ИЗУЧЕНИЕ ВЛИЯНИЯ ЛЕГИРОВАНИЯ МЕТАЛЛАМИ (Co, Ni, Cu) НА СТРУКТУРНЫЕ И ЭЛЕКТРОННЫЕ СВОЙСТВА ОДНОСЛОЙНЫХ УГЛЕРОДНЫХ НАНОТРУБОК: ТЕОРЕТИЧЕСКИЙ АНАЛИЗ

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Широко параметризованный самосогласованный квантово-химический метод GFN2-xTB был использован для исследования влияния легирования металлами Co, Ni и Cu на структурные и электронные свойства однослойных углеродных нанотрубок (CNT). Результаты вычислений энергии взаимодействия, порядка связей и зарядов атомов по Мулликену показали, что легированные металлы образуют химические связи с поверхностью CNT через металло-углеродные связи. Было отмечено значительное перенесение заряда от атомов металла к CNT, особенно в случае Cu/CNT. Анализ значений энергии ионизации (IP), сродства к электрону (EA) и глобального индекса электрофильности (GEI) показал, что присутствие металлов увеличивает значения IP, EA и GEI по сравнению с чистыми CNT. Эти изменения свидетельствуют о повышении реакционной способности и стабильности легированных нанотрубок. Кислотность Льюиса исследуемых систем увеличивается в следующем порядке: Ni/CNT < Co/CNT < Cu/CNT. Вычисления плотности, взвешенной по дробному числу заполнения, показали, что в системах с легированными металлами CNT плотность горячих и химически активных электронов преимущественно сосредоточена на атомах металла. Анализы молекулярных орбиталей продемонстрировали вклад атомов металла в HOMO и LUMO, что существенно влияет на электронные свойства нанотрубок. Кроме того, центральное расстояние (Dij) между HOMO и LUMO систем M/CNT (M = Co, Ni, Cu) зависит от легирования металлами. Среди исследованных систем, Co/CNT имеет наименьший энергетический зазор между LUMO и HOMO и наибольшее значение Dij, что указывает на его пригодность для фотокаталитических приложений. Эти результаты могут быть полезны для разработки новых материалов на основе углеродных нанотрубок с улучшенными свойствами для различных практических применений.

Ключевые слова: CNT, легированные металлами CNT, GFN2-xTB, электронные свойства

UNDERSTANDING THE IMPACT OF METAL DOPING (Co, Ni, Cu) ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES: THEORETICAL INSIGHTS

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The broadly parametrized self-consistent tight-binding quantum chemical method – GFN2-xTB was employed to investigate the impact of Co, Ni, and Cu metal doping on the structural and electronic properties of single-walled carbon nanotube (CNT). Computational results for interaction energy, bond order, and Mulliken atomic charge indicated that the doped metals form chemical bonds with the CNT surface through metal-carbon bond formation. Significant charge transfer from the metal atoms to the CNT was observed, most notably in the case of Cu/CNT. Analysis of ionization energy (IP), electron affinity (EA), and global electrophilicity index (GEI) values revealed that the presence of metals increases IP, EA, and GEI values compared to the pristine CNT. The Lewis acidity of the studied systems increases in the order of Ni/CNT < Co/CNT < Cu/CNT. Calculations of the fractional occupation number weighted density (FOD) indicated that in the metal-doped CNT systems, the density of hot and chemically active electrons is predominantly concentrated on the metal atoms. Molecular orbital analyses demonstrated the contribution of metal atoms to the HOMO and LUMO of the system. Additionally, the centroid distance (Dij) between the HOMO and LUMO of the M/CNT (M = Co, Ni, Cu) is influenced by metal doping. Among the studied systems, Co/CNT exhibits the lowest energy gap between the LUMO and HOMO and the highest Dij value, suggesting its suitability for photocatalytic applications.

