

Structure, Interaction, and Dynamics of Au/Pd Bimetallic Nanoalloys Dispersed in Aqueous Ethylpyrrolidone, a Monomeric Moiety of Polyvinylpyrrolidone

by

Aditi Gupta, Bundet Boekfa, Hidehiro Sakurai, Masahiro Ehara, U Deva Priyakumar

in

Physical chemistry

Report No: IIIT/TR/2020/-1



Centre for Computational Natural Sciences and Bioinformatics
International Institute of Information Technology
Hyderabad - 500 032, INDIA
May 2020

Structure, Interaction, and Dynamics of Au/Pd Bimetallic Nanoalloys Dispersed in Aqueous Ethylpyrrolidone, a Monomeric Moiety of Polyvinylpyrrolidone

Aditi Gupta,[†] Bundet Boekfa,[‡] Hidehiro Sakurai,[§] Masahiro Ehara,^{*,‡} and U. Deva Priyakumar^{*,†}

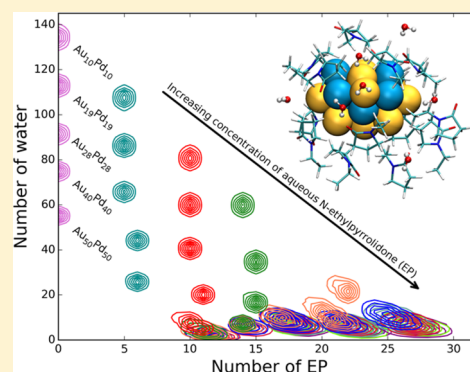
[†]Center for Computational Natural Sciences and Bioinformatics, International Institute of Information Technology, Hyderabad 500 032, India

[‡]Research Center for Computational Science, Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan

[§]Division of Applied Chemistry, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan

S Supporting Information

ABSTRACT: Bimetallic nanoparticles (NPs) have been shown to exhibit certain advantages over pure NPs in catalysis due to a synergistic effect. It is common to disperse NPs in a polymer matrix such as polyvinylpyrrolidone (PVP) to prevent flocculation, which imparts considerable electronic effects on the NPs. In the present study, the interactions between aqueous solutions of *N*-ethylpyrrolidone (EP, system chosen to model the monomeric form of PVP) and Au/Pd bimetallic NPs, which are relevant in catalysis, have been investigated using molecular dynamics simulations and density functional theory (DFT) method. The adequacy of the force fields used was assessed based on their ability to reproduce the structures and adsorption energies obtained using DFT calculations. The interactions of NPs with the environment were studied at various concentrations of aqueous solutions of EP to examine the strength of NP–EP and NP–water interactions. Free energy calculations and local mole fraction enhancement values show that the EP adsorption on NPs is preferred over the adsorption of water. Extensive analysis of the interactions of the NPs with various concentrations of aqueous EP suggests the existence of isolated water molecules that may take part in reactions. Adsorption of unexpectedly large numbers of EP molecules was found to be possible leading to accumulation of the electron density on the Au/Pd NPs, which have previously been shown to enhance the catalytic activity of NPs. This study emphasizes the importance of including the electronic effects on the NPs due to the adsorption of stabilizing agents in modeling and demonstrates the utility of MD simulations to generate appropriate model chemistries for studying catalysis at higher level quantum chemical and density functional theory calculations.



INTRODUCTION

Metal nanoparticles (NPs) find potential applications in wide ranging areas such as catalysis, microelectronics, solar energy, sensing, photonics, information storage, and medicine due to their unique electronic, optical, and mechanical properties.^{1–8} This is in part because the NPs in the nanometer length scale exhibit unique shape- and size-dependent properties that are completely different from those of individual atoms or bulk matter. Lately, the use of nanoparticles in catalysis has gained interest since heterogeneous catalysis has enormous applications in chemical manufacturing processes.⁹ A few of the examples of the use of nanoparticles in catalysis include the use of Au nanoparticles in the low-temperature oxidation of CO, water–gas shift reaction, and the partial oxidation of hydrocarbons.^{10–13} Pd-based nanocatalysts are also employed in alkaline fuel cells for chemicals and energy cogeneration.¹⁴ Due to its wide applicability, nanocatalysis is currently perceived as a huge leap in the field of catalysis. Lopez et al. have shown that CO oxidation by gold NPs depends primarily on the particle

size.¹⁵ It has been suggested that small metal clusters display nonmetallic properties with low coordinated atoms in high densities. In addition to the size of NPs, their shape has also been shown to dictate their catalytic efficiency. Tian et al. have reported the enhanced catalytic activity of tetrahedral Pt nanoparticles for the electro-oxidation of formic acid and ethanol as compared to equivalent Pt surface areas of NPs with different shapes (e.g., nanospheres).¹⁶

There is growing evidence that suggests the advantages of utilizing bimetallic NPs (nanoalloys) like Au/Pd NPs that often exhibit synergistic effect in catalysis.^{17–23} It is possible to design bimetallic NPs with the desired physicochemical properties by varying the composition, size, and atomic ordering of the clusters. TiO₂-supported Au/Pd NPs have been shown to catalyze the direct synthesis of H₂O₂ from H₂ and O₂

Received: May 20, 2016

Revised: July 16, 2016

Published: July 19, 2016

significantly better than TiO_2 -supported pure Pd or Au NPs.²² Similar results were obtained when Au/Pd catalysts supported on Fe_2O_3 were used for H_2O_2 synthesis.²¹ The reaction rate of CO oxidation reaction has been shown to be remarkably high at a Au/Ag molar ratio of 3:1 at 250 K, whereas neither of the monometallic species shows any activity at this temperature.²³ Recently, a unique homocoupling reaction via C–Cl bond activation has been achieved with Au/Pd NPs at low temperature.²⁰

Pristine metal NPs in solution tend to lower their energy by adsorbing molecules from the surroundings or by lowering their surface energy through coagulation. Nanoparticle coagulation decreases the active surface area, thereby reducing their catalytic activity. Stabilizing agents are commonly used to prevent this, which can broadly be classified as electrostatic, steric, and their combination, electrosteric stabilizers. In the electrostatic stabilization, the stability is achieved by the Coulombic repulsion between NPs that arises from the electric double layer of ions adsorbed at the particle surface. Steric stabilization is attained by adsorption of bulky organic molecules such as polymers, and electrosteric stabilization combines the two mechanisms.^{24,25}

Polyvinylpyrrolidone (PVP), a water-soluble polymer (Figure 1a), is a commonly used steric stabilizer that adsorbs on metal

pyrrolidinone are selectively adsorbed on silver and gold colloid surfaces preferably via the nonbonding electrons of the carbonyl group.³⁰ These results were further supported by a combined DFT/FTIR structural study of monodispersed PVP adsorbed Au and Ag NPs.³¹ While the effect of the adsorbed stabilizers is indispensable, the atomistic details of the structure and dynamics of polymer-dispersed NPs are not well understood.

