



## Size dependent noble metal nanoparticles modified DNA: MD-simulation studies

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### ABSTRACT

Coinage metal nanoparticles (CMNPs) have unique physical and optical properties. Herein we have analyzed the size effect of Copper, Silver and Gold Nanoparticles (NP) on DNA. Molecular docking was first examined with nanoparticles modelled as metal clusters of different sizes. Then Molecular Dynamics (MD) simulation was carried out on energy minimized docked structures. The interaction of different sizes of NPs is evaluated from parameters, viz. docking score analysis, H-bond formation, and conformational changes of the composites. NP docked DNA realised higher values of RMSD compared to free DNA. The structure of the DNA was seen to alter due to interaction with metal nanoclusters. A detailed assessment of the results revealed that the size of the nanoparticles controls the stability of the nanoparticle modified DNA assemblies.

### Introduction

Copper nanoparticles (NP) can be used as fluorescent probes and sensors in DNA [1]. The optical properties of Ag-NP are used for multiplexed disease diagnostics [2]. Gold NP is used for various genetic and microbial therapies [3]. Magnetic nanoparticles (iron, cobalt, nickel oxides, mixed oxides etc.) are used for drugs themselves along with carriers for targeted drug delivery [4]. Both anti-fungal and anti-bacterial activities have been shown by Copper NPs. Silver nanomaterial is available in the market today as nano-gel for antibiotic surface applications [5]. There are numerous other nanomaterials, inorganic, organic, polymeric, biomolecular, and hybrid, which are either proto-drugs or drug molecules, currently in use or undergoing testing or waiting for final approval [6–8]. Due to antimicrobial efficacy, antibacterial effects, and electrochemical sensing properties on biological systems, coinage materials are of interest to researchers [9]. However, the exact mechanism of action of nanoparticles on live organisms is not yet fully known. The action of NPs on live cells is being slowly unravelled. It has been seen that the same nanoparticle acts differently on different organisms [10] and produces enormous complexity in even simple biological systems. In this regard understanding the mechanism of nanoparticle modified DNA as-

sembly is very important as the size of the nanoparticle determines the stability of this assembly [5]. The DNA's major and minor grooves are known to bind to Cu(II) compounds, resulting in cleavage and interfering with cellular biological function, viz. groove binding or modulation of electrostatic surface [6,11]. Similarly, Cu(II) complexes with arginine, and bipyridine, ph, dpq and dppy demonstrated groove binding and breaking of photosensitized double strands by the reactive singlet oxygen species generation with the same two DNA models [12,13]. Both these results were explained by docking studies [12]. The interaction between one tetranuclear and dinuclear copper(II) compounds with supercoiled plasmid DNA (pBR322) was also supported by a docking study [14]. DNA cleavage was caused by hydrolytic (tetranuclear) and oxidative (dinuclear) pathways. The compounds showed marked activity against *E. coli* and *S. aureus*. The Ni(II), Cu(II) and Zn(II) compounds with isatin and tyramine also showed groove binding and cleavage of DT and pUC19 [15]. They were also active against *K. pneumoniae*, *S. aureus*, *B. subtilis*, *E. coli*, and *S. typhi*. This was also verified with docking studies [12]. In another study, Co(II) and Ru(II) derivatives comprising 2-(1H-indol-3-yl)-1H-imidazo-[4,5-f]-1,10-phenanthroline and 4,4'-dimethyl-2,2'-bipyridine displayed groove binding to CT DNA, which was suggested by docking analysis [16]. They also showed

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## Physica E: Low-dimensional Systems and Nanostructures

journal homepage: [www.elsevier.com/locate/physa](http://www.elsevier.com/locate/physa)CO<sub>2</sub> activation on transition metal decorated graphene quantum dots: An insight from first principlesKingkar Ghosh<sup>a</sup>, Niranjana Kumar Mridha<sup>b</sup>, Abdul Ashik Khan<sup>c</sup>, Nabajyoti Baildya<sup>d</sup>,  
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## ABSTRACT

Herein electrolytic reduction of CO<sub>2</sub> on transition metal decorated graphene quantum dot (M@GQD) has been investigated by using first-principles calculations. Comparative study of geometrical properties and charge distribution of CO<sub>2</sub> adsorbed M@GQD revealed that while GQD is unable to activate CO<sub>2</sub>, the transition metal decorated sites of M@GQD are available for CO<sub>2</sub> adsorption, activation and dissociation. Charge distribution and molecular orbital analysis indicate that metal centre on GQD act as a Lewis base and the overall activation process is guided by the transfer of electron density from the corresponding metal centre to the π\* orbital of CO<sub>2</sub>. The extent of CO<sub>2</sub> activation is also analysed by the projected density of states (PDOS) which demonstrates that among the transition metal series Ti sites are available for CO<sub>2</sub> activation and dissociation while activation does not occur involving Cu and Zn, due to their poor adsorption energy and lowest coupling of valence band state with the GQD. Overall transition metal decorated GQD opens up unlimited possibilities for designing new and highly selective and efficient catalysts for electrolytic CO<sub>2</sub> reduction.