Keywords: CNT, metal doped CNTs, GFN2-xTB, electronic properties

INTRODUCTION

Carbon nanotubes (CNTs) are renowned for their exceptional mechanical, electrical, and thermal properties, making them suitable for various applications, including electronics, energy storage, sensors, and environmental remediation [1-3]. However, challenges such as aggregation, difficulty in achieving uniform dispersion, and limited control over their electronic properties hinder their performance [4-6]. Metal doping presents a promising solution by enhancing these properties and mitigating the disadvantages of CNTs. Specifically, doping with transition metals increases active sites and improves chemical affinity, significantly enhancing the adsorption capacities for pollutants and improving the conductivity of single-walled carbon nanotube (SWCNT) networks [7-14].

Understanding the fundamental impact of metal doping on the structure and properties of CNTs is crucial. This knowledge will significantly enhance our ability to clarify and explain the various behaviours of these materials in a wide range of applications, including catalysis, sensors, and beyond. Several theoretical studies on metal-doped CNTs have shown that doping metals onto the surface of SWCNTs is energetically favourable and results in charge transfer from the metal atoms to the CNTs [15-17]. For example, research by Chen et al. on the structure of transition metal-doped (5,5) CNT systems (TM/CNT) reveals that TM-doped SWCNTs are predominantly metallic or narrow-gap semiconductors. As the transition metal dopant shifts from Sc to Zn within the same period of the periodic table, or from the top to the bottom within the same platinum group, the energy of the highest occupied crystal orbital in the TM-doped SWCNTs decreases, signifying a diminished electron-donating capability [15]. Moreover, transition metals can have varying impacts on the electronic properties of SWCNTs.

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For instance, doping metallic isolated (3,3) SWCNTs with Mn, Fe, or Co transforms them into semi-metals, whereas doping with Ni results in semiconductor behaviour [18]. These modifications consequently impact the activities of CNTs. Specifically, transition metal doping has been shown to significantly enhance the H_2 storage potential of SWCNTs compared to other metals, as evidenced by optical spectra analysis [19]. Additionally, this doping method improves the adsorption capacity for other gases, such as NO_2 and CO [20, 21].

Although numerous experimental and theoretical studies on metal-doped single-walled carbon nanotube (M/CNT) systems exist, the effects of metals have primarily been analysed in terms of interaction energy and charge transfer. However, the nature of the bonding between metal atoms and the CNT surface, as well as the influence of metals on other electronic properties, has received less attention. In this study, we provide valuable insights into the nature of the interactions between metals and the CNT surface and analyse their effects on specific electronic parameters, which are crucial for evaluating the activities of M/CNT systems.

MODELS AND COMPUTATIONAL METHODS

Models

The pristine carbon nanotube model was constructed similarly to our previously published studies [9]. This model features an armchair structure, formed by rolling a graphene sheet into an open-ended cylinder comprising 240 carbon atoms arranged in hexagonal rings. The terminal carbon atoms at both ends of the CNT are hydrogen-saturated. The M/CNT structures (where M = Co, Ni, Cu) were developed by positioning metal atoms atop the hexagonal carbon rings of the CNT. The formation of M/CNT systems from M and CNT can be represented by the following equation: M + CNT → M/CNT. This process is characterized by the interaction energy, E_{int}, which is determined using the following formula:

$$E_{int} = E_{(M/CNT)} - E_{(M)} - E_{(CNT)}$$

where, $E_{(M/CNT)}$, $E_{(M)}$, $E_{(CNT)}$ are the energies of the M/CNT, M, and CNT structures, respectively. The nature of the interaction between the metal atoms and the CNT is elucidated by analyzing structural parameters such as the shortest distance from M to the CNT surface (d_{min}), the total Mayer bond order (BO) formed between M atom and the carbon atoms on the surface, and the Mulliken atomic charge on the atoms (q).

