单分子层保护纳米 Au 粒子表面配位催化剂的制备及其应用

贾丽凤, 何 涛, 李志鹏, 李雪梅

南京工业大学材料化学工程国家重点实验室, 江苏南京 210009

摘要: 贵金属纳米粒子由于其小尺寸效应而表现出特殊的催化性能. 综述了纳米 Au 粒子表面配位催化剂的制备方法及其在催化中的应用. 由于 Au 可与硫化物形成配位键, 所以硫化物可在 Au 表面形成有序单分子膜. 单分子膜保护的 Au 纳米粒子具有非常好的溶解性、分散性、稳定性, 以及由不同的表面功能团而导致的不同的催化性能. 该催化体系兼具均相催化剂和多相催化剂的特点, 这对开发新型催化剂具有重要的理论和实际意义.

关键词: Au 纳米粒子; 配位催化; 多相催化; 表面络合催化剂

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Monolayer-Protected Gold Nanoparticle Surface-Bound Catalysts: Preparation and Application

JIA Lifeng, HE Tao*, LI Zhipeng, LI Xue-Mei*

State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, Jiangsu, China

Abstract: Precious metal nanomaterials have shown significantly different reactivity and catalytic activity because of their small-size effects. In this report, we focused on gold nanoparticle-based catalysts, especially gold nanoparticle surface-bound catalysts, their preparation and application. Because of its special surface properties, gold can form stable bonds with sulfur containing molecules including sulfides and thiols. These molecules form well ordered self-assembled monolayers on gold nanoparticles, which render monolayer-protected gold nanoparticles (MPGs) with good solubility, easy characterization, extraordinary stability, and versatility. With attached functional groups, we used MPGs as surface-bound catalysts. These catalysts show the combined characteristics of a homogeneous and a heterogeneous catalyst, which is critical for theoretical aspects and in the development of new types of surface-bound catalysts.

Key words: gold nanoparticle; coordination catalysis; heterogeneous catalysis; surface-bound catalyst

单分子层保护的 Au 纳米粒子 (MPGs) 是一个跨学科的研究领域^[1~3]. 由于硫醇可以和 Au 配位形成稳定的金硫键^[4], 所以表面包覆单分子层的纳米粒子不仅表现出很好的分散性, 而且具有溶剂溶解性^[5]. MPGs 具有纳米粒子的小尺寸效应, 特别是量子效应^[6]和表面效应. 表面效应的最直接体现是 MPGs 表面功能团决定了它的溶解性^[7]、反应活性^[2,8~10]、生物相容性^[11,12]和催化性能^[2]. 此处催化性能并非源自 Au 纳米粒子, 而是其表面因接枝具有催

化作用的功能团而获得的表面配位催化体系. 该催化体系不仅催化效率高, 而且兼具络合催化剂和多相催化剂的特点. 即纳米粒子具有溶解性, 可以均匀地分散在反应体系中, 类似于络合催化过程; 同时也可通过沉淀或离心得以分离, 所以又具有多相催化剂的特点. 因此, 研究制备具有催化活性的 MPGs 具有特定的意义. 由于是新兴领域, 相关报道较少, 本文主要结合作者的一些工作, 对 Au 纳米粒子表面配位催化剂的制备及其在催化中的应用进行总结.

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联系人: 李雪梅. Tel/Fax: (025)83587775; E-mail: xuemeili@njut.edu.cn

何 涛. E-mail: taohe@njut.edu.cn

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1 MPGs 的制备及表面功能团的引入

1.1 MPGs 的制备

Au 纳米粒子具有较高的表面能, 易团聚, 因此分散性好、粒径单一的 Au 纳米粒子的制备成为挑战. Schmid 等^[3,13,14]首次合成了配体保护的 Au 纳米团簇 $\text{Au}_{55}[\text{PPh}_3]_{12}\text{Cl}_6$. 该粒子粒径为 1.4 nm, 具有双层结构, 内层为 55 个金原子, 外层为 12 个氯原子和 6 个三苯基磷. 该纳米团簇粒径均一, 稳定性好, 但制备过程复杂. Brust 等^[5]利用相转移试剂四辛基溴化铵将水溶性的四氯金酸根 (AuCl_4^-) 与四辛基铵根 ($\text{N}(\text{C}_8\text{H}_{17})_4^+$) 络合成油溶性物质而被萃取到甲苯中. 在十二烷基硫醇中, 以 NaBH_4 为还原剂在甲苯和水的界面制备了十二烷基硫醇保护的 MPGs (见图式 1). 该制备方法简易, 重复性好, 具有实际应用价值.

