



# Optical properties of transition metal atom adsorbed graphene: A density functional theoretical calculation



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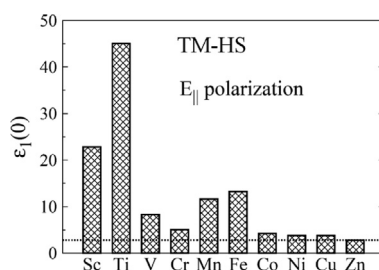
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## HIGHLIGHTS

- Optical properties of graphene are modified after transition metal adsorption.
- Appreciable modifications of band structure occur around Fermi level.
- Low energy optical absorption lines emerge due to band structure alteration.
- Significant enhancement of static dielectric constant is achieved.
- Reflectivity increases in the infrared part.

## GRAPHICAL ABSTRACT

*Ab-initio* calculation of optical properties of different transition metal adsorbed graphene reveals significant modification, where element type and its adsorption site play the crucial role.



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## ABSTRACT

Electronic and optical properties of 3d-transition metal adsorbed graphene system, theoretically studied in the framework of density functional theory, reveals significant modification compared to the pristine system. Due to adsorption of transition metal, the emergence of closely separated electronic bands leads to substantial amount of low energy optical absorption below 2.0 eV photon energy. Very significant enhancement of static dielectric constant and large value of reflectivity in the low optical energy regime has been identified for different adsorbed systems. In the different 3d-transition metal adsorbed systems, particularly up to the half filled *d*-shell transition metal atom, pronounced emergence of optical absorption line in the deep ultraviolet regime beyond 30.0 eV photon energy is observed.

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## 1. Introduction

In recent years, the carbon based two dimensional nano-material, graphene have fostered and played an important key role in the advancement of nanoscience and nanotechnology along with the pure academic interest [1–6] after its successful synthesis in 2004 by Novoselov et al. [7]. Among the various possible allotropes of carbon (C) atoms in low dimension, this material (graphene) has the unique honeycomb like two dimensional (2D)

structure. The existence of graphene was predicted by Wallace in 1947 [8], but it was not believed to observe a purely 2D crystalline material because of thermodynamic instability [9,10]. In a short time span after its birth [7], several interesting works involving graphene suggest that this material possesses the capability to be a promising candidate in the field of material science as well as from purely theoretical point of view also [11–25]. One of the most fascinating features of graphene is that it exhibits linear electronic band dispersion relation around the Fermi level or Fermi energy ( $E_F$ ) showing exactly zero band gap energy ( $E_g$ ); consequently, charge carriers in graphene act as mass-less Dirac fermions [3]. However, the band structure and electronic density of states (DOS)

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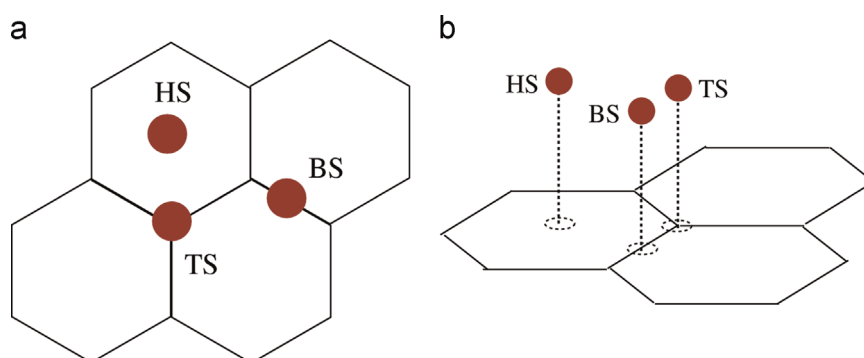
as well as the chemical properties of graphene can be modulated substantially by introducing impurities/defects in the graphene network [12–23]. Recently, two different theoretical works reveal that due to substitutional doping of N and B in graphene, its electronic, dielectric and related optical properties are modified appreciably [26,27]. Experimentally, the dielectric response of graphene has been studied by Reed et al. [28] through inelastic x-ray scattering (IXS) measurements. This interesting work reports a small value ( $\sim 0.14$ ) of the effective fine structure constant of pristine graphene. Apart from doping, strain engineering in graphene system crucially alters its electronic properties. In-plane strain on graphene system breaks its electron-hole symmetry and as a result band gap opening is observed [24,25]. It is also to be mentioned that apart from mono layer graphene (doped or undoped), the electronic properties of bilayer graphene (BLG) systems exhibit some interesting features beyond its single layer counterpart, particularly depending on the stacking geometry and interlayer separation [29–33].