Computational Details

All optimization calculations were performed using the GFN2-xTB method, a highly accurate and extensively parameterized self-consistent tight-binding quantum chemical approach [22, 23]. The energy derived from the GFN2-xTB method comprises multiple components: repulsive energy between atomic pairs, extended Huckel-type energy, isotropic electrostatic and exchange-correlation energy, anisotropic electrostatic energy, and the chemical potential of electrons. Furthermore, the method incorporates the D4 London dispersion model, which is dependent on atomic partial charges [24]. The GFN2-xTB method, with parameters optimized for 86 elements of the periodic table, has demonstrated greater efficiency compared to other computational methods, especially for large systems. In this study, calculations were performed at an electron temperature of 300K, with energy convergence criteria set at $0.1 \cdot 10^{-5}$ Hartree, and wavefunction convergence at $0.1 \cdot 10^{-3}$ e.

To assess the impact of metal doping on the structural and electronic properties of CNT, we calculated several key parameters: vertical ionization energy (IP), vertical electron affinity (EA), global electrophilicity index (GEI), and fractional occupation number weighted density (FOD). Additionally, molecular orbital analyses were performed to determine the energy gap between the HOMO and LUMO (E_g), the centroid distance between the HOMO and LUMO (D_{ij}), and the contribution ratio of the metal atom M to the HOMO and LUMO (denoted as C_{ij}(HOMO) and C_{ij}(LUMO), respectively). The GFN2-xTB method was implemented in the open-source xTB code [https://xtb-docs.readthedocs.io/en/latest/].

RESULTS AND DISCUSSIONS

Structural properties of M/CNT (M = Co, Ni, Cu)

The optimized structures of M/CNT along with the parameters characterizing the formation of M/CNT are presented in Fig. 1 and Table 1.

The formation of M/CNT systems (M = Co, Ni, and Cu) is energetically favorable, as evidenced by the negative values of interaction energy. Among these, the energy released during the formation of Ni/CNT and Cu/CNT systems is notably similar, indicating comparable stabilization upon doping with these metals.

A detailed analysis of the minimal distance from the metal atoms to the CNT surface reveals that these distances are slightly larger than the sum of the covalent radii of the metal atoms (Co = 1.26 Å, Ni = = 1.24 Å, Cu = 1.32 Å) and the covalent radius of Csp^2 (0.73 Å) [25]. This suggests that the metal atoms are not merely physisorbed but also have the potential to form covalent bonds with the carbon atoms on the CNT

surface. The significant bond order values further corroborate the presence of these covalent bonds. Additionally, the formation of these covalent bonds results in a partial charge transfer from the metal atoms to the CNT. This charge transfer is most pronounced in the Cu/CNT system, indicating a higher degree of interaction between the copper atoms and the CNT surface. Conversely, the least charge transfer is observed in the Co/CNT system, suggesting relatively weaker interaction compared to Ni and Cu. This differential charge transfer can influence the electronic properties of the CNT, potentially enhancing its applicability in various electronic and catalytic applications.
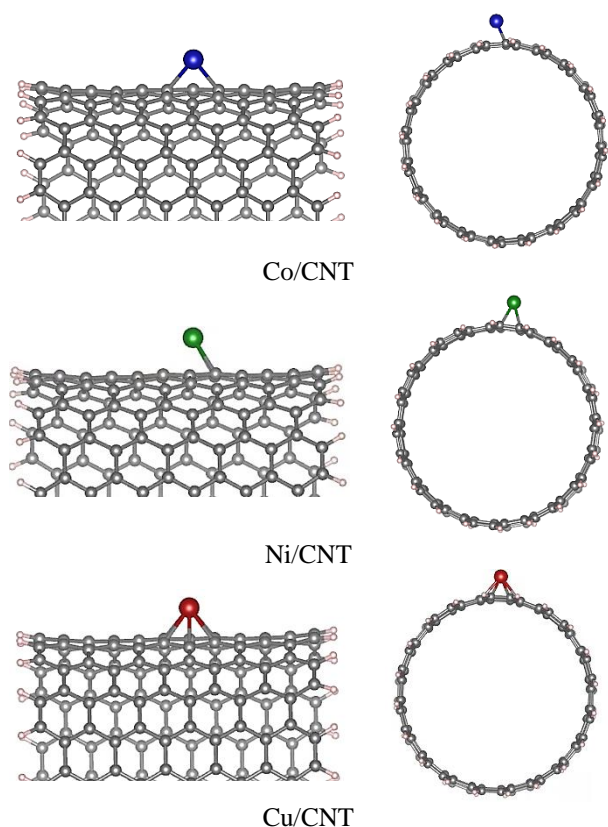