1.2 MPGs 表面功能团的引入

Brust 法又称两相法, 制得的样品多为油溶性物质, 其溶解性取决于表面的功能团. 表征 MPGs 的方

法也较为广泛, 如核磁共振^[5]、红外^[15]、紫外、甚至质谱^[7,16]都可以使用. 另外, MPGs 体系表现出量子效应^[17]、小尺寸效应和表面效应. 表面效应表现为纳米粒子表面功能团决定了它的溶解性和催化性能. 现已有 $\text{C}_3\sim\text{C}_{24}$ 烷基硫醇^[1]、二烷基二硫化物^[18]、树枝型分子^[19~21]、硫醇化的聚乙二醇 (PEG)^[22,23]、酰胺类^[24]和羰基铁^[25]等被用于制备 MPGs. 另外, 微流体法^[26]、微波法^[27]、电化学法^[28]、柠檬酸钠、琥珀酸^[29]还原法等也用于 Au 纳米粒子的制备. 目前合成 Au 纳米粒子的技术已相当成熟, 但如何控制纳米粒子的单分散性和接枝理想保护基团仍是 Au 纳米粒子研究的主要难点^[30].

同硫醇相比, 硫醚与 Au 的结合力较弱, 但化学稳定性较高; 而且当一个分子中含有多个硫醚配体时, 该分子与 Au 的结合力较强, 因而也可形成稳定的单分子层, 如杯芳烃和环糊精等^[31~33]. Li 等^[34]首次以硫醚为保护基团制备了 Au 纳米粒子, 所用硫醚分子式如图式 2 所示. 该系列硫醚分子所含的硫醚

图式 1 Brust 法合成单分子层保护的 Au 纳米粒子

Scheme 1. Brust's synthesis of monolayer-protected gold nanoclusters (MPGs)^[5].

图式 2 用于 MPGs 制备的硫醚分子

Scheme 2. Molecular structure of the thioethers used for MPG formation^[34].

配体的数量从 1 到 4 不等,并且端基的功能团也不相同. 研究表明,对只有一个硫醚功能团的分子而言,链长越长,所获得的 MPGs 稳定性越好;链上的功能团越复杂,稳定性越差. 另外,功能团数量和硫醚头部配体大小匹配程度决定了粒子的稳定性. 相对而言,该体系纳米粒子的稳定性较差,但 Hasan 等^[35]利用该体系中 Au 与硫醚相对较弱的结合力而以硫醇取代硫醚进行配位基交换,并采用核磁共振对该交换过程进行了追踪. 这为确定硫醇与 Au 结合过程硫氢键的存在方式提供了非常有力的证据.

将不同功能团引入到纳米粒子表面是制备纳米粒子表面配位催化体系的关键. 为将配体引入到纳米粒子表面,该配体必须具有硫醇功能团. 硫可与很多过渡金属形成配位化合物,而过渡金属是催化剂的主要组分,因此在 Au 纳米粒子表面引入配体的工作是一种挑战. 其中代表性的工作是 Hostetler 置换法^[9]和混合功能团法^[36].

Hostetler 置换法主要从 Brust 法合成的纳米粒子出发,在溶剂中将 MPGs 与具有理想功能团的硫

醇进行置换,从而制得具有混合功能团的纳米粒子. 该法的优点是可选择硫醇范围广.

虽然置换法可以获得具有不同功能团的粒子,但是影响因素较多,如已包覆基团的空间位阻、氢键、交换过程的离子强度、溶液的 pH 等,并且较难控制置换度;所以 Friggeri 等^[36]采用了混合功能团法,以目标摩尔比来投入混合硫醇,利用 Brust 法一步制备了癸基硫醇与 11-羟基十一烷基硫醇混合基团保护的 MPGs. 该方法简单有效. 另外,进一步利用表面羟基上的酯化反应,将三苯基磷接枝到纳米粒子表面,得到三苯基磷改性的纳米粒子(见图式 3),该粒子进一步反应可制得 Grubbs 催化剂,但目前尚未见有关催化性能方面的报道.