## 1. Introduction

Reduction of CO<sub>2</sub> to fuels like methane, methanol is an ample option for storing renewable energy and balancing global warming [1,2]. The converted fuel can be kept for long term fossil fuel alternative, chemicals for laboratory synthesis and can also be utilised, giving back CO<sub>2</sub> as the main waste, terminating the overall loop. However stable linear geometry of CO<sub>2</sub> has a strong C=O bond (750 kJ mol<sup>-1</sup>) making it challenging for electrochemical conversion [3]. Furthermore high activation barrier, multi-electron and proton transfer during the processes of different intermediates and products making the overall process highly complex [4, 5]. During the recent decades several catalysts have been reported for the electrocatalytic transformation of CO<sub>2</sub> but still remains as the biggest challenge. Metal oxides [6], zeolites [7] and carbon nanotubes (CNTs) [8], metal-organic frameworks (MOFs) [9] and graphene have been reported as CO<sub>2</sub> adsorber both experimentally and theoretically [10–12, 47,48]. Graphene can be easily decorated and modified for catalytic

reduction of CO<sub>2</sub> to valuable energy resources [13]. Due to the unique characteristics like high thermal conductivity, zero bandgap semiconductor [14], large surface area [15], good tensile strength and high electron mobility, graphene offers various catalytic applications [16–18]. The electronic properties can be tuned by doping or adsorbed other materials or atoms with destroying the symmetry of the isolated graphene [19–21]. Due to the presence of mono-vacancy site of defected graphene, the binding affinity of Fe, Al and Ni nanoparticles are significantly enhanced thereby increasing the surface reactivity of the nanoparticle decorated graphene surface [22–24]. 0D graphene quantum dots (GQDs) due to their tunable bandgap arising due to their reduced size, offer outstanding physical and chemical properties among the carbon based family. Significant applications for graphene like electronics, catalysis, biomedicine, magnetism, energy storage ability [25], optical devices [26], bio-sensors [27] for detecting hazardous analytes including pesticides, antibiotics, heavy metals, and poisonous gases [28–31]. Previous studies showed that catalytic GQD-transition

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## Comparative study of the efficiency of silicon carbide, boron nitride and carbon nanotube to deliver cancerous drug, azacitidine: A DFT study

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### ABSTRACT

Herein we have made a comparative study of the efficiency of three different nanotubes viz. Carbon nanotube (CNT), boron nitride nanotube (BNNT) and silicon carbide nanotube (SiCNT) to deliver the cancerous drug, Azacitidine (AZD). The atomistic description of the encapsulation process of AZD in these nanotubes has been analyzed by evaluating parameters like adsorption energy, electrostatic potential map, reduced density gradient (RDG). Higher adsorption energy of AZD with BNNT ( $-0.66\text{eV}$ ), SiCNT ( $-0.92\text{eV}$ ) compared to CNT ( $-0.56\text{eV}$ ) confirms stronger binding affinity of the drug for the former than the later. Charge density and electrostatic potential map suggest that charge separation involving BNNT and CNT is more prominent than SiCNT. Evaluation of different thermodynamic parameters like Gibbs free energy, enthalpy change revealed that the overall encapsulation process is spontaneous and exothermic in nature and much favorable with BNNT and SiCNT. Stabilizing interactions of the drug with BNNT and SiCNT has been confirmed from RDG analysis. ADMP molecular dynamics simulation supports that the encapsulation process of the drug within the NT at room temperature. These results open up unlimited opportunities for the applications of these NTs as a drug delivery system in the field of nanomedicine.

### 1. Introduction

In the past few decades, different attempts have been made to develop efficient drug delivery systems to overcome the limitations of conventional drug therapies, including restricted solubility, limited circulating time, insufficiency of selectivity, negative pharmacodynamics, and unfavorable side effects [1–4]. Normally, the available traditional drugs have inherent limitations viz. They are hydrophobic and poor water soluble, restricting their pharmacological effectiveness and presenting difficulties for systemic delivery [5,6]. A small fraction of the administered drug molecules reaches the target site of interest while

gastrointestinal system, kidneys, liver, and other organs of the body inactivate or remove the drugs. Therefore, higher doses of drugs should be delivered in order to achieve an optimized concentration which invites the risk of side effects [7,8]. The toxicity profile of the drug like azacitidine is quite high and results in myelosuppression, mostly manifesting itself as neutropenia and thrombocytopenia. However, patients with severe cytopenias from their disease may find it difficult to assess toxicity [2,9,10]. In this context, innovative drug delivery systems are needed urgently to overcome the limitations of traditional drug delivery methods.

The discovery of nanotechnology paves the way in developing the

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