# AGGREGATION MECHANISMS OF 1-NM DIAMETER NIO NANOCLUSTERS

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**Abstract.** The aggregation processes of NiO nanoparticles have been studied to some extent in ideal environments, i.e., gas and aqueous solutions, but their interaction mechanisms between aqueous media and nanoclusters are still not fully understood. In this work, the environmental effect on the aggregation process of NiO nanoclusters with a size of about 1 nm has been studied using molecular dynamics simulations. Obtained results show that (1) nanoclusters are located at a longer distance from each other in aqueous media in comparison to vacuum due to the hydrodynamic shell (with a thickness of 0.08 nm) formed around the NiO nanoaggregates affected by the aqueous environment, and (2) the stability of NiO nanoclusters in the water environment decreases as a result of the formation of the hydrodynamic shell. Overall, these results suggest that a better understanding of the tuning of nanocatalyst size will lead to the selective synthesis of nanomaterials with unique properties, which are the basis of nanotechnology.

***Keywords:*** *nickel oxide nanocluster, aggregation, stability, reactive molecular dynamics, hydrodynamic shell.*

## Introduction

Currently, nanomaterials, especially, nanoparticles with unique mechanical, optical and electronic properties, which are fundamentally different from the properties of micro-sized particles, are of great importance in modern nanotechnology [1-3]. In particular, in current nanotechnology, one of the priority tasks is to obtain nanoparticles that can replace expensive metal (such as Au, Ag, and Pt) nanoparticles and their industrial application [4].

One such nanoparticle is nickel oxide (NiO) nanoparticles, which are widely used nowadays in creating catalysts [7, 8], solar panels [9], gas sensors [10, 11], and high-thermal-conductivity nanofluids [12] due to their wide bandgap (3.6–4.0 eV) [5, 6] and photocatalytic properties [13], as well as their low cost [14]. In this respect, their homogeneity and monodispersity are key factors for the aforementioned applications [15].

Several experimental studies reported that the aggregation of NiO nanoparticles, followed by their synthesis, significantly affects the surface-related properties of the nanoparticles, thereby leading to a considerable reduction of their catalytic activity [16,17]. In particular, in the sol-gel method, a high calcination temperature of 1073 K is generally required for the synthesis of homogeneous NiO nanoparticles [18,19]. However, temperatures higher than the optimum result in a drastic increase in the rate of nanoparticle aggregation, causing the formation of large-sized NiO nanoparticles [16-20]. In addition, controlling the size of nanoparticles in different environments [10], interpreting the mechanisms of diffusion phenomena [21] that occur due to the interaction of nanoparticles with the molecules of the environment, as well as increasing the heat transfer efficiency of nanofluids [22], the study of processes of nanoparticle aggregation is of fundamental importance [23].

Although the aggregation processes of NiO nanoparticles have been partially studied in ideal environments (i.e., in gas and liquid media) [24-27], their characteristics in the liquid environment have not been sufficiently studied at the molecular level [28,29]. In particular, while the heat transfer property of nanofluid is improved due to the increase in the concentrations of NiO nanoparticles [12], the increase in the concentration of nanoparticles above the limit (e.g., 0.6% mass fraction [30]) leads to the formation of nano-aggregates in a nanofluid. As a result, the sedimentation of nanoparticles (i.e., a layer) occurs, and "solid-liquid" phases emerge in the nanoparticle solution [31]. This leads to a change in the state of the nanoparticle solution and a deterioration in the heat dissipation properties of the nanoparticle solution [32,33]. To determine the size of nano-aggregates using transmission electron microscopy (TEM) in a liquid environment, the sample needs to be kept at a very low temperature. Because such experimental conditions affect the processes of interaction between the environment and nanoparticles, it remains difficult to create a complete scientific picture of the basic mechanisms of the interaction of nano-aggregates in the environment [34,35]. Therefore, in this study, the influence of the water environment on the process of aggregation of NiO nanoclusters at room temperature is investigated by computer simulations.

## Simulation details

Reactive molecular dynamics (MD) simulations are performed to study the aggregation processes of NiO nanoparticles. In the MD simulations, the position and velocity of each atom in the thermodynamic system are determined by solving Newton's equations of motion. In the simulations, the interaction between Ni and O atoms in the system is described using the ReaxFF potential, which is based on the parameters developed by Zou and others [36].

