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GREEN SYNTHESES AND CHARACTERIZATION OF ZINC OXIDE AND CERIUM ION DOPED ZINC OXIDE NANOPARTICLES ASSISTED BY *MANGIFERA INDICA*

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ABSTRACT

Green synthesis of zinc oxide nanoparticles and Ce ion doped ZnO nanoparticles were carried out using the leaf extract of *Mangifera Indica* (mango leaves). The UV-Vis spectrum 4.5eV for undoped ZnO, 4.0eV for 1% Ce: ZnO, 3.9eV for 2% Ce: ZnO, 4.0eV for 3% Ce: ZnO, 5.4eV nanoparticles. XRD behavior exhibits the size of doped and undoped ZnO nanoparticles. The crystallite size was found to 58.65 nm for ZnO nanoparticles and 49.98 nm for Ce ion doped ZnO nanoparticles. TEM micrographs also confirmed the particle size of the doped and undoped samples are in the nanoscale range and the size of the undoped ZnO and Ce ion doped ZnO nanoparticles were found to be 100 nm respectively. Green synthesis using *Magnifera Indica* found to be the best capping agent for synthesizing nanoparticles.

KEYWORDS: Green synthesis, Zinc oxide nanoparticles, Ce ion doped ZnO nanoparticles, *Magnifera Indica*, UV-Vis, XRD, TEM.

1. INTRODUCTION

Zinc oxide is a widely used semiconductor found in our daily lives. From its uses in the rubber and concrete industries to food additives, pigments and UV blockers, ZnO is exploited for its optical and physical properties. ZnO has a wide direct band gap (Eg ~3.37 eV at 300 K) and an exciton binding energy of 60 meV. This wide band gap allows devices to operate at higher temperatures and brings the electronic transition energy into the energy range of visible light creating light emitting devices in the visible spectrum.[1] ZnO is a biofriendly oxide semiconductor and an inexpensive luminescent material. It has attracted intensive research efforts for its unique properties and versatile applications in antireflection coatings, transparent electrodes in solar cells, ultraviolet (UV) light emitters, diode lasers, varistors, piezoelectric devices, spin-electronics, surface acoustic wave propagator, antibacterial agent[2], photonic material[3] and for gas sensing. In general, ZnO is considered “generally recognized as safe” (GRAS)[4] but ZnO nanoparticle system may be toxic. Among all the inorganic semiconducting nanoparticles, zinc oxide nanoparticles have attracted increasing attention because ZnO nanoparticles can be easily synthesized and ZnO is a “green” material that is biocompatible, biodegradable, and nontoxic for medical applications and environmental science. Recently, there are several physical or chemical synthetic methods of preparing ZnO, such as thermal evaporation[5], pulsed laser deposition (PLD)[6], ion implantation[7], reactive electron beam evaporation[8], thermal decomposition[9] and sol–gel technique.[10] Due to their excellent optical and electrical properties, ZnO nanoparticles have become predominant semiconductor materials for nanoscale devices, such as nano-generators, gas sensors, highly efficient solar cells, field-emission transistors, ultra violet photo detectors, and biomedical systems ZnO is attracting considerable attention for its possible application to UV light emitters, spin functional devices, gas sensors, transparent electronics and surface acoustic wave devices.[11]

Ceria (CeO_2) is the most widely used compound of cerium. The main application of ceria is as a polishing compound, e.g. chemical-mechanical planarization (CMP). In this application, ceria dioxide has replaced other metal oxides for the production of high quality optical surfaces.[12] Green synthesis techniques make use of moderately pollutant free chemicals to synthesis nanomaterials and embrace the use of benign solvents such as water, natural extracts. Green chemistry seeks to reduce pollution at source.[13,14] It is enhanced to prevent waste than to treat or clean up waste after it is formed. This principle focuses on choosing reagents that facade the least risk and generate only benevolent by products. Though physical and chemical methods are trendier for nanoparticles synthesis, the biogenic fabrication is a better choice due to eco-friendliness.[15,16] Metabolites, proteins[17] and chlorophyll present in the plant extracts were found to be acting as capping agents. Our present study focused on the preparation of ZnO nanoparticles and Ce ion doped ZnO nanoparticles by green syntheses using cost- effective, ecofriendly *Mangifera Indica* leaf extracts as reductant and stabilizing agent. The prepared nanoparticles were characterized using UV-Vis spectrometer, XRD (X-Ray diffraction) analysis, and TEM (Transmission Electron microscopy).