Molecular dynamics (MD) simulations have been used to investigate NPs interacting with adsorbents such as polymers, surfactants, proteins, DNA, lipids, and dendrimers.^{32–39} However, interactions of polymers with metal NPs and the associated change in the solvation dynamics and electronic effects are still not clear. In the present study, MD simulations and DFT methods have been used to investigate the interactions between aqueous solutions of a monomeric form of PVP (*N*-ethylpyrrolidinone referred to as EP in the rest of the manuscript) and five Au/Pd bimetallic NP model systems (Figure 1). Since it has been shown that adsorption of EP on metal NPs affects their catalytic activity and that inclusion of this effect is crucial in accurate modeling of reaction energy pathways, we have explored the use of MD simulations to obtain appropriate model chemistries that could be used in QM/DFT calculations. A systematic study has been performed by validating the results from MD simulations using DFT calculations, and the EP–NP interactions have been studied at various concentrations of aqueous EP.

■ COMPUTATIONAL METHODS

Five bimetallic Au/Pd NPs of different sizes were chosen as the model systems for the MD simulations: $\text{Au}_{10}\text{Pd}_{10}$, $\text{Au}_{19}\text{Pd}_{19}$, $\text{Au}_{28}\text{Pd}_{28}$, $\text{Au}_{40}\text{Pd}_{40}$, and $\text{Au}_{50}\text{Pd}_{50}$ (Figure 1b). The topological structures of these Au/Pd NP models were generated using the Birmingham Genetic Algorithm (GA) calculations.^{40,41} The Gupta potentials with three parameter sets (DFT-fit, experimental-fit, and averaged) proposed in the previous work⁴² have been adopted in GA calculations to locate the stable structures. The most stable structures of the fcc-type cuboctahedral shape were obtained with the DFT-fitted parameters and were utilized in the MD simulations. The $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$ structures are energetically preferred in agreement with the previous DFT studies.^{29,42,43} The core of these structures is mostly formed by Pd atoms with the shell dominated by Au atoms (see Figure S1).

All MD simulations were performed using the NAMD program⁴⁴ employing the Lennard-Jones (LJ) potentials for metals obtained by Heinz et al.,⁴⁵ CHARMM force field for EP recently reported by Fichthorn and co-workers,⁴⁶ and the TIP3P water model.⁴⁷ Solvent boxes of various concentrations of aqueous EP (Table 1) of sizes $30 \times 30 \times 30 \text{ \AA}^3$ (Au_nPd_n , $n = 10$ and 19) and $40 \times 40 \times 40 \text{ \AA}^3$ (for $n = 28, 40$, and 50) were obtained by including a requisite number of EP molecules in pre-equilibrated water. The box dimensions were chosen based on the dimensions of the NPs considered here (8.11, 8.99, 10.66, 12.21, and 14.74 $\text{\AA}$ for $\text{Au}_{10}\text{Pd}_{10}$, $\text{Au}_{19}\text{Pd}_{19}$, $\text{Au}_{28}\text{Pd}_{28}$, $\text{Au}_{40}\text{Pd}_{40}$, and $\text{Au}_{50}\text{Pd}_{50}$ respectively). The concentration of aqueous EP is defined here in terms of the percentage of EP molecules relative to the number of water molecules (eq 1). The five NP model systems were immersed in the solvent boxes; overlapping water/EP molecules were deleted; and the resultant systems were subjected to energy minimization with weak harmonic constraints on the NPs. MD simulations in the NPT ensemble were performed on these configurations for 1 ns

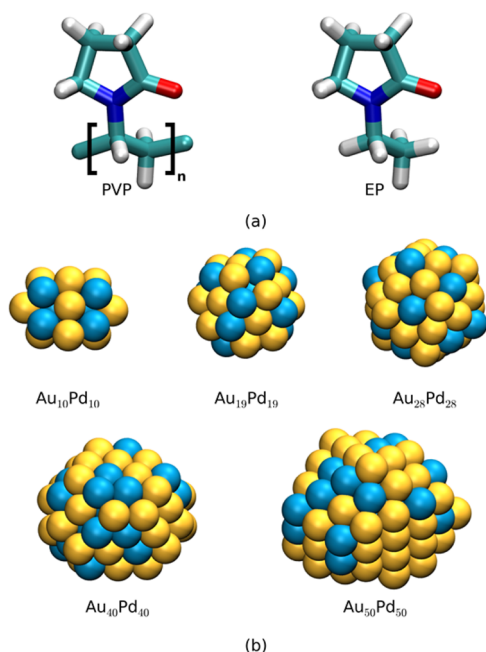


Figure 1. (a) Structures of PVP and EP. (b) Nanoparticles of different sizes having Au:Pd ratio of 1:1 used as the models: $\text{Au}_{10}\text{Pd}_{10}$, $\text{Au}_{19}\text{Pd}_{19}$, $\text{Au}_{28}\text{Pd}_{28}$, $\text{Au}_{40}\text{Pd}_{40}$, and $\text{Au}_{50}\text{Pd}_{50}$. Au and Pd atoms are represented by yellow and blue colors, respectively.

NP surfaces and prevents agglomeration. Previous studies have suggested that stabilizing agents have a significant effect on the catalytic properties of metal NPs.^{26,27} However, in theoretical modeling of reactions involving metal NPs, pristine metal clusters are often employed as model systems ignoring the electronic effects the stabilizer may have on the NPs. Studies have shown that the electronic structure of the metal NPs is significantly modified upon adsorption of PVP.^{28,29} Employing surface-enhanced Raman spectroscopy and DFT calculations, Revaprasadu et al. showed that pyrrolidinone and *N*-methyl-2-