As model systems, $Ni_{55}O_{55}$ nanoclusters with a diameter of about 1.15 nm are used. The size of these nanoclusters is close to the experimentally reported size of 1.48 nm [37] and other MD results, i.e., 1.30 nm [38]. To study the effect of the medium on the aggregation of Ni and NiO nanoclusters, simulations are carried out in a vacuum and water. The structural, static and dynamic parameters of the water model selected as the environment in the simulations are consistent with the theoretical and experimental values [39]. In particular, the length of the chemical bond between hydrogen and oxygen atoms in the water environment is 0.098 nm and the H-O-H bond angle is 104.50, which correspond to the experimentally [40] and theoretically [41, 42] obtained results. In a vacuum, the thermodynamic system consists of two $Ni_{55}O_{55}$ nanoclusters (220 atoms in total), and in a water environment, the system contains two $Ni_{55}O_{55}$ nanoclusters and 2055 water molecules (6385 atoms in total) (Fig. 1). Before the simulations, two NiO nanoclusters are placed at the same distance (1.56 nm) from each other in both environments.

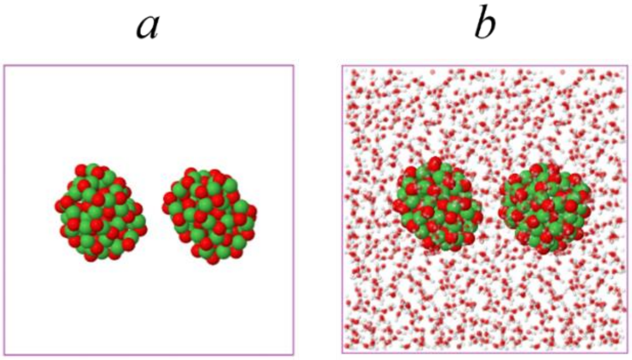

**Fig. 1. NiO nanoclusters in vacuum (a) and water (b) environments. Here, Ni, O, and H atoms are shown in green, red, and white colors, respectively.**

The size of the simulation box is 4×4×4 $nm^3$. Taking into account the interaction radius of atoms with each other, $r_{cut}$ = 1 nm [35], the dimensions of the simulation box are chosen sufficiently large ($>2r_{cut}$). Periodic boundary conditions are applied along all directions of the simulation space. The energy of the model system is initially minimized using the steepest descent and conjugate gradient methods. Then, the system is heated up to 300 K with a heating rate of 1 K/ps employing the Nose-Hoover thermostat [43] in the NVT ensemble and kept at this temperature for 2 ns. In all simulations, a time step of 0.5 fs is chosen. The stability of NiO nanoparticles is estimated by the molar Gibbs free energy ($\delta$G) [44]:

$$\delta G = E_{coh} - \sum \chi_i \, \mu_i \tag{1}$$

where $E_{coh}$ is the cohesive energy per atom of the system, $\chi_i$ and $\mu_i$ are the ratio of the concentration of type *i* atoms in the system to the concentration of total atoms in the system, and chemical potential of type *i* atom, which is equal to -4.45 eV and -2.8 eV for Ni and O atoms, respectively [44].

## Results and discussion

The approach of NiO nanoclusters in vacuum and aqueous media is evaluated by the distance between the surfaces of the nanoclusters. Fig. 2*a* demonstrates a dependence of the distance between the surfaces of nanoclusters as a function of simulation time.

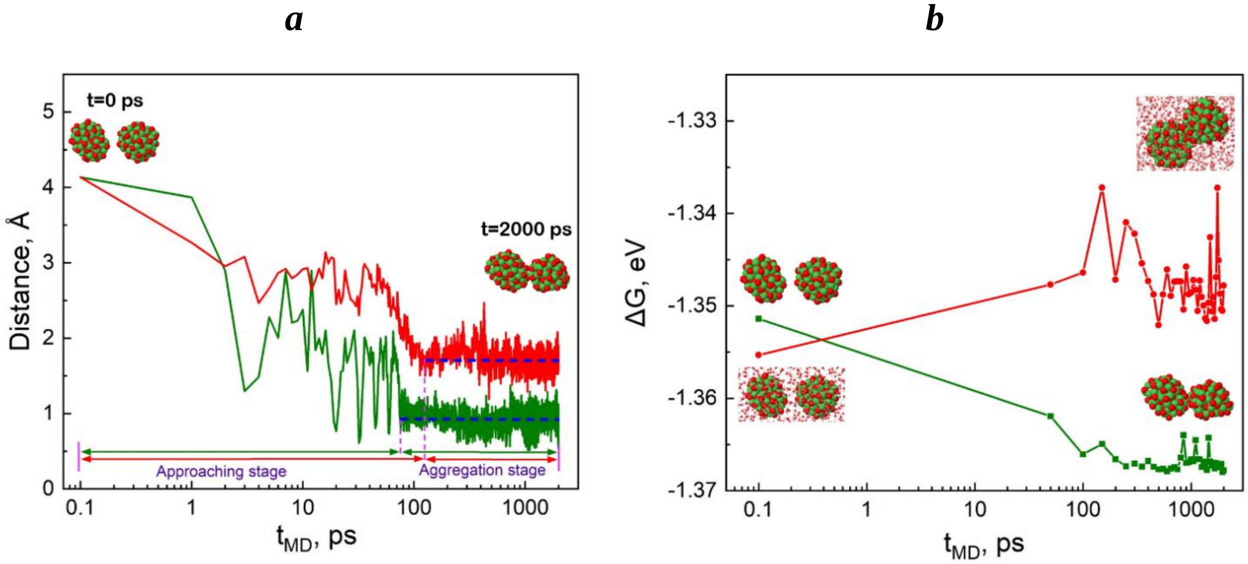

**Fig. 2. (a) Time dependence of the average distance between the surfaces of NiO nanoclusters in vacuum (green) and water (red), and (b) molar Gibbs free energy of the system.**