Co/CNT

Ni/CNT

Cu/CNT

Fig. 1. Optimized structures of M-CNT: Co/CNT (a); Ni/CNT (b); Cu/CNT (c), colour codes: grey – C, ivory – H, dark blue – Co, green – Ni, red – Cu

Рис. 1. Оптимизированные структуры M-CNT: Co/CNT (a); Ni/CNT (b); Cu/CNT (c), цветовая кодировка: серый – C, кремовый – H, темно-синий – Co, зеленый – Ni, красный – Cu

Table 1

Calculated results for M/CNT systems (M = Co, Ni, Cu)
Таблица 1. **Результаты расчетов для систем M/CNT (M = Co, Ni, Cu)**

System	E_{int}, (kJ mol^{-1})	d_{min}, Å	BO	q(M), e
Co/CNT	-220.7	2.126	1.492	+0.241
Ni/CNT	-256.6	2.176	1.613	+0.415
Cu/CNT	-257.0	2.148	0.947	+0.493

Electronic properties of M/CNT (M = Co, Ni, Cu)

The computational results at the same theoretical level for pristine CNT show ionization potential (IP), electron affinity (EA), and global electrophilicity index (GEI) values of 5.578 eV, 3.473 eV, and 4.866 eV, respectively [12]. An analysis of the electronic parameters of the M/CNT systems (Table 2) reveals significant enhancements in IP, EA and GEI due to the incorporation of Co, Ni, and Cu compared to the pristine CNT. The IP values for Co/CNT and Ni/CNT systems are quite similar and higher than those for Cu/CNT. This similarity in ionization energy between Co/CNT and Ni/CNT can be attributed to their position in Group VIIIB of the periodic table, where they share similar electron shell structures, differing mainly in the number of electrons in the 3d subshell. Conversely, Cu, a Group IB element, has a distinctly different electron configuration with only one electron in its outermost shell, explaining relatively lower ionization energy of Cu/CNT.

Table 2

Electronic parameters calculated for M/CNT (M = Co, Ni, Cu) systems
Таблица 2. **Электронные параметры, рассчитанные для систем M/CNT (M = Co, Ni, Cu)**

System	IP, eV	EA, eV	GEI, eV
Co/CNT	6.0140	4.1486	6.9206
Ni/CNT	6.0164	3.9580	6.0418
Cu/CNT	5.6015	3.9848	7.1054

Furthermore, the doping of metal atoms notably increases the GEI values relative to the original CNT. The GEI serves as an indicator of the Lewis acidity of the material's surface [26]. Lewis acid sites are crucial in various chemical processes, including photochemical reactions and the adsorption of organic compounds [27]. The ascending order of GEI values: Ni/CNT < Co/CNT < Cu/CNT, suggests that Cu-doped CNTs exhibit the highest Lewis acidity, followed by Co-doped and Ni-doped CNTs. The enhanced Lewis acidity in metal-doped CNTs can facilitate more efficient electron transfer, enhancing the catalytic activity.

Fig. 2 presents the fractional occupation density maps for the M/CNT systems. The FOD analysis is a valuable theoretical method for examining complex electronic structures. Its main benefit is its ability to quickly and accurately identify where "hot" electrons – those that are strongly correlated and highly reactive – are located within a molecule [28].