Table 1. Description of the Systems Chosen for MD Simulations^a

S. no.	Au ₁₀ Pd ₁₀			Au ₁₉ Pd ₁₉			Au ₂₈ Pd ₂₈			Au ₄₀ Pd ₄₀			Au ₅₀ Pd ₅₀		
	N _{ep}	N _w	% EP	N _{ep}	N _w	% EP	N _{ep}	N _w	% EP	N _{ep}	N _w	% EP	N _{ep}	N _w	% EP
1	0	710	0	0	695	0.00	0	2021	0.00	0	2007	0.00	0	1992	0.00
2	6	693	0.87	6	681	0.88	5	2004	0.25	5	1990	0.25	5	1975	0.25
3	11	677	1.62	11	669	1.64	10	1990	0.50	10	1976	0.51	10	1961	0.51
4	16	662	2.42	16	663	2.41	15	1975	0.76	15	1961	0.76	15	1944	0.77
5	22	644	3.42	22	654	3.36	23	1952	1.18	23	1938	1.19	22	1925	1.14
6	31	621	4.99	31	631	4.91	33	1928	1.71	33	1915	1.72	32	1902	1.68
7	47	570	8.25	46	562	8.19	45	1893	2.38	43	1882	2.28	43	1869	2.30
8	66	482	13.69	64	475	13.47	60	1854	3.24	57	1843	3.09	57	1830	3.11
9							83	1779	4.67	79	1768	4.47	79	1755	4.50
10							120	1673	7.17	116	1661	6.98	116	1649	7.03
11							164	1557	10.53	159	1546	10.28	159	1534	10.37

^aN_{ep} and N_w are the numbers of EP and water, respectively, that form the simulation box. % EP is the percentage of EP in the system as given in eq 1.

retaining the harmonic restraints followed by production simulations of 100 ns without any restraints. Constant temperature and pressure were employed by using Langevin dynamics and Langevin pressure piston approaches, respectively. An integration time step of 2 fs was used in all the MD simulations, and the SHAKE algorithm⁴⁸ was used to constrain all covalent bonds involving hydrogen atoms. All results presented from the 100 ns MD simulations here are based on calculations done every 5 ps for the last 80 ns of the trajectories.

$$\% \text{ EP} = \frac{N_{\text{ep}}}{N_{\text{w}}} \times 100 \quad (1)$$

Free energy calculations using the thermodynamic integration method were performed to quantify the binding affinity of the Au₁₀Pd₁₀ NP in different environments. The transfer free energies corresponding to the NP going from the gas phase to the water/aqueous EP solution phase and vice versa were calculated. In the alchemical transformation setup involving transformation of one chemical species to another, a hybrid Hamiltonian is used that is a function of the coupling parameter λ , which smoothly connects the two states (eq 2). Here, $H_{\text{a}}(x, p_x)$ and $H_{\text{b}}(x, p_x)$ describe the interactions of the group of atoms representing the initial state (a) and the final state (b) with the rest of the system, and $H_0(x, p_x)$ describes the atoms that do not undergo any transformation.

$$H(x, p_x; \lambda) = H_0(x, p_x) + \lambda H_{\text{b}}(x, p_x) + (1 - \lambda) H_{\text{a}}(x, p_x) \quad (2)$$

The thermodynamic integration method calculates the free energy difference by taking the derivative of the free energy with respect to λ . The derivative is collected for a series of discrete λ values, and the total free energy is determined by integrating over the whole range of λ (eq 3).⁴⁹

$$\Delta A = \int_0^1 \left\langle \frac{\partial H(x, p_x; \lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda \quad (3)$$

The structures obtained after the 100 ns production simulations were used for these calculations with the desolvated and solvated NPs as the initial and final states, respectively. The value of the coupling parameter λ was varied from 0 to 1 over steps of 0.01. For each intermediate value of λ , 600 ps (a cumulative time of 62 ns for each of the eight systems) of NPT simulations were performed using soft-core van der Waals

potential for robust sampling of the free energy of the system. Convergence of the transfer free energies was verified by comparing the calculated solvation and desolvation free energy values.

For the structural, dynamic, and energetic analyses, CHARMM⁵⁰ and VMD⁵¹ programs were employed. Interaction energies were calculated based on the potential energy function as defined by the CHARMM force field,⁵² and the numbers of molecules adsorbed were calculated with a cutoff distance of 4.5 Å between any atom on the NP and the carbonyl oxygen of EP/oxygen of water. The cutoff distance of 4.5 Å was decided based on the radial distribution functions corresponding to the interactions between Au/Pd and the oxygen atom of EP (see Results and Discussion). The preference of NPs toward EP versus water molecules was quantified by calculating the local mole fraction enhancement (LMFE) which is the ratio of the local mole fraction and the bulk mole fraction (eq 4).

$$L_{\text{ep}}(r) = \frac{1}{x_{\text{ep}}} \left[\frac{\text{NI}_{\text{ep}}(r)}{\text{NI}_{\text{ep}}(r) + \text{NI}_{\text{water}}(r)} \right] \quad (4)$$

Here, x_{ep} is the mole fraction of EP, and NI is the number integral or the number of molecules of each type up to a distance $r = 4.5$ Å from the NPs.^{53,54} LMFE represents the change in the mole fraction of EP in the local domain of the nanoparticle due to preferential adsorption of EP molecules at the nanoparticle surface.

DFT calculations using the M06-L functional⁵⁵ were performed for the Au₁₀Pd₁₀ NP structure to which different numbers of EP molecules are adsorbed. M06-L has been shown to describe the stability of different spin states of Au/Pd NPs adequately, which has been validated by coupled cluster reference calculations.²⁹ Geometry optimizations were performed for the structures of Au₁₀Pd₁₀:EP_{*m*} employing the LANL2DZ relativistic effective core potential (RECP)^{56,57} for the Au and Pd atoms and 3-21G basis set⁵⁸ for the C, N, O, and H atoms. Single-point energy calculations were performed using the LANL2DZ and 6-31G(d,p)^{59–62} to calculate the adsorption energies. Molecular mechanics (MM) was also used to calculate the adsorption energies of these model systems using the results from energy minimization with the force fields mentioned above. All the DFT and MM calculations were performed using the Gaussian 09⁶³ and the CHARMM⁵⁰ programs, respectively.