2 MPGs-表面配位络合催化剂的制备及应用

Bartz 等^[38]以末端为己二烯功能团的硫醇为单一配体来制备 MPGs,然后通过 RuCl_3 与己二烯基团配位,制得的样品结构与 Grubbs 催化剂类似的结构

图式 3 癸基硫醇、11-羟基十一烷基硫醇混合配体保护的 MPGs 的制备及表面酯化过程

Scheme 3. Use of a decanethiol and 11-hydroxyundecanethiol mixture as ligands for the preparation of MPGs and coupling to 4-(diphenylphosphino)benzoic acid^[36,37].

(见图式 4). 这种负载于 Au 纳米粒子表面的催化剂可催化降冰片烯交互置换开环聚合反应. 因为 MPGs 表面上催化剂的取向性有利于单体的相互作用和聚合物链的增长, 所以该 Au 纳米粒子表面配位催化剂活性是同类均相催化剂的 5 倍. 在催化反应中, 纳米粒子体系均匀分散于反应体系中, 表现出均相催化剂的特点; 反应结束后, 通过改变溶剂, 可将催化剂沉降回收, 又表现出多相催化剂的特点. 这充分体现了 Au 纳米粒子表面配位催化剂的优点.

基于配位基置换法, Li 等^[39]将一种用于制备手

性邻二醇的催化剂连接到了 Au 纳米粒子上, 并用于芳香不饱和烯烃的二元醇化反应 (见图式 5). 由于反应在水溶液中进行, 无需严格除氧和除水. 另外, 该表面催化剂性能与负载于聚合物的同样催化剂相似. 值得指出的是, 该催化体系并非基于过渡金属.

Belser 等^[40]制备了基于过渡金属 Co(III) 的可催化环氧树脂不对称水解的表面配位催化剂 (见图式 6). 通过功能团置换法将手性 Salen 硫醇化合物接到 MPGs 上, 进一步与乙酸亚钴 (II) 反应, 制得具有催化活性的、基于 MPGs 的 Salen 配位 Co(III) 催化体系.

图式 4 用于烯烃置换开环聚合反应的 Au 纳米粒子表面附载催化剂

Scheme 4. Gold nanoparticle surface-bound catalyst for olefin metathesis polymerization: the ligand used for colloid preparation, the homogeneous catalyst, and the surface-bound catalyst^[38].

图式 5 基于 MPGs 的络合催化剂及其在烯烃不对称双羟化反应中的应用

Scheme 5. Gold nanoparticle surface-bound catalyst and its application in the dihydroxylation of aromatic olefins^[39].

图式 6 基于 MPG 可催化环氧基团不对称水解的含 Co(III) 的催化剂

Scheme 6. Synthesis of a Co(III) containing MPG-based catalyst for the asymmetric hydrolysis of epoxy functional groups^[40].

结果表明,当催化剂加入量为 0.01 mol% 时,反应 5 h 即可获得高于 99.9% ee 的动力学拆分效果,而对于非表面络合催化剂,为达到类似结果,在催化剂投入量为 0.1 mol% 的情况下,需反应 24 h. 可见,该催化体系的性能优于非表面络合催化剂,且催化剂回收容易.

由于 Brust 法采用相转移试剂,所以不能用于制备水溶性纳米粒子. 另外,从相转移试剂分离出产品也很费时. 因此,改变纳米粒子的制备方法尤为重要. 磺酸基保护的 MPG 的制备方法改变了必须用两相法制备 Au 纳米粒子的传统. 特别是该纳米粒子表现出非常好的催化性能,因此具备特别的意义^[41]. 将带有磺酸钠保护的 MPG 通过离子交换可以得到磺酸 (MBS-H⁺) 修饰的单分子层保护的 Au 纳米粒子,可用于催化溶液中三甲基硅醚 (TMS) 的水解 (见图式 7). 该催化剂具有均相催化剂的特性,可溶于极性溶剂如甲醇;也可以用作多相催化剂,通过微接触印刷技术,作为油墨印刷到 TMS 单分子层上,实现选择性催化水解,在 TMS 单分子层表面制备出具有不同功能团区域的表面^[31,41]. 由于 Au 纳米粒子粒径与原子力探针针尖具有近似的几何尺寸,因而它为开

发催化探针技术提供了易于表征的模型催化体系 (见图式 8)^[42].