2. MATERIALS AND METHODS

All the chemicals and reagents used in this study were of analytical grade. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99.9%) and Cerium nitrate ($Ce(NO_3)_3$) obtained from Himedia Chemicals were used as received without further purification. Ultra-pure deionized water was used throughout the experiments. The leaves of *Mangifera Indica* used in the present study were procured from the surroundings of Thoothukudi district, Tamil Nadu.

2.1 Synthesis of Zinc Oxide Nanoparticles

2.1.1 Preparation of *Mangifera Indica* leaves extract

The leaves of *Mangifera Indica* were dried and washed separately thoroughly with double distilled water and filtered through Whatman No.41 filter paper and used for further studies respectively. The dirt and other foreign materials in the leaves were removed by thorough washing with tap water and finally with double-distilled water.

To prepare the leaf extract, 10g of thoroughly washed and finely cut leaves were boiled in 100 ml double distilled water in a 250 ml glass beaker. The mixture of distilled water and fine cut dried leaves were then heated for 60 minutes until the color of the solution changes to yellow. The leaf extract of plant material was finally filtered through Whatman No.41 filter paper. The extract was stored in a refrigerator for further experiments. All the experiments were carried out with this extract unless otherwise mentioned.

2.1.2 Synthesis of ZnO nanoparticles using *Mangifera Indica* leaf extract:

For the synthesis ZnO nanoparticles, 50 ml of *Mangifera Indica* leaf extract was taken and boiled to 60-80^{0}C using a stirrer-heater. 5g of Zinc Nitrate was added to the extract at a temperature of about 60^{0}C. The solution is then boiled until a deep yellow colored paste is formed. This paste was then collected in a ceramic crucible and heated in an air heated furnace at 400^{0}C for 2 hours. A light yellow colored powder of ZnO nanoparticles was obtained and this was carefully collected and preserved in the air-tight vials for further studies. The powder was mashed in a mortar-pestle to get a finer nature of the sample for further characterization studies.

2.1.3 Synthesis of Ce ion doped ZnO nanoparticles using *Mangifera Indica* leaf extract

For the synthesis Ce ion doped ZnO nanoparticles, 50 ml of *Mangifera Indica* leaf extract was taken and boiled to 60-80^{0}C using a stirrer-heater. 5g of Zinc Nitrate and 1% of cerium nitrate solution were added to this extract and the temperature reached 60^{0}C. The resulting solution was then boiled until it was reduced to a paste. This paste was then collected in a ceramic crucible and heated in an air heated furnace at 400^{0}C for 2 hours. A light yellow coloured powder of ZnO nanoparticles was obtained and this was carefully collected and preserved in the air-tight vials for further studies. The powder was mashed in a mortar-pestle so as to get a finer nature of the sample for further characterization studies. Similar procedure was adopted for the synthesis of different percentage of Ce ion content in the doped samples by varying the amount of cerium nitrate in the range of 2 - 3%.

3. RESULTS AND DISCUSSION

Nanosized ZnO particles of specific morphology were synthesized using the plant leaf extracts of *Mangifera Indica* (Mango leaves). The structures, morphology, optical properties of these fabricated undoped and doped ZnO nanoparticles were characterized by UV-Vis spectroscopy, XRD and TEM of the nanoparticles were studied. The leaves of *Mangifera Indica* provided reducing as well as stabilizing agents for the synthesis of nanoparticles.

3.1 UV-visible spectroscopy

The UV-Vis spectrum of undoped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract was shown in Fig.1. An absorption at 290 nm were observed which is effectively blue shifted with respect to the wavelength of bulk ZnO appeared at 385 nm [18]. It is clear that the absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle. This pronounced and systematic shift in the absorption edge is due to the quantum size effect.