In the M/CNT systems, the "hot" electrons are predominantly situated on the metal atoms. The density of active electrons on Co and Ni is significantly

higher than on Cu. This could be attributed to the activity of the 3d subshell electrons in Co and Ni compared to the saturated 3d subshell electrons in Cu. Nonetheless, the concentration of these active electrons on the metal atoms is notable, as it suggests that the metal atoms are likely to serve as the primary active centers in chemical reactions taking place on the surface of the M/CNT. The presence of these active centers is crucial for catalysis and other surface-related chemical processes, as they can enhance the reactivity and selectivity of the CNTs in various applications.
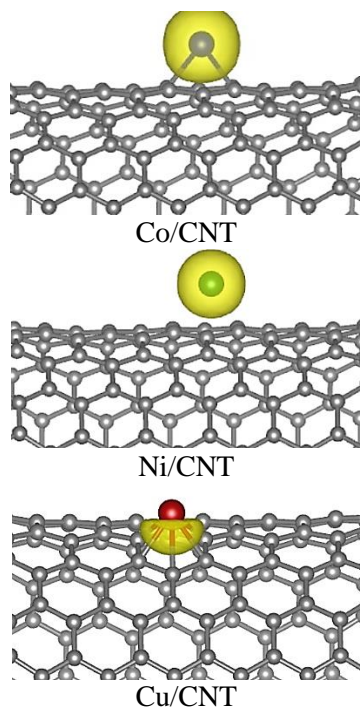

Co/CNT

Ni/CNT

Cu/CNT

Fig. 2. FOD maps of M/CNT (M = Co, Ni, Cu) depicted at an isovalue of 0.001 e Å⁻³
Рис. 2. Карты FOD для M/CNT (M = Co, Ni, Cu), изображенные при изозначении 0.001 e Å⁻³

Molecular orbital analysis for M/CNT (M = Co, Ni, Cu)

The frontier molecular orbitals play a crucial role in modulating chemical reactivity. Therefore, a thorough investigation into their composition becomes essential for understanding and predicting chemical interactions. The depiction of the HOMO and LUMO of the M/CNT systems, as illustrated in Fig. 3, highlights the significant contribution of the d orbitals of the metal atoms to these frontier molecular orbitals. An in-depth analysis of the HOMO and LUMO characteristics across the M/CNT configurations yields insightful observations. In the case of the Co/CNT composite, the HOMO demonstrates notable involvement from cobalt atoms, accompanied by partial engagement from carbon constituents, whereas the LUMO predominantly

localizes across the entire carbon nanotube (CNT) structure. Conversely, in the contexts of Ni/CNT and Cu/CNT, both the HOMO and LUMO are primarily situated on the CNT, indicating a distinct electronic distribution within these systems.
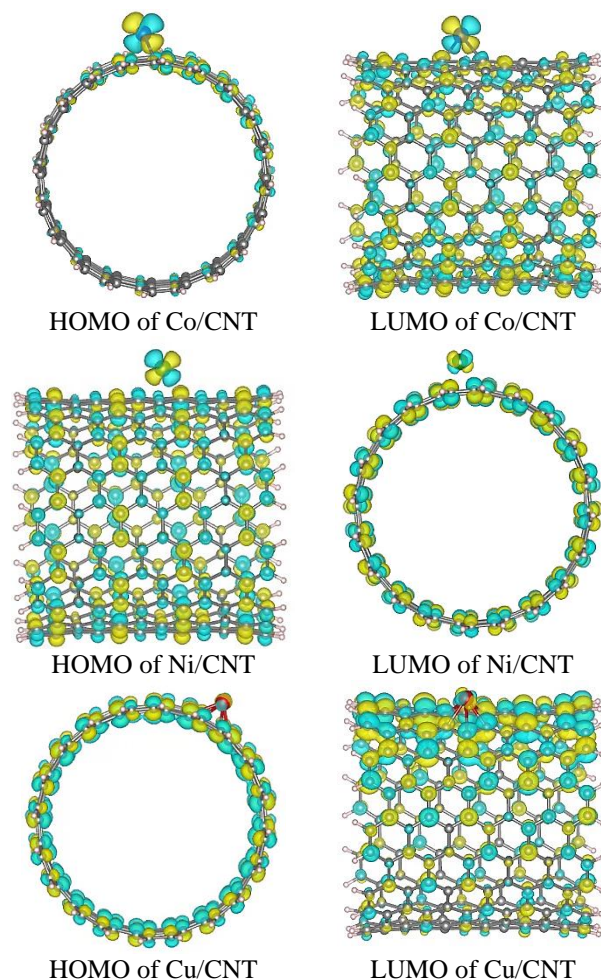

