SO₄. As a benchmark, we

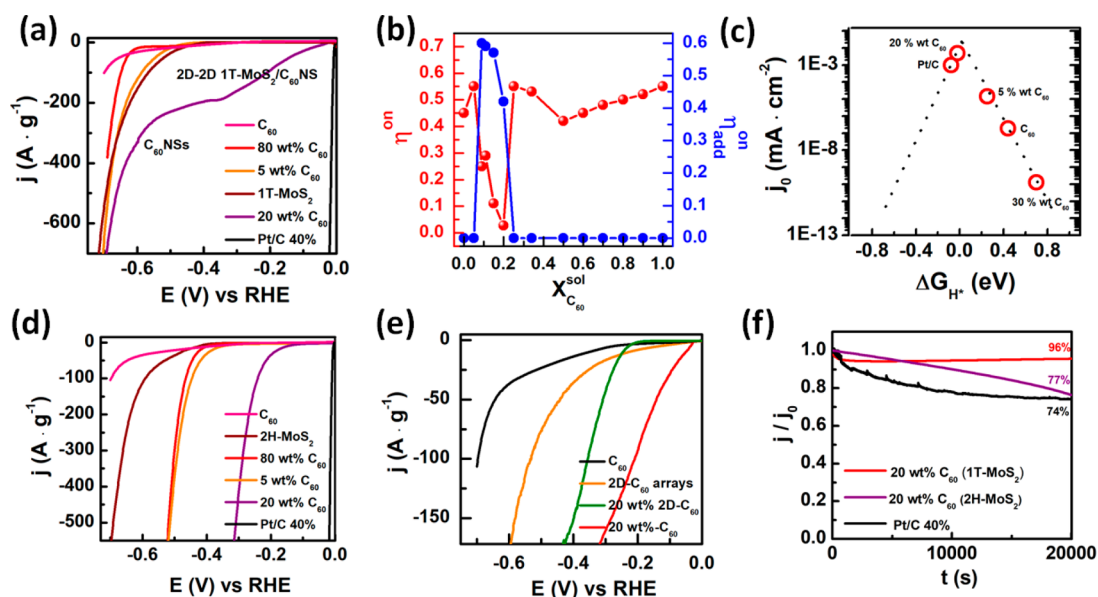


Figure 2. (a) Mass-normalized catalytic currents for C_{60} , 1T-MoS₂, commercial Pt/C 40%, and the 1T-MoS₂/C₆₀ heterostructures with 5, 20, and 80 wt% of C₆₀ at 2 mV·s⁻¹ in 0.5 M H₂SO₄. (b) HER onset overpotential values as a function of the C₆₀ volume fraction in solution. (c) Volcano plots of the as-synthesized vdW 1T-MoS₂/C₆₀. (d) Mass-normalized catalytic currents for C₆₀, 2H-MoS₂, commercial Pt/C 40%, and the 2H-MoS₂/C₆₀ heterostructures with 5, 20, and 80 wt% of C₆₀ at 2 mV·s⁻¹ in 0.5 M H₂SO₄. (e) Mass-normalized LSVs for C₆₀, C₆₀ NSs, 20 wt% 2D-C₆₀, and 20 wt% C₆₀ at 2 mV·s⁻¹ in 0.5 M H₂SO₄. (f) Chronoamperometric curves of 2H-MoS₂/20 wt% C₆₀ and 1T-MoS₂/20 wt% C₆₀ at -0.35 V vs RHE.