RESULTS AND DISCUSSION

Structures of EP-Adsorbed Nanoparticle Model Systems. Molecular dynamics simulations were performed on five different Au/Pd NPs (Figure 1) in water and in the presence of different concentrations of aqueous EP. Initially, the adequacy of the force-field parameters used here was assessed by comparing the structures of selected model systems and interaction energies between the NP and EP molecules with DFT results. Configurations where Au₁₀Pd₁₀ NP directly interacts with 1, 2, 4, 6, 8, 10, 12, and 14 EP molecules were obtained from the MD trajectories and were subjected to MM minimization. These configurations were also subjected to geometry optimization at the M06-L level of theory. Irrespective of the number of EP molecules adsorbed, the structures of NP (without the adsorbed EP molecules) obtained using the two levels are almost identical. This further demonstrates the versatility and suitability of the model proposed by Heinz et al.⁴⁵ Figure 2 compares the structures

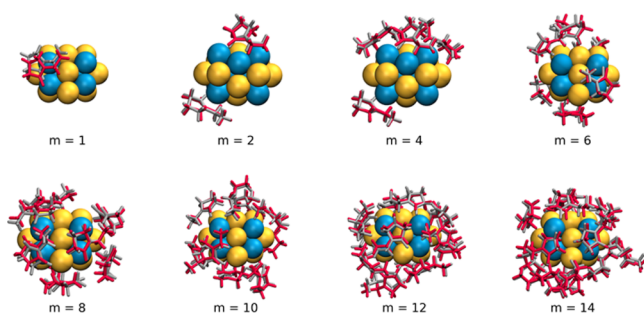


Figure 2. Optimized structures of the Au₁₀Pd₁₀–EP_{*m*} complexes. The geometries of the EP molecules obtained by MM and DFT-M06-L methods are depicted in red and gray colors, respectively. The structures were aligned with respect to the NP.

obtained after optimization using MM and M06-L methods. To examine the differences in the orientations of the EP molecules with respect to the metal NP, the optimized structures of each of the model systems obtained using the two methods were aligned by superimposing one on the other—the alignment was done considering only the NPs and not the adsorbed EP molecules. Marginal differences between the two structures were observed exhibiting root-mean-square deviation values in the range of 0.28–1.49 Å indicating good agreement between the MM and DFT results on their structures. Notable differences in the Au/Pd–O (oxygen of the carbonyl group of EP) distances were observed though the overall structures are very similar. Previous studies have successfully used such models to study the PVP interactions with Ag and Au surfaces^{35,46,64} though rigorous comparison with higher levels of theory on metal NPs is reported here for the first time.

Adsorption Energies of NP–EP Model Systems. In addition to examining how well the MM parameters agree with DFT in terms of obtaining reliable geometries, calculations were done to compare the NP–EP adsorption energies in the complexes shown in Figure 2. Total adsorption energy was calculated as the difference between the energy of the EP adsorbed complex and the sum of the energy of NP and energy of EP molecule multiplied by the number of EP molecules adsorbed. Adsorption energies per EP molecule were calculated by dividing the total adsorption energy by the number of adsorbed EP molecules.²⁹ The adsorption energies per EP molecule obtained using the MM potential energy function and

M06-L level of theory are given in Figure 3. At the DFT level, the magnitude of the adsorption energy gradually decreases

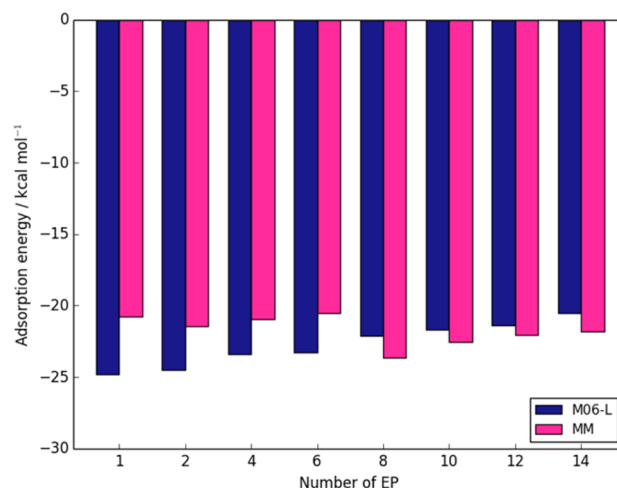


Figure 3. Adsorption energies (kcal mol⁻¹) per EP molecule obtained using the MM potential energy function (magenta) and M06-L level of theory (blue).

with respect to increasing number of adsorbed EP molecules (−24.8 to −20.5 kcal mol⁻¹ when *m* varies from 1 to 14). Such a gradual change of the adsorption energy with respect to the number of adsorbed EP molecules is not observed in the case of the MM method. However, the magnitudes of the interaction energies obtained from the two methods are consistent with each other in all the model systems with minor quantitative differences. Good agreement of the structures and energetics supports the validity of the results of the MD simulations reported here. Discussion in the following sections is based on the MD simulations done on all five NPs in the presence of different concentrations of aqueous EP.

Higher Concentrations of EP Stabilize the NP System.

Initial configurations of all the systems taken for MD simulations correspond to the NP in the center of the box and randomly distributed EP molecules in pre-equilibrated water. During the MD simulations, the EP molecules get adsorbed onto the NPs in the picosecond time scale in all the cases indicating high affinity between the two. Radial distribution functions for the atoms in NPs were calculated (Figure S2 in the Supporting Information), which showed that the NPs were not affected by the environment and retained their structural integrity irrespective of the concentration of EP.

It is very well-known that PVP keeps metal NPs isolated and prevents flocculation. However, the strength of interactions between the two and how they compare at different concentrations are not understood. Initially, the interaction energies between the NP and the surrounding molecules were calculated to examine this. The interaction energies were calculated as the difference between the potential energy of the whole system and sum of the potential energies of the NP and surrounding molecules. The mean interaction energies along with the standard deviations calculated over the last 80 ns of the simulations are presented in Figure 4 (the probability distributions of the interaction energies are given in Figures S3–S7 in the Supporting Information). In all five systems, the interactions between the NP and the surroundings become more favorable with respect to inclusion of EP molecules. However, the energy, which decreases initially, saturates

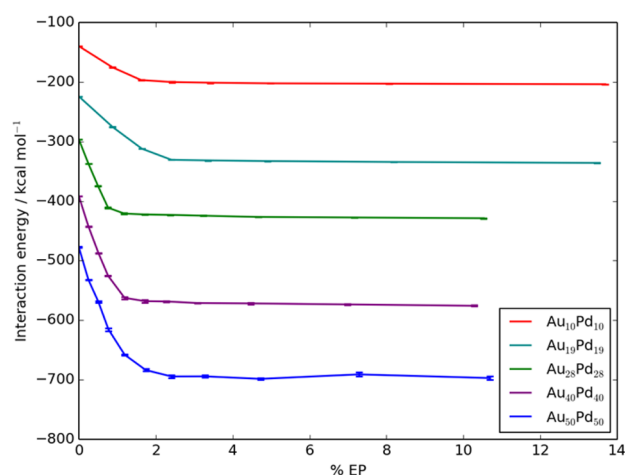


Figure 4. Mean interaction energies of the NPs with the surroundings (EP + water in the simulation box) of each of the systems considered plotted against the % EP in the solution.

beyond a point when no more EP molecules can interact directly with the NP.