HOMO of Co/CNT   LUMO of Co/CNT

HOMO of Ni/CNT   LUMO of Ni/CNT

HOMO of Cu/CNT   LUMO of Cu/CNT

Fig. 3. HOMO and LUMO of M/CNT systems (M = Co, Ni, Cu)
Рис. 3. HOMO и LUMO систем M/CNT (M = Co, Ni, Cu)

Table 3
HOMO-LUMO analysis for M/CNT (M = Co, Ni, Cu)
Таблица 3. Анализ HOMO-LUMO для систем
M/CNT (M = Co, Ni, Cu)

System	E_g, eV	D_{ij}, Å	C_{ij}(HOMO),%	C_{ij}(LUMO),%
Co/CNT	0.3399	5.2650	84.19	36.03
Ni/CNT	0.3937	0.2049	14.09	0.83
Cu/CNT	0.4629	3.3596	0.56	1.84

Particularly, the contribution of copper's d atomic orbitals to the HOMO and LUMO states is less distinct compared to cobalt and nickel. This discrepancy is underscored by the tabulated data in Table 3, which shows the varying percentage contributions of metal atoms to the HOMO and LUMO across the

M/CNT structures. Indeed, Co contributes approximately 84% to the HOMO and 36% to the LUMO of Co/CNT, whereas Cu contributes only 0.56% and 1.84%, respectively.

The energy gap between the HOMO and LUMO of the systems follows the increasing order: Co/CNT < Ni/CNT < Cu/CNT. Consequently, the excitation of electrons from the HOMO to the LUMO in Co/CNT occurs more readily than in Cu/CNT. This ease of electron excitation may significantly contribute to the enhanced catalytic efficiency of these materials in photocatalytic applications.

To further investigate, we calculated the centroid distance between the HOMO and LUMO (D_{ij}) for the studied systems using Multiwfn [29]. The D_{ij} value is critical as it provides insights into electron transitions when the system is excited. A larger D_{ij} indicates a greater potential for photoinduced electron separation. Based on the increasing D_{ij} values, the materials are ordered as follows: Ni/CNT < Cu/CNT < Co/CNT. This ordering suggests that Co/CNT is likely to exhibit the highest electron separation and transfer capability, followed by Cu/CNT and then Ni/CNT. The superior performance of Co/CNT in these aspects can be attributed to its smaller HOMO-LUMO gap and larger D_{ij}, making it the most promising candidate for applications requiring efficient photocatalytic activity.

CONCLUSIONS

The GFN2-xTB method has been employed to investigate the influence of doping metals (Co, Ni, and Cu) on the structure and electronic properties of CNTs. Computational results reveal that doping metals onto the surface of CNTs is advantageous energetically due to the formation of covalent chemical bonds between metal atoms and carbon atoms of CNTs. Significant charge transfer from metal atoms to the surface of CNTs is observed, particularly in the case of Cu/CNT. The presence of metals increases the values of IP, EA, as well as the Lewis acidity of the material surface. Computational results also indicate that chemically active electrons in the M/CNT systems are predominantly localized on metal atoms. Analysis of molecular orbital compositions reveals varying degrees of contributions from metal atoms to the HOMO and LUMO components, with Co contributing the most and Cu – the least. Among the studied systems, Co/CNT exhibits the smallest E_g and the highest centroid distance between HOMO and LUMO, indicating its potential for excellent performance in photocatalytic applications.

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