The aggregation process of NiO nanoclusters can be analyzed by dividing it into two stages: (i) “ the approach” and (ii) “aggregation” stages. In the first stage, the average distance between nanocluster surfaces continues to decrease over time. However, in the second stage, the average distance between nanocluster borders remains constant throughout the simulation time. In a vacuum, the first and second stages proceed for 74 ps (0–74 ps) and 1926 ps (74–2000 ps), whereas in a water environment, these stages last for 125 ps (0–125 ps) and 1875 ps (125–2000 ps), respectively. As is clear, the process of nanocluster aggregation occurs with a delay of 51 ps in water compared to vacuum. This phenomenon can be explained by a decrease in the diffusion coefficient of NiO nanoclusters in an aqueous medium, according to the Stokes-Einstein rule [46], due to an increase in the viscosity of the “nanocluster-aqueous medium” system [45]. The average distance between nanocluster borders is initially ($t = 0$ ps) equal to 0.41 nm in both vacuum and aqueous environments. In the first stage, this distance decreases sharply to approximately 0.09 nm in a vacuum and 0.17 nm in a water environment, which indicates that NiO nanoclusters are located a little far from each other in an aqueous environment compared to a vacuum.

The results also show that the thickness of the layer formed between the surface of NiO nanoclusters and the liquid phase is about 0.08 nm. Experimental studies conducted by Yu and others [47, 48] reported the formation of a hydrodynamic shell around the nanoclusters in an aqueous solution, with a maximum size of 0.1 nm. Hence, the simulation results are consistent with these experimental outcomes.

The molar Gibbs free energy (see formula (1)) is used to evaluate the stability of the nanoaggregates [26]. In particular, Fig. 2*b* shows the molar Gibbs free energies over time for NiO nanoclusters in vacuum and water. The results indicate that in a vacuum, the initial value of the molar Gibbs free energy of NiO nanoclusters (-1.351 eV) decreases slowly during the approaching stage, while during the aggregation stage, the energy remains almost constant at around -1.367 eV. In the case of a water environment, different results are obtained compared to the case of a vacuum. In particular, the molar Gibbs free energy of the nanoclusters in water initially starts at the smallest value of -1.355 eV and gradually increases up to a constant value of -1.35 eV. The obtained results suggest that the interaction between the nanoaggregate and water leads to a decrease in its stability compared to that in a vacuum. Although Y. Zang et al. reported that the aggregation of various metal oxide nanoparticles in an aqueous medium is more stable than in a vacuum [49], data on the aggregation of exactly NiO nanoparticles are not found in the literature. The fact that our results on NiO nanoparticles do not correspond to the results of experimental studies on the stability of other nanoclusters in aqueous media can be explained by the fact that the nanoclusters have a relatively small size. Specifically, the size of the NiO nanoclusters in this study is relatively small (approximately 10–20 times smaller) than the size of the nanoparticles studied in experimental measurements [47], which suggests that their stability may also be reduced due to a decrease in the size of the cluster in a water environment, by the results reported in other studies [50]. Based on the abovementioned considerations, our results suggest that the stability of the nanoaggregates formed as a result of the aggregation of small (1.15 nm in size) NiO nanoclusters in an aqueous environment is decreased due to the formation of a hydrodynamic shell [45, 46].

## Conclusions

In this work, the mechanisms of the aggregation process of NiO nanoclusters were studied by the reactive molecular dynamics (MD) method. The results showed that due to the formation of a hydrodynamic shell between NiO nanoclusters with a thickness of about 0.08 nm in the aqueous environment, the nanoclusters are located at a greater distance from each other than in a vacuum. This distance is consistent with the experimental thickness, and the obtained results help to better understand the formation mechanisms of the hydrodynamic shell on the aggregation process. In addition, the decrease in the stability of NiO nanoclusters in the water environment as a result of the formation of a hydrodynamic shell was evaluated by the molar Gibbs free energy. Also, this phenomenon does not correspond to experimental evidence, the results of the simulations can be interpreted as a decrease in the size of the nanoclusters, which has not been experimentally studied. Overall, this study helps to understand the nature of the aggregation of NiO nanoclusters with a diameter of around 1 nm at the atomic level and gives suggestions about the control of the monodispersity of nanocatalysts.

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