Fig 2. shows the UV-Vis absorption spectra of Ce ion doped ZnO nanoparticles with various concentrations synthesized using *Mangifera Indica* leaf extract. Here the absorption band were observed at 322, 328 and 320 nm for 1% Ce:ZnO, 2% Ce:ZnO and 3% Ce:ZnO respectively. This in turn is considerably blue-shifted when compared to the bulk phase ZnO.

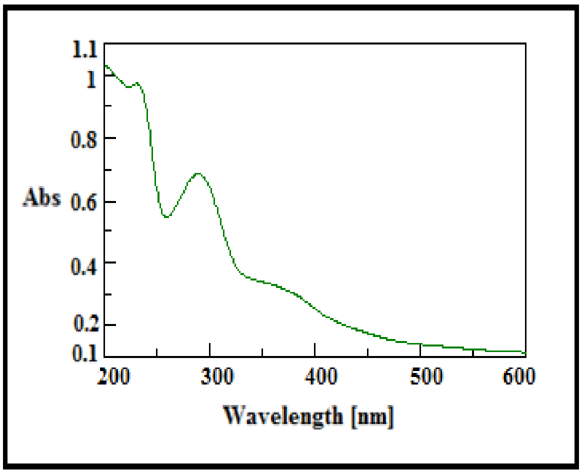

Fig. 1 UV-Vis absorption spectra of, undoped ZnO nanoparticles, synthesized using, *Mangifera Indica* leaf extract.

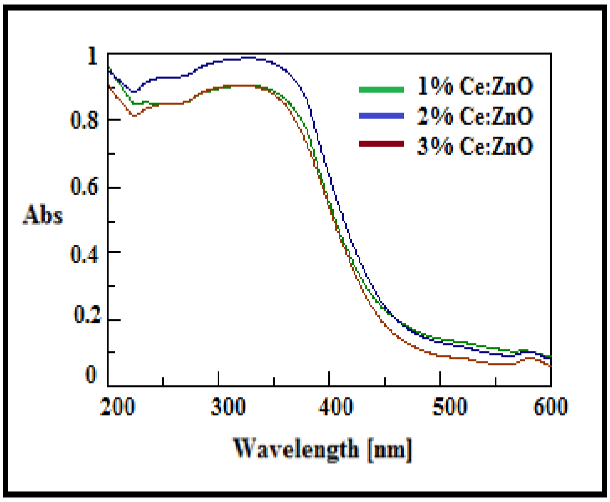

Fig.2 UV-Vis absorption spectra of, Ce ion doped ZnO nanoparticles at, different concentration synthesized using *Mangifera Indica* leaf extract.

The band gap energy of undoped ZnO and Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract are shown in Table.

Table 1: Band gap energy of undoped ZnO, Ce ion doped ZnO n anoparticles.

Type of Plant Material	Nanoparticles	Band Gap Energy in eV
Mangifera Indica	ZnO	4.5 (λ_{max} =290nm)
	1% Ce:ZnO	4.0 (λ_{max} =322 nm)
	2% Ce:ZnO	3.9 (λ_{max} =328 nm)
	3% Ce:ZnO	4.0 (λ_{max} =320 nm)

The band gap energy (Table 1) of doped ZnO nanoparticles was more when compared to the undoped ZnO nanoparticles, as a result the size of doped samples get decreased. The high band gap energy obtained for doped samples is attributed to the fact that there is decrease in particle size.

3.2 XRD Analysis

Structural parameters of doped and undoped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extracts was calculated from the XRD pattern. Calcination at 400^{0}C is essential for complete removal of water and to obtain higher crystallinity. The prominent peaks obtained for doped and undoped samples corresponding to the diffraction planes {100}, {002}, {101}, {102}, {110}, {103} and {112} agree well with the JCPDS Card No. 36-1451.[19] The prepared doped and undoped material was of hexagonal wurtzite crystalline structure. Presence of several peaks indicates random orientation of the crystallites, confirming the hexagonal wurtzite structure of the ZnO nanoparticles. The average crystallite size (D) was calculated using the well-known Scherer's formula.

$D = k\lambda / \beta\cos\theta$

Table 2: JCPDS Card No. 36-1451.

JCPDS 36-1451	
Hkl	**2θ(^{0})**
100	31.770
002	34.422
101	34.353
102	47.539
110	56.603
103	62.864
200	66.378
112	67.961
201	69.100

The X-ray diffraction pattern of undoped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract was shown in Fig.3. The spectrum of ZnO nanoparticles exhibits sharp peaks at 2θ equal to 11.05^0, 13.86^0, 16.47^0, 21.99^0, 25.13^0, 32.16^0, 44.75^0, 48.63^0, 50.32^0 and 58.40^0.[20] These peaks are identified to originate from {111}, {102}, {002}, {102}, {002}, {102}, {112},{002},{111} and {002} planes of the hexagonal ZnO phase resectively. This XRD pattern was well matched with standard JCPDS Card No. 36-1451.[21] The above mentioned XRD parameters is shown in Fig. 3. The average crystallite size (D) of synthesized nanoparticles was found to be 58.65 nm.

Fig. 4 shows the XRD pattern of Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract. The spectrum of Ce:ZnO exhibits sharp peaks at 2θ equal to 31.86^0, 34.50^0, 36.33^0, 47.63^0, 56.64^0, 62.88^0, 67.99^0, 69.10^{0}and 77.06^0. These peaks are identified to originate from pattern {111}, {111}, {102}, {002}, {002}, {111}, {111} and {002} planes of JCPDS 36-1451.[21] The above mentioned XRD parameters is shown in Fig. 4. The increase in FWHM suggests that Ce is incorporated into the ZnO matrix.[20] Polycrystalline nanoparticles with a hexagonal wurtzite structure (zincite,) and cubic structure CeO_2 from the JCPDS (No.75-0390) card. The average crystallite size (D) of synthesized nanoparticles was found to be 49.98 nm.

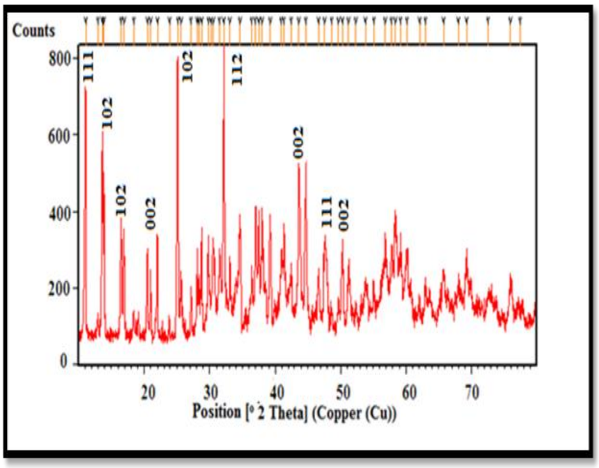

Fig 3: XRD spectrum of undoped ZnO Nanoparticles synthesized using *Mangifera Indica* leaf extract.

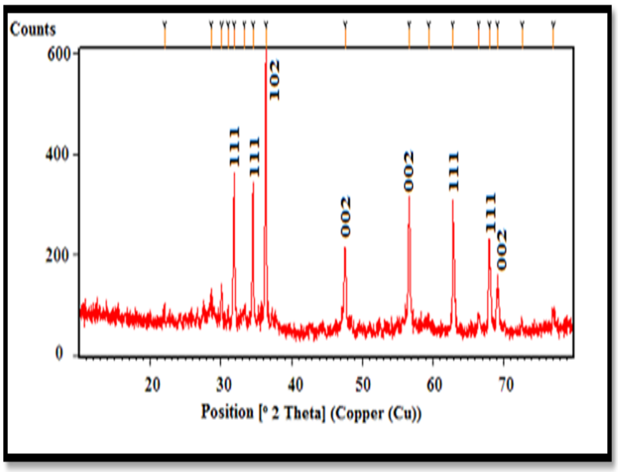

Fig 4: XRD spectrum of Ce ion doped ZnO Nanoparticles synthesized using *Mangifera Indica* leaf extract.