have also characterized the catalytic performance of commercial Pt/C, which exhibited a near-zero HER overpotential. Figure 2a,d shows the LSVs of both 1T-MoS₂/C₆₀ and 2H-MoS₂/C₆₀ heterostructures constructed using 5, 20, and 80 wt% of C₆₀, where the catalytic currents were normalized by the mass of the nano-heterostructures to obtain a deeper understanding of their intrinsic catalytic activities. The polarization curves recorded with the 1T-MoS₂/C₆₀ nanocatalytic system displayed unique electrochemical features (Figure 2a). The onset potentials of the structures were plotted as a function of the C₆₀ weight content (Figure 2b). As shown, the appearance of an additional onset potential value took place in a low range of fullerene concentrations, mostly between 8% and 20% (Figure S5). Particularly, the 20 wt% C₆₀ vdW heterostructures exhibit two well-defined catalytic waves, which, to the best of our knowledge, have not been reported for HER processes. This unusual catalytic behavior has been detected for other water-splitting reactions.²⁰ For instance, the oxygen electroreduction of laccase–AuNPs nanosystems displayed two electrocatalytic contributions, which were ascribed to the different electronic wiring properties of laccases adsorbed onto nanoparticles and glassy carbon (GC) surfaces.²⁰ It is worth noting that the first electrocatalytic process shows an ultrasmall onset potential of -0.027 V vs RHE, which is better than the catalytic activity of their individual components and is comparable with those using Pt/C (-0.004 V vs RHE) and other state-of-the-art HER catalysts (Table S1), while the second catalytic onset potential is -0.42 V vs RHE, which is also better than those of the other heterostructures. Accordingly, the 1T-MoS₂/20 wt% C₆₀ displayed two Tafel slopes (Figure S6). The smaller slope, which belongs to the first catalytic wave (57 mV·s⁻¹), is by far the value closer to that obtained with Pt/C (35 mV·s⁻¹) among all the heterostructures, demonstrating their electrokinetic efficiency. Electrochemical impedance spectroscopy

(EIS) plots further confirmed the faster electron transfer kinetics of the 1T-MoS₂/20 wt% C₆₀ heterostructures (Figure S7), which exhibited a lower charge resistance value (19 Ω). Additionally, the volcano plots revealed that 1T-MoS₂/20 wt% C₆₀ has almost the same position as Pt/C, close to the peak, indicating a Pt-like catalytic activity (Figure 2c). We have observed similar catalytic trends using 2H-MoS₂ platforms to form the heterostructures (Figure 2d). 2H-MoS₂/20 wt% C₆₀ was the heterostructure with the most effective onset overpotential value (-0.17 vs RHE). As it was revealed in the microscopic characterization, the 20 wt% C₆₀ nano-heterostructures show the presence of well-ordered fullerene nanosheets that are either forming free-MoS₂ domains or intercalated into the MoS₂ layers. To get in-depth electrocatalytic information on these interesting LD materials, the LSVs of C₆₀ NSs and C₆₀ NSs physically mixed with 1T-MoS₂ layers (20 wt% 2D-C₆₀) were obtained (Figure 2e, Figure S8). The onset overpotentials of both nanostructures are larger than the onset overpotential of the first 20 wt% C₆₀ catalytic wave, suggesting that the 2D-2D 1T-MoS₂/C₆₀ NS domains are responsible for the most efficient HER electrocatalysis. Also, the onset potentials of the as-synthesized C₆₀ NSs (-0.36 V vs RHE) and the second electrocatalytic wave are very similar, which indicates that the lower catalytic efficiency occurs at the C₆₀ NS domains. These findings can be understood on the basis of (i) the interconnected conductive 2D-2D 1T-MoS₂/C₆₀ NS network, which promotes faster electron transfer rates from the glassy carbon electrodes to the catalytically active sites, confirmed by the lower R_{CT} , and (ii) its optimal interfacial interactions that decrease the uphill energy states of each catalytic step, thus improving the HER performance. The 1T-MoS₂/20 wt% C₆₀ structures delivered excellent stability, keeping 96% of the initial current density after 20 000 s, thus surpassing the stability of Pt/C (Figure 2f).

To further understand the catalytic performance of the 1T-MoS₂/C₆₀ nanostructures and unravel the origin of the excellent catalytic activity of the 2D-2D 1T-MoS₂/C₆₀ NS domains, density functional theory (DFT) calculations (see Supporting Information for computational details) were performed. Different C₆₀ weight percentages (5%, 20%, and 30%) were added onto 1T-MoS₂ surfaces (Figure 3a, Figure

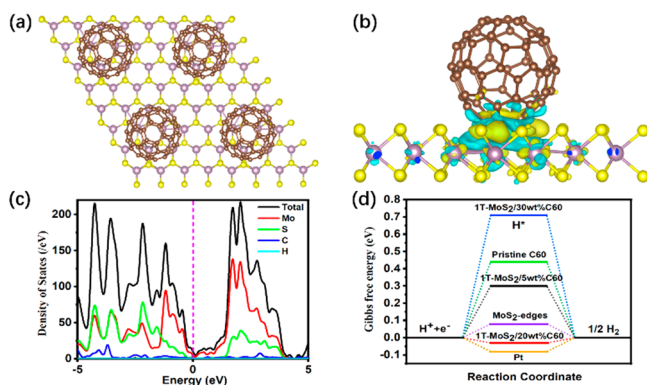


Figure 3. (a) Top view of the optimized model and (b) the calculated charge density difference for the 1T-MoS₂/C₆₀ heterostructures. (c) Total electronic density of states for 2D-2D domains of the MoS₂/20 wt% C₆₀ heterostructure (pink dashed line represents the Fermi level). (d) Calculated HER free energy diagrams. Color code in (a) and (b): S, yellow; Mo, light violet; C, brown.

S9) to simulate the 1T-MoS₂/C₆₀ interfaces. First, the HER active sites of the 1T-MoS₂/C₆₀ nanostructures were identified by calculating the binding energies of the adsorbed hydrogen at different sites. The binding strength of the hydrogen on top of the C₆₀ (0.74 eV) and on the in-plane MoS₂ (1.81 eV) were very weak, which leads to low kinetics for H* generation. On the other hand, the C atoms located at the 1T-MoS₂/C₆₀ interfaces exhibited moderate binding energy values (−0.33 eV), indicating that they are the active catalytic sites for the HER process, as is stated by the Sabatier principle.²¹ Second, the charge density differences of the 1T-MoS₂/C₆₀ nanostructures were calculated (Figure 3b). The results suggest that the charge transfer process mainly takes place from the C atoms at the interface of the composite to the in-plane MoS₂, which is in good agreement with previous reports.^{17,22} Such charge transfer could also polarize the Mo–S bonds, which decreases the enthalpy for hydrogen adsorption, thus giving rise to active HER sites at the 1T-MoS₂/C₆₀ interfaces.²² Importantly, the density of states of the 2D-2D 1T-MoS₂/C₆₀ NS domain was analyzed (Figure 3c). It showed that the electronic states of C atoms are overlapped with those of the Mo and S atoms, implying effective interfacial interactions between the C₆₀ and MoS₂. Based on these facts, we believe that the 1T-MoS₂/C₆₀ interfacial interactions are mainly based on both vdW and weak covalent interactions. The large number of electronic states close to the Fermi level indicates high electroconductivity and carrier density at the 1T-MoS₂/C₆₀ NS interfaces, which strongly supports our experimental results. Figure 3d displays the ΔG_{H^*} values for the heterostructures with 5%, 20%, and 30% of C₆₀ as well as the pristine C₆₀ and the MoS₂ edges. As is well known, the ideal HER catalyst requires a value of ΔG_{H^*} close to zero.^{23,24} It is clear that the 2D-2D 1T-MoS₂/C₆₀ NS structure ($\Delta G_{H^*} = -0.03$ eV) exhibits the best HER catalytic activity, outperforming both pristine C₆₀ ($\Delta G_{H^*} = 0.44$ eV) and MoS₂ edges ($\Delta G_{H^*} = 0.08$

eV) as well as the other two heterostructures, placing it among the five best-performing HER catalysts (Table S2). This is attributed to the moderate interfacial interactions between the C₆₀ and MoS₂, which lead to optimal binding strengths of H atoms on the active sites.

In summary, we have demonstrated that the structural and catalytic properties of 1T-MoS₂/C₆₀ heterostructures can be tuned at the nanoscale level by changing the C₆₀ weight contents via a simple synthetic strategy. 1T-MoS₂/C₆₀ materials with 20 wt% C₆₀ showed different fullerene arrangements, which were directly connected to the two catalytic HER waves. The 2D-2D 1T-MoS₂/C₆₀ NSs domains exhibited impressive catalytic performances, rendering Pt-like onset potentials and ultralow ΔG_{H^*} values. This work provides in-depth insights into the rational design of highly active non-precious 0D-2D catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c08867>.

Synthetic strategy details; structural characterization of the MoS₂ nanoplateforms; Raman and XPS spectra of the heterostructures; LSVs of 1T-MoS₂/C₆₀ with different fullerene weight contents; Tafel plots; Nyquist plots for the 1T-MoS₂/C₆₀ heterostructures; SEM of C₆₀ NSs; computational details (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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