3 结语

总结了近年来新兴的基于单分子层保护的 Au 纳米粒子表面配位催化剂的发展状况. 由于 Au 纳米粒子的小尺寸效应和表面效应,该催化剂既表现出络合催化剂的特性,如溶解性、高效性,又表现了多相催化剂的可回收性. 该催化体系中参与催化过程的不是 Au 纳米粒子,而是粒子表面功能团. 另外,由于 Au 纳米粒子比表面积高,同时可能由于表面络合催化剂与 Au 粒子的相互作用而产生的协同效应,该类催化剂的活性远高于一般络合催化剂. 另一方面, Au 纳米粒子表面配位催化剂也可以作为新型模型化合物,研究不同催化剂的催化特性,特别是用来研究一些特殊反应的催化动力学,这将促进新型催化剂的开发. 然而,目前有关这类催化剂的研究还不多,面临的主要问题是单分散的 Au 纳米粒子的制备,以及如何在粒子表面引入不同的配体. 这些问题的解决有利于制备出更多高效的表面配位催化剂,提高催化反应效率,并使配位催化剂再生成为可能.

图式 7 磺酸基保护的 Au 纳米粒子的制备及其催化水解 TMS 反应

Scheme 7. Preparation of a sulfonic acid functionalized gold nanoparticle and its application in the hydrolysis of TMS silyl ether^[41].

图式 8 MBS-H⁺改性催化探针技术用于表面制作

Scheme 8. Schematic illustration of the use of a catalytic probe nanolithography (CPL) process based on MBS-H⁺ modified gold coated atomic force microscope tip pattern creation on a self-assembled monolayer on gold^[42].

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英 译 文

English Text

The preparation and application of monolayer-protected gold nanoparticles (MPGs) is a novel interdisciplinary area [1–3]. Because of the very strong gold-sulfur interaction [4], gold nanoparticles are very stable after coated with thiols by the formation of self-assembled monolayers (SAM), which render the MPGs with good dispersibility and solubility in a certain solvent [5]. Because of their nanometer size, MPGs show small size effects, especially quantized size effects [6] and surface effects. The surface effects are expressed by that surface functional groups determine their solubility [7], reactivity [2,8–10], biocompatibility [11,12], and catalytic activity [2]. It is noteworthy that the catalytic activities are mainly because of the surface-bound catalytically active functional groups. Owing to the high surface-to-volume ratio of the nanoparticles, these colloid-bound catalysts exhibit higher catalytic efficiency than their homogeneous counterparts. Moreover, these surface-bound catalysts show the characteristics of both homogeneous catalysts and heterogeneous catalysts. Specifically, the surface-bound catalysts can be well dispersed in a solvent just like a homogeneous catalyst but can also be recovered by precipitation and centrifugation. Therefore, the preparation and application of these catalysts are an interesting subject. Because there have been limited reviews in this area, we summarize previous work and recent progress with a special focus on nanoparticle preparation, surface functionalization, and application in catalysis in this report.

1 Preparation of MPGs and introduction of functional ligands to MPGs

1.1 Preparation of MPGs

Gold nanoparticles tend to aggregate due to their high surface energy. It has been a challenge to prepare gold nanoparticles with good dispersibility and uniform size until Schmid reported in 1981 for the first time a type of ligand-protected gold nanocluster, $\text{Au}_{55}[\text{PPh}_3]_{12}\text{Cl}_6$ [3,13,14]. This gold nanocluster has a double-layer structure with a gold core consisting of 55 gold atoms and an outer layer of 12 chlorine and 6 triphenylphosphine ligands. This ligand-protected gold cluster is uniform in size and is chemically very stable, but its preparation involves typical organometallic synthesis. In 1998, Brust et al. [5] reported a two phase preparation of monolayer protected gold nanoparticles (Scheme 1). This process involves the use of a phase transfer reagent tetraoctylammonia bromide to transfer the tetrachloroaurate ligand from water into toluene, which is then reduced by NaBH_4 in the presence of dodecane thiol. Although the resulting MPGs are not as uniform in size as those of Schmid, particles of various sizes ranging from 1.5 to 20 nm were prepared according to this method.

1.2 Introduction of functional ligands to MPGs

Brust's method is a two-phase method, and most products are lipophilic with the outer functional groups determining the final solubility and reactivity of the MPGs. Moreover, because of their small size, these MPGs can be characterized just like common chemical compounds. Many characterization methods are applicable including NMR [5], infrared spectroscopy [15], ultraviolet spectroscopy, and mass spectrometry [7,16]. Moreover, MPGs show quantized effects [17], small size effects, and surface effects. Surface effects are of special relevance because the surface functional groups determine their solubility, reactivity, and even catalytic activity. Based on Brust's method, a wide variety of thiols with chain lengths of C_3 – C_{24} [1], dialkyldisulfides [18], dendrimers [19–21], and thiolated polyethylene glycol (PEG) [22,23] have been used as coating ligands for MPG preparation. There have also been reports on the use of other ligands including amides [24] and iron carbonyls [25]. Other methods for the preparation of MPGs include microfluidic [26], microwave [27], and electrochemical methods [28]. Gold nanoparticles, however, are usually prepared by citrate or succinic acid reduction [29]. Currently, the preparation methods are rather versatile but the control of monodispersity and the attachment of desired functional groups are still major challenges [30].

Compared with thiols, thioether interacts less strongly

with gold but it is chemically more stable. Moreover, when multiple attachment points exist in a molecule, for example, the presence of many thioether end groups, a well-ordered SAM can still be formed on gold, for example, the thioether derivatives of calix arene and β -cyclodextrin [31–33]. In 2001, Li et al. [34] reported the use of thioethers as protecting ligands for MPGs. The molecular structures of the series of thioethers used are shown in Scheme 2 with 1–4 thioether ligands and different head functional groups. Results show that compared to thiols, thioethers also yield gold nanoparticles but with shorter time stability. The combination of rigid headgroups and multiple attachment points afford gold nanoparticles with comparable stability to thiolated MPGs. Hasan et al. [35] made use of this weak gold thioether interaction to study the ligand exchange process of a thioether with dodecanethiol and monitored the exchange by ^1H NMR, which provided a powerful proof of the fate of hydrogen in RS-H during the SAM formation process on gold.

The introduction of functional groups, especially catalytically active functional groups, is critical in the preparation of a surface-bound catalyst. A prerequisite for the ligand is that it must have a thiol moiety. It is well known that sulfur can form a complex with many transition metals that constitute the major components of catalysts. Therefore, it has been a challenge to introduce a complex catalyst to a gold nanoparticle surface. Two representative methods have been developed to introduce functional groups to MPGs: place-exchange as developed by Hostettler et al. [9] and mixed ligands as developed by Friggeri et al. [36].

In a typical place-exchange approach, MPGs capped with an alkanethiol prepared using Brust's method are placed in a solvent containing the desired functional thiol. During the exchange process, the surface thiolate desorbs and makes place for the thiol in solution, which then adsorbs onto the gold nanoparticle surface. The advantage of this process is that a broad range of end functional groups are available.

Although many end-functional groups can be introduced to the surface of gold, this method suffers from difficulties in controlling the degree of exchange. Moreover, the steric hindrance of bulky groups, hydrogen bonding, ionic strength of the exchange solution, and pH of the solution affect the exchange process. Irreversible aggregation can also result in some cases. In the mixed ligand approach, Friggeri et al. [36] used the desired molar ratio of the initial mixture of thiols to prepare MPGs. Decanethiol and mercapto-11-undecanethiol were used in a 4:1 ratio to prepare MPGs providing a simple method to obtain MPGs with mixed functional groups. Moreover, analysis demonstrated that the final product had the same molar ratio of ligands as the initial ratio. By further esterification of the hydroxyl end groups with 4-(diphenylphosphino)benzoic acid, triphenylphosphine functionalized MPGs were obtained, which might be useful for the prepa-

ration of a surface-bound Grubbs type of catalyst (Scheme 3).

2 Preparation of MPG surface-bound catalysts and their application

Bartz et al. [38] reported the first preparation and catalytic activity of an MPG surface-bound catalyst for the ring-opening metathesis polymerization of norbornene. Bartz et al. used the thiol derivative of hexadiene as a protecting ligand for gold nanoparticles, which were then reacted with RuCl_3 to form a hexadiene-Ru complex, similar to the well known metathesis catalyst (Scheme 4). They found that the surface-bound catalyst catalyzed the ring-opening polymerization of norbornene with much higher catalytic efficiency. They suggested that the orientation of the catalyst on the surface facilitates its interaction with the monomer and the growth of the polymer chain. It is noteworthy that in the catalytic process, the MPGs were well dispersed in the reaction mixture and they showed the characteristics of a homogeneous catalyst. After the completion of the reaction, the MPGs were recovered by precipitation, which is typical of a heterogeneous catalyst. The results of Bartz et al. are very interesting but the preparation of the surface-bound catalyst requires organometallic chemistry, which limits its accessibility. Nevertheless, it has been demonstrated that these surface bound catalysts show the combined characteristics of both a homogeneous catalyst and a heterogeneous catalyst.

Based on a place-exchange reaction, Li et al. [39] attached a dihydroxylation catalyst, which showed reactivity in the dihydroxylation of aromatic olefins to yield chiral diols (Scheme 5). The catalytic reaction was carried out in an aqueous mixed solvent, where no exclusion of air or water was needed. Moreover, the catalytic reactivity of this surface-bound catalyst is similar to the polymer supported alkaloid ligands.

Belser et al. [40] prepared a MPG surface-bound catalyst for the asymmetric hydrolysis of epoxy functional groups based on Co(III) (Scheme 6) also by a place-exchange approach. A thiol derivative of chiral salen was attached to a gold nanoparticle by place-exchange, which was then reacted with Co(II) acetate. After oxidation, a catalytically active system was formed on the MPGs surface. Catalytic reaction tests showed that at a load of 0.01 mol%, a higher than 99.9% ee kinetic resolution was achieved over a reaction time of 5 h. For the catalyst without surface-attachment similar results

could only be obtained for 0.1 mol% catalyst loading and a reaction time of 24 h. Apparently, the catalytic reactivity of the surface-bound catalyst is much better than the unbound catalyst with advantages of easy regeneration and recovery.

In the Brust approach to prepare MPGs, a phase transfer reagent was used to transfer the aurate to the organic phase and the final product was lipophilic. Moreover, the phase transfer reagent needs to be removed to yield a pure product. On the other hand, this method is not suitable for the preparation of water-soluble gold nanoparticles. In 2004, Li et al. [41] reported the preparation of water-soluble, sulfonated MPGs in a one-step approach. Moreover, these particles showed reasonable catalytic reactivity. The MPGs were prepared by reduction of tetrachloroauric acid in the presence of 5-mercapto-2-benzimidazole sulfonate sodium salt (MBS) in water. Sulfonic acid functionalized gold nanoparticles were obtained by ion exchange using a Dowex- H^+ ion exchanger. The sulfonic acid functionalized gold nanoparticles catalyzed the hydrolysis of trimethylsilylether (TMS) adsorbate in solution (Scheme 7). The MPGs were further applied as ink in a microcontact printing process, which catalyzed the hydrolysis of the TMS SAM selectively in the area of contact yielding patterned surfaces of different functional groups [31,41]. Because gold nanoparticles have a similar geometric size as the tip of an atomic force microscope, these MPGs provided a powerful and easily monitored model system for later catalytic probe nanolithography during nanofabrication (Scheme 8) [42].

3 Conclusions

We summarize recent developments in surface-bound catalysts based-on monolayer protected gold nanoparticles. Because of their small size effects and surface effects, MPG surface-bound catalysts show characteristics of both a homogeneous catalyst and a heterogeneous catalyst. Because of their high surface-to-volume ratio and possibly the cooperative effects of the gold nanoparticles, these catalysts show significantly higher catalytic efficiency than their homogeneous counterparts. These catalysts can also be used as model systems to study the kinetics of a certain reaction, which may help in the development of new catalysts.

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