3.3 Transmission Electron Microscopy (TEM).
The size of the synthesized undoped ZnO and Ce ion doped ZnO nanoparticles using aqueous leaf extracts of *Mangifera Indica* was further confirmed by TEM. The TEM monograph (Fig.5 and Fig.7) clearly shows the distribution of spherical and rod like appearance for undoped ZnO and Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of *Mangifera Indica*.

The diffraction pattern in SAED images shows the highly crystalline nature of nanoparticles were shown in Fig.6 & Fig.8. The size of undoped ZnO and Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of *Mangifera Indica* was found to be 100 nm. The morphology of the synthesized undoped ZnO and Ce ion doped ZnO nanoparticles was found to be spherical like appearance.

Electron diffraction of the selected area using a 2.1nm aperture of the undoped ZnO, Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of *Mangifera Indica* were shown in Fig.6, Fig.8. There are four circular rings appeared for undoped ZnO nanoparticles, six circular rings appeared for Ce ion doped ZnO nanoparticles. The patterns display distinct reflections as opposed to being the powder pattern type confirm that the crystal growth is epitaxial with respect to the monolayer and demonstrate that this lattice correspondence is maintained even in regions of denser crystal coverage. The appearance of some darker particles results from an enhanced diffraction contrast due to their orientation with respect to the electron beam**.** The selected area diffraction pattern of undoped ZnO nanoparticles synthesized using *Mangifera Indica* are shown in Fig.6. It revealed that the samples are highly crystalline and are identified to originate from the planes {111}, {102}, {002}, {102}, {002}, {102}, {112}, {002}, {111} and {002}**.** The selected area diffraction pattern of Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* are shown in Fig.8. It revealed that the samples are highly crystalline and are identified to originate from the planes pattern {111}, {111}, {102}, {002}, {002}, {111}, {111} and {002}**.** From the results obtained it has been demonstrated that the size of undoped ZnO and Ce ion doped ZnO nanoparticles are found to be 100 nm. The SAED pattern exhibiting several uniform bright rings suggested that the nanoparticles have high crystalline nature.

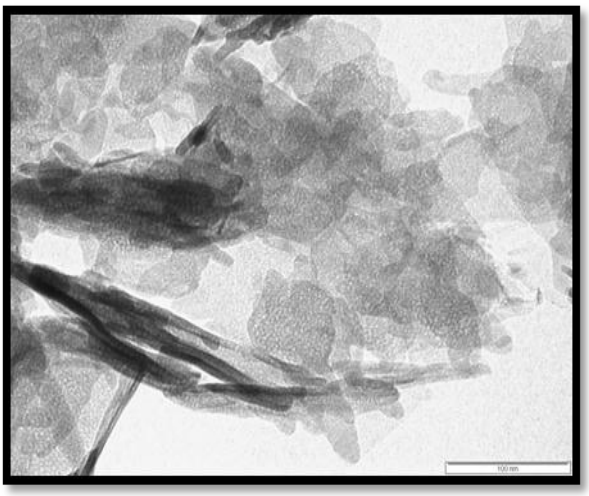

Fig.5 TEM image of undoped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract.

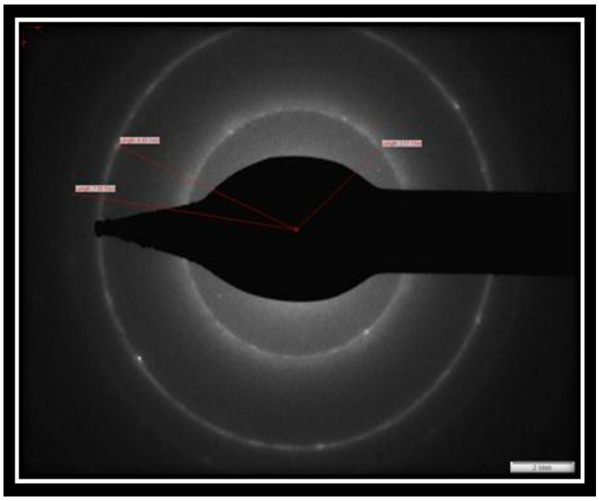

Fig.6 SAED pattern undoped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract.

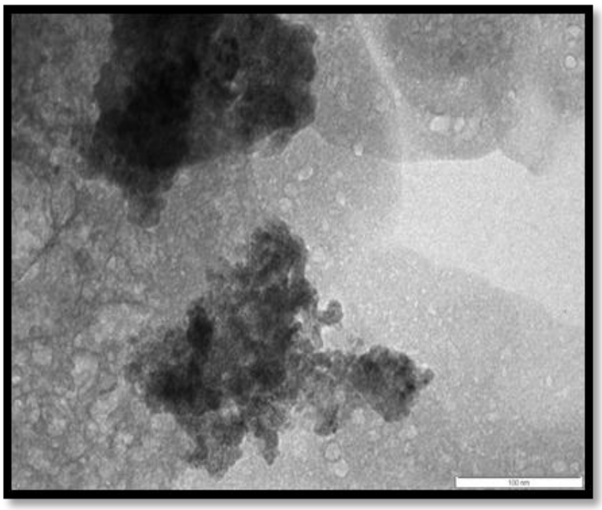

Fig.7 TEM image of Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract.

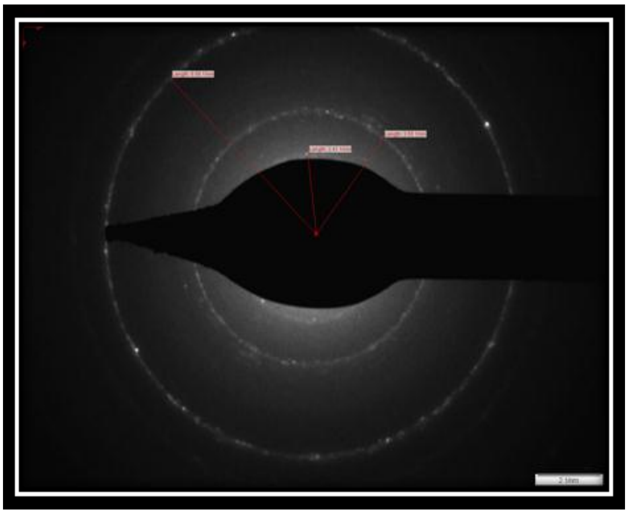

Fig.8 SAED pattern of Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract.

4. CONCLUSION

In the present work we reported that the simple method for the syntheses of Zinc oxide and Ce ion doped zinc oxide nanoparticles by green method (simple and cost effective) using aqueous leaf extract of *Mangifera Indica* (Mango leaves). The highly blue shifted UV-Vis absorption peak confirmed the nano-size of the synthesized ZnO nanoparticles. The absorbance increases in the metal ion doped ZnO nanoparticles. The optical direct band gap energy was found to be 4.5eV for undoped ZnO, 4.0eV for 1% Ce:ZnO, 3.9eV for 2% Ce:ZnO, 4.0eV for 3% Ce:ZnO, 5.4eV nanoparticles synthesized using *Mangifera Indica* leaf extract. XRD behaviour exhibits the size of doped and undoped ZnO nanoparticles. The crystallite size was found to 58.65 nm for ZnO nanoparticles and 49.98 nm for Ce ion doped ZnO nanoparticles synthesized using *Mangifera Indica* leaf extract. TEM micrographs also confirmed the particle size of the doped and undoped samples are in the nanoscale range and the size of the undoped ZnO and Ce ion doped ZnO nanoparticles were found to be 100 nm respectively.This method is best against conventional method and is less expensive and eco-friendly. ZnO nanoparticles can be used in different industries like rubber, electronic and electrotechnology industry, textile industry, pharamaceutical industry due to their amazing properties like antiseptic, anticorrosive, antibacterial. Thus, the ZnO nanoparticles synthesized using aqueous leaf extract of *Mangifera Indica* find use for medical applications and environmental science.

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