Transition metal (TM) adsorbed graphene systems are promising representative to be nano-spintronic materials as they exhibit magnetic ordering [15,34,35]. 3d-TM atoms adsorbed on graphene plane can give rise to stable structures having non-vanishing value of magnetic moment in contrast to non-magnetic graphene nano-sheet; however, zig-zag graphene nano-ribbon possesses an intrinsic magnetism due to its edge states. Recently, Sevinçli et al. [35] have examined the adsorption site dependent structural stability of TM adsorbed graphene and corresponding magnetic behavior. Interestingly, it is pointed out through theoretical calculations by different research groups [35–38] that most of the 3d-TM atoms prefer to be adsorbed at the top of the center of hexagonal ring of graphene network as a consequence of larger value of adsorption energy compared to other adsorption sites. Besides, it is also observed that the value of elevation height of the adsorbed TM atoms on the graphene network strongly depends on the choice of adsorption sites as well as TM atomic species [37,38]. According to Mao et al. [36], all of the Mn, Fe and Co adsorbed graphene systems possess non-zero magnetic moment associated with the adsorbed 3d-TM atom. Moreover, non-vanishing DOS at the Fermi level are observed in these adsorbed systems in contrast to pristine graphene. Furthermore, magnetic properties of TM atom adsorbed at monovacancy and divacancy sites on graphene network are also investigated [15]. Interestingly, such systems also exhibit appreciable local magnetic ordering. Moreover, the amount of magnetic moment strongly depends on the choice of TM atom species [15]. In a recent experimental work by Sessi et al. [39], the *d*-shell electron configurations and magnetism have been investigated for various 3d-TM atoms when adsorbed on highly oriented pyrolytic graphite (HOPG) and also on few layer graphene. Interestingly, it is noticed that these two different adsorbed systems exhibit difference in *d*-shell occupation of TM atoms after

adsorption [39]. It is also interesting to note that graphene sheet embedded on a slab (or substrate) of TM, the TM substrate interacts with graphene; however, the graphene–substrate interactions are classified in two broad classes: strong and weak depending on the TM type [40,41]. Weakly interacting systems keep the linear band dispersion of graphene intact whereas strong interaction breaks the electron–hole symmetry of Dirac fermions in graphene leading to profound change in graphene band structure. Low energy Ar<sup>+</sup> ion irradiation on graphene produces point defects in graphene network and such local defects give rise to strong graphene–substrate interaction even with the weakly interacting substrate [41]. In a recent theoretical work, Dai et al. [13] have reported that Mn adsorbed graphene can be a promising candidate regarding gas sensor and gas storage devices due to strong coupling between Mn and the foreign gas molecules such as O<sub>2</sub>. It is clear that TM atoms adsorbed on graphene network, modify the electronic band structure of graphene substantially. In this present theoretical work, we have investigated the electronic and optical properties of 3d-TM atom adsorbed graphene systems considering various TM atoms along with their different adsorption sites on graphene network. This will eventually trigger to choose appropriate TM atoms at specific sites for opto-electronic device application.

## 2. The model and computational details

In this computational work, the electronic and optical properties of TM atom adsorbed graphene systems (abbreviated as TM-GR) have been carried out in the frame work of density functional theory (DFT). The optical properties are studied for both parallel polarization ( $E_{\parallel}$  polarization) of electric field vector *i.e.* polarization is parallel to graphene plane and perpendicular polarization ( $E_{\perp}$  polarization) of electric field vector *i.e.* polarization is perpendicular to graphene plane. The theoretical calculations were performed with the help of Vienna *Ab-initio* Simulation Package (VASP) [42–45] using the plane wave pseudo-potential method implemented in this DFT code. We have considered a graphene super cell containing ( $4 \times 4$ ) graphene unit cell *i.e.*, the graphene structure under study contains 32 carbon (C) atoms. It is assumed that graphene network is lying on the *x*–*y* plane and the *z*-axis is chosen normal to the graphene plane. Periodic boundary condition has been considered in the *x*–*y* plane and in addition 16 Å vacuum separation is considered along the *z*-axis to avoid any unwanted interlayer interaction with its periodic copy. Now, a series of 3d-TM atoms are considered to be adsorbed on graphene plane. The adsorption sites are chosen systematically by noting the symmetry of graphene crystal [35]. The honeycomb like symmetry provides three different possible adsorption sites: (i) just above of the center of the hexagonal ring or hollow site (HS), (ii) at the top of a



**Fig. 1.** The schematic representation of transition metal atom adsorbed graphene on different adsorption sites; (i) transition metal on hollow site (TM-HS), (ii) transition metal on bridge site (TM-BS) and (iii) transition metal on top site (TM-TS). (a) Represents the top view and (b) represents the side view of different adsorbed systems.

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