The interaction energies were further decomposed into contributions from EP and water to understand the relative affinities of the two to interact with the NPs. Figure 5 depicts the two-dimensional probability distributions corresponding to the interaction energy contributions from water molecules and EP molecules calculated using the last 80 ns of the MD trajectories. All the individual contour plots are given in Figures S8–S12 in the Supporting Information. With respect to an increase in the concentration of aqueous EP, NP–EP interaction energies become more favorable, and expectedly the NP–water interactions become less favorable. While this effect is more pronounced at lower concentrations of aqueous EP, no substantial change is observed at higher concentrations. Convergence of the probability distributions with respect to the increase in the EP content in the surroundings indicates that further adsorption of EP molecules may not be possible even if its concentration is increased in the system. This is further examined by analyzing the structural aspects and adsorption isotherms, which are discussed in the following sections. Any marginal change in the interaction energies after the complete coverage of the NP by EP molecules is deemed to be due to long-range interactions between the NP and EP molecules that are not directly adsorbed. The interactions also are more favorable with respect to the size of the NP expectedly due to an increase in the surface area available for interaction. The solvation free energies of the $\text{Au}_{10}\text{Pd}_{10}$ model system in water and in different concentrations of aqueous NP were calculated using the thermodynamic integration method. Figure 6 depicts the free energies corresponding to transferring of the NPs from the gas phase to water and different concentrations of aqueous EP. Inclusion of EP molecules in the medium leads to substantial stabilization of the system due to favorable NP–EP interactions. The qualitative trends of the strength of NP interactions with the environment obtained using the interaction energies and the free energies are consistent with each other. The structural details of these interactions are presented in the following section.

Substantial Preference of EP Molecules over Water by NPs. The structural details of NP–EP/water interactions were examined by analyzing the number of molecules adsorbed on

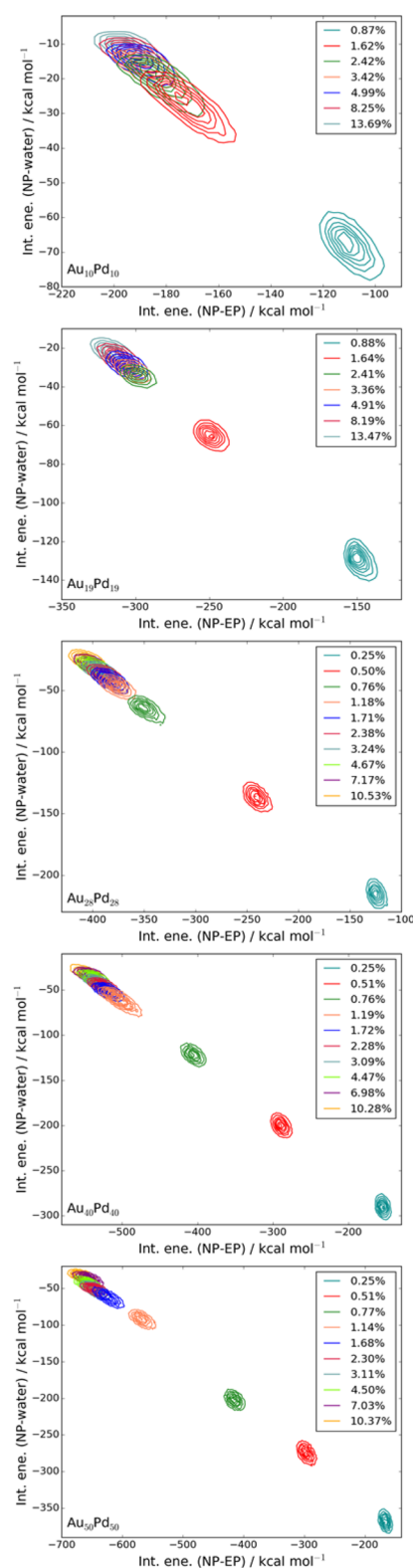


Figure 5. Two-dimensional probability contours of the interaction energies of NP with water and EP molecules for different concentrations of aqueous EP (given in percentage in the insets) for the five nanoparticles.

the NPs and the local mole fraction enhancement. Calculation of the radial distribution functions corresponding to the Au and Pd atoms present on the nanoparticle surface with the oxygen of EP indicates that binding of EP to Au/Pd atoms is equally

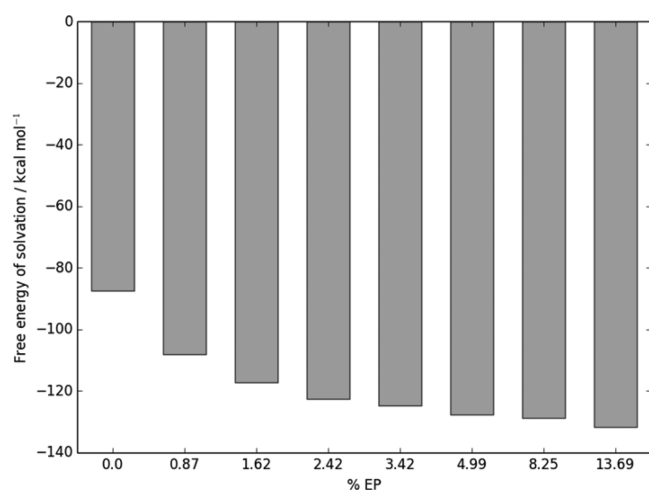


Figure 6. Free energy of solvation (kcal mol^{-1}) of the $\text{Au}_{10}\text{Pd}_{10}$ NP with respect to different environments obtained using the thermodynamic integration method.

preferred (Figures 7 and S28). Probability distributions corresponding to the number of EP and water molecules

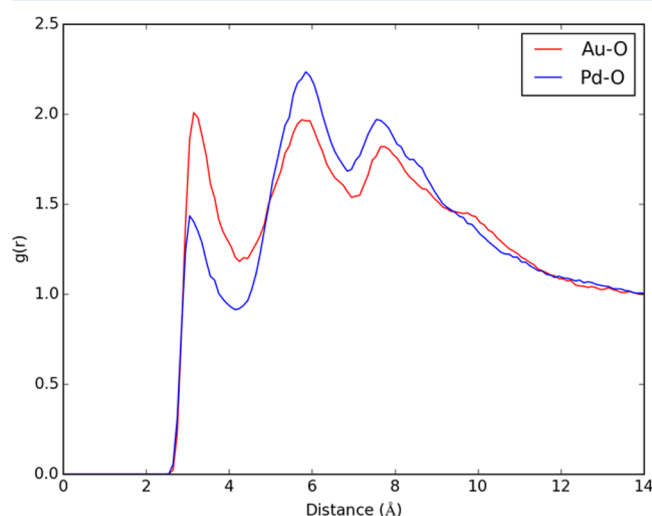


Figure 7. Radial distribution function obtained for Au-O_{EP} (oxygen of the carbonyl group of EP) and Pd-O_{EP} for 13.69% aqueous EP solution of $\text{Au}_{10}\text{Pd}_{10}$.

adsorbed on to the NPs with respect to all the systems are depicted in Figure 8. The individual distributions and one-dimensional probability distributions are depicted in Figures S13–S27 in the Supporting Information. An EP molecule was considered to be adsorbed to the NP if its oxygen atom lies within $4.5 \text{ \AA}$ of the NP. Since a minimum is observed in the $\text{Au/Pd-O}_{\text{EP}}$ radial distribution function approximately at $4.5 \text{ \AA}$, this distance was chosen as the cutoff for determining whether a molecule is adsorbed on the NP or not (Figure 7). Similarly a water molecule is considered to be directly bound to the NP if its oxygen atom lies within $4.5 \text{ \AA}$ of the NP. At lower concentrations of aqueous EP, it is noted that all the EP molecules present in the solvent box get adsorbed to the NP consistent with the energetics discussed above. Accordingly, the number of water molecules directly interacting with the NP decreases with respect to an increase in the number of EP molecules in the solution. The numbers of both EP and water

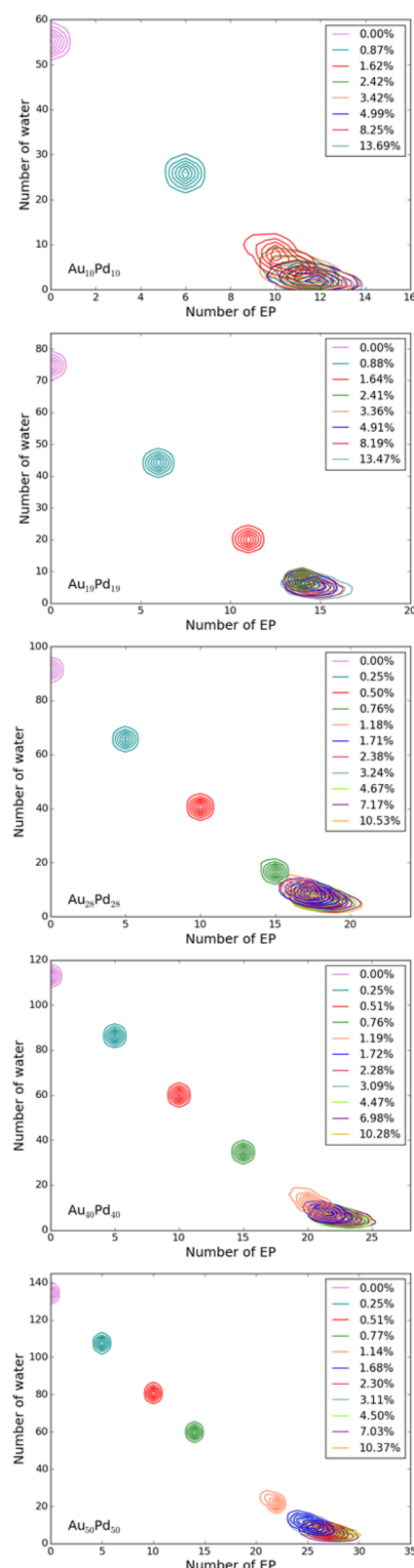


Figure 8. Two-dimensional probability distributions of the number of water and EP molecules interacting with the NPs for different concentrations of aqueous EP (given in percentage in the insets) for the five nanoparticles.

molecules adsorbed on the NP saturate with respect to increasing the total number of EP in the system. Importantly, though NP–EP interactions are substantially stronger than

NP–water interactions, the number of water molecules directly interacting with the NP is nonzero with values of 3 to 6 in the five systems considered here even at saturating concentrations of aqueous EP. This number is expected to be dependent on the shape and size of the NP. The existence of water molecules directly interacting with the NPs is due to the inability of EP to completely cover the NP surface due to size effects. For example, when EP molecules are adsorbed on the surface of a given NP, there may exist a part of the surface too small to accommodate another EP molecule. Such voids between the adsorbed EP molecules accommodate isolated water molecules. This effect will be more pronounced in the presence of polymeric PVP since the individual monomeric units are structurally constrained by the covalent bonds connecting them.^{35,64} Further evaluation shows that these water molecules that directly interact with the NPs are devoid of hydrogen bonds with other water molecules in the system (see below).

From the above sections, it is evident that NPs preferentially interact with EP over water molecules. Enhancements in local mole fraction of EP molecules around NPs were calculated for all the systems to quantify this phenomenon using eq 4 and are depicted in Figure 9. LMFE gives a measure of difference in the

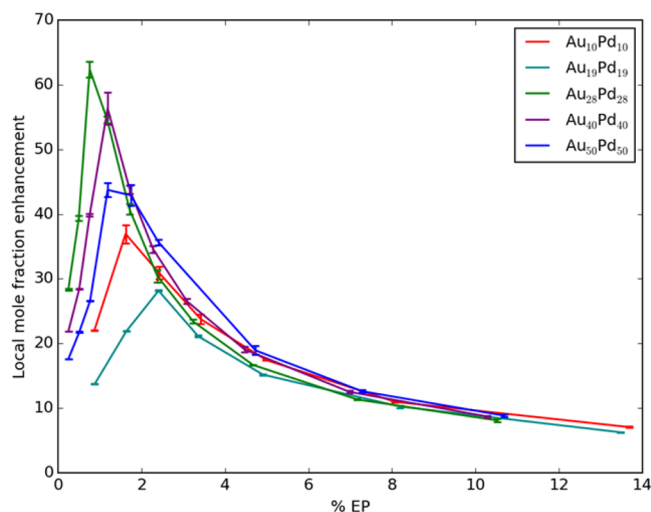


Figure 9. Enhancement in local mole fraction of EP around NPs obtained using eq 4 for each nanoparticle plotted against the % EP in the solution.

change in the concentration of EP closer to the NP versus its concentration in the bulk. A value of 1 for the coefficient means that the concentration of EP near the NPs and the bulk solvent are the same, indicating no enrichment of EP molecules around the nanoparticles. However, irrespective of the concentration of aqueous EP solution, the LMFE values are considerably greater than 1, indicating strong preference of EP over water molecules by the NPs. Lower concentrations of aqueous EP exhibit large values of LMFE since all the EP molecules are adsorbed on the NPs leaving only water in the bulk. The LMFE values fairly converge to a constant value of close to 10 and are independent of the particle size and the simulation box parameters.

The above sections illustrate that irrespective of the high affinity between NPs and EP compared to that between NPs and water few water molecules are found in the first adsorption layer. The nature of Au/Pd–water interactions was further examined by calculating the radial distribution functions corresponding to the Au/Pd atoms with the oxygen atoms of

water (Figures 10a and S29). At lower concentrations of aqueous EP and in pure water, the distribution functions exhibit

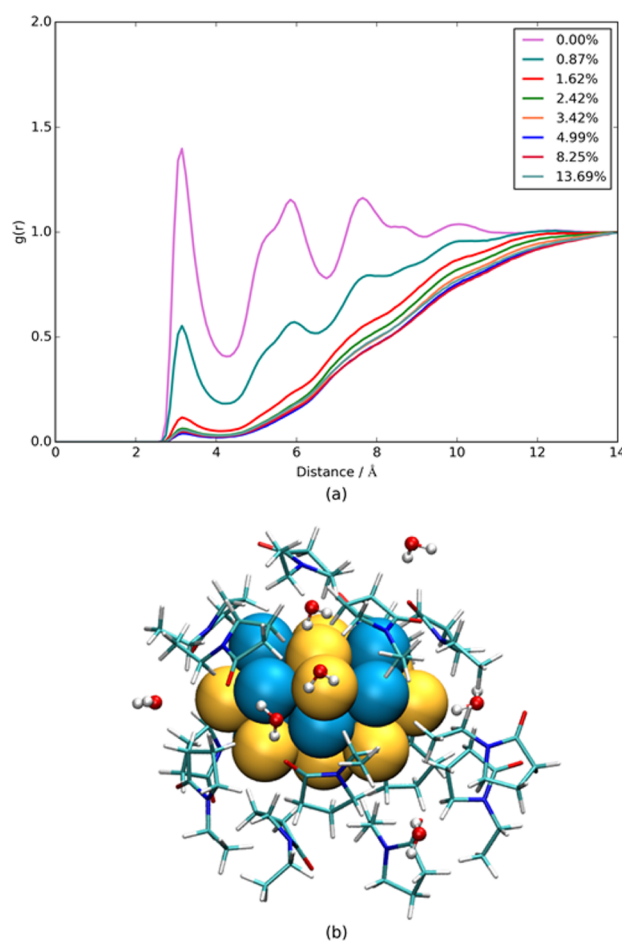


Figure 10. (a) Radial distribution function obtained for Au/Pd–O_{water} for different concentrations of aqueous EP (given in percentage in the insets) for Au₁₀Pd₁₀. (b) High energy water molecules along with EP present at the surface of Au₁₀Pd₁₀.

clear peaks corresponding to the first layer of adsorbed water and second solvation shell. The presence of distinct peaks for the second solvation shell in 0.0 and 0.87% aqueous EP solutions is demonstrative of the hydrogen-bonded interactions that the adsorbed water molecules have with the bulk. However, at higher concentrations of aqueous EP, the radial distribution functions indicate no such hydrogen-bonded interactions between the NP-adsorbed water molecules and the rest of the water molecules in the system. As discussed above, these water molecules fill the voids created by EP-adsorbed NPs when the exposed surface of the NP is not large enough to occupy an additional EP molecule. The absence of the typical second peak suggests that these isolated water molecules present in the first adsorption layer are at a higher energy state compared to bulk water. A snapshot showing the structure of such water molecules present on the surface of Au₁₀Pd₁₀ is given in Figure 10b. Though the surface is mostly devoid of water, such high-energy water molecules may readily participate in reactions that occur on the nanoparticles.⁶⁵ Indeed, water has been shown to assist double proton transfer from DMF (dimethylformamide) to Au/Pd NP, which is the rate-determining step of the reaction and stabilizes the transition state.⁶⁶

Extent of Coverage of the NPs by EP. A straightforward question that arises from the previous discussions is if water directly interacts with the NP, to what extent are the NPs protected by the EP layer? The percentages of the surface area of NPs covered by EP molecules were calculated and were plotted against the number of EPs that are adsorbed on the NPs (Figure 11). The surface area of the NP covered by EP was

$$\% \text{ SA} = \frac{KN_{\text{ep}}^{1/n}}{1 + N_{\text{ep}}^{1/n}} \times 100 \quad (5)$$

Electronic Effects Due to EP Adsorption to NPs.

Investigations of reactions catalyzed by NPs using computational methods are routinely done on small metal clusters, and the changes in the electronic nature of the NPs upon adsorption of the protecting agents such as PVP are often not considered.⁶⁷ Mulliken charges obtained from the DFT M06-L calculations on the $\text{Au}_{10}\text{Pd}_{10}\text{-EP}_m$ systems were analyzed to understand the extent of electron donation by EP molecules to the NPs. The charges on the NP with respect to different numbers of EP molecules adsorbed are given in Table 2. As expected, all of them reveal that the NP gains electronic

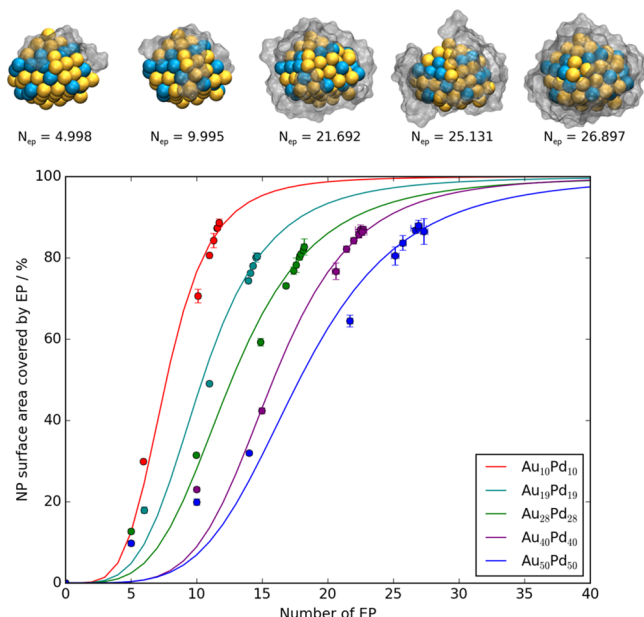


Figure 11. Percentages of the surface area of NPs covered by EP molecules plotted against the number of EP molecules interacting with the nanoparticle. The best fits based on the Langmuir–Freundlich isotherm are given as continuous lines. Select configurations of the $\text{Au}_{50}\text{Pd}_{50}$ NPs with varying percentage coverage are depicted above the graph.

calculated by taking the difference between the solvent-accessible surface area of the NP and the solvent-accessible surface area (SASA) of the NP that is covered by water molecules. The SASA calculations were performed by using a probe with radius 1.4 Å. Initially the increase in concentration of aqueous EP leads to an increase in surface coverage by EP molecules. However, irrespective of the concentration of the aqueous EP, the surface of the NP is not completely covered by EP molecules. In all the cases, a residual surface of the NPs is not covered by EP as given in Figure 11. This is consistent with the radial distribution functions that some water molecules are still in contact with the NP surface. The data from this analysis were fit to the Langmuir–Freundlich adsorption isotherm (eq 5). In the equation, SA is the surface area of NP covered by EP molecules; N_{ep} is the number of EP molecules adsorbed at the NP surface; and K and n are fitting parameters. The fitting parameter K represents the adsorption-to-desorption ratio for the EP adsorption, and the parameter n is suggested to account for the chemical nature of the adsorbed species. Reasonable correlation between the surface area covered and number of EP molecules directly bound to the NP was obtained based on the Langmuir–Freundlich isotherm. However, it is to be noted that the surface area covered by EP or even the polymeric PVP is not expected to attain 100% as seen in the figure. Representative snapshots of the surface covered are depicted for a select number of EP molecules adsorbed on the $\text{Au}_{50}\text{Pd}_{50}$ in the figure.

Table 2. Mulliken Charges on the NP Obtained from the M06-L Calculations on the $\text{Au}_{10}\text{Pd}_{10}\text{-EP}_m$ Systems with Respect to the Number of Adsorbed EP Molecules (m)

number of EP (m)	charge on NP
1	−0.20
2	−0.49
4	−0.80
6	−0.97
8	−1.35
10	−1.57
12	−1.87
14	−2.03

charge from EP. A charge of about 0.2 e can transfer from the EP to the $\text{Au}_{10}\text{Pd}_{10}$ cluster per EP molecule. The electronic charge on the NP increases with respect to an increase in the number of EP molecules adsorbed, which is limited by the maximum number of EP molecules that can directly interact with a given NP. It has been shown previously that adding an electron to metal clusters and tagging of small molecules such as DNA bases have a significant electronic effect on the physicochemical properties of metal nanoclusters.^{29,68–70} This clearly suggests that model chemistries chosen for studying reactions catalyzed by NPs should also appropriately consider the environment of the system. Molecular dynamics simulations can effectively be used to generate initial model systems for further QM or DFT calculations. For example, the structures depicted in Figure 2 may be chosen for studying the catalytic efficiency of the $\text{Au}_{10}\text{Pd}_{10}$ cluster.

CONCLUSIONS

The current study reports a systematic study of the interactions between different concentrations of aqueous solutions of EP with NPs of different dimensions using MD simulations and DFT calculations. Good agreement between the adsorption energies calculated using MM and DFT for EP adsorption on NP was obtained supporting the validity of the MD approach employed in this study. It was observed that the EP adsorption is substantially preferred over water by the large difference in the interaction energies of the two with the NPs. Due to the difference of affinities between the NPs with EP and NPs with water, the surface of the NP is covered mostly by EP molecules at high concentrations of aqueous EP, which can be clearly seen by the values of local mole fraction enhancement. Free energy calculations indicate that the NP system is more stabilized in high concentrations of aqueous EP, leading to high desolvation

energy for flocculation to happen. Such desolvation penalty in addition to steric repulsion is deemed to be responsible for preventing flocculation of any two polymer-dispersed NPs. Analysis of the structural aspects of the adsorbed NP systems using the radial distribution functions reveals that there exist few water molecules directly interacting with the NP. These water molecules have minimal interactions with the bulk water devoid of the regular tetrahedral structure and hence exist in the high energy state. These water molecules that are present close to the surface are proposed to play an important role in reactions that occur on the NP surface. It is also observed that EP has similar preference to adsorb on the Au and Pd sites on the NP surface. The surface area of the NP protected by the EP molecules with respect to the concentration of aqueous EP behaves according to the Langmuir–Freundlich isotherm. Increasing negative charge on the NP with respect to increasing number of adsorbed EP molecules emphasizes other electronic effects that these molecules have on the NP and the necessity of choosing model chemistries that include adsorbed stabilizing agents for theoretical modeling of catalysis. Further investigations on the mechanism by which adsorption of EP and PVP molecules prevents flocculation of NPs and the size dependency of this effect are in progress.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05097.

Figures of the radial distribution functions and probability distributions of the interaction energies and number of adsorbed molecules on the NP surface (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ehara@ims.ac.jp.

*E-mail: deva@iiit.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

UDP thanks Indian National Science Academy for financial assistance and JSPS for an invitation fellowship. M.E. acknowledges the financial support from a Grant-in-Aid for Scientific Research from the JSPS, ACT-C program of JST, Nanotechnology Platform Program of the MEXT of Japan. The computations were partly performed using the RCCS in Okazaki, Japan.

■ REFERENCES

- (1) Haruta, M. Novel Catalysis of Gold Deposited on Metal Oxides. *Catal. Surv. Jpn.* **1997**, *1*, 61–73.
- (2) Schön, G.; Simon, U. A Fascinating New Field in Colloid Science: Small Ligand-Stabilized Metal Clusters and Their Possible Application in Microelectronics. *Colloid Polym. Sci.* **1995**, *273*, 202–218.
- (3) Kamat, P. V. Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion. *J. Phys. Chem. C* **2007**, *111*, 2834–2860.
- (4) Katz, E.; Willner, I.; Wang, J. Electroanalytical and Bioelectroanalytical Systems Based on Metal and Semiconductor Nanoparticles. *Electroanalysis* **2004**, *16*, 19–44.
- (5) Huang, Y.; Duan, X.; Lieber, C. M. Nanowires for Integrated Multicolor Nanophotonics. *Small* **2005**, *1*, 142–147.
- (6) Wei, J.; Liu, S.; Geng, Y.; Wang, Y.; Li, X.; Wu, Y.; Dun, A. Nano-Optical Information Storage Induced by the Nonlinear Saturable Absorption Effect. *Nanoscale* **2011**, *3*, 3233–3237.
- (7) Dittlbacher, H.; Krenn, J. R.; Lamprecht, B.; Leitner, A.; Aussenegg, F. R. Spectrally Coded Optical Data Storage by Metal Nanoparticles. *Opt. Lett.* **2000**, *25*, S63–S65.
- (8) Rosi, N. L.; Mirkin, C. A. Nanostructures in Biodiagnostics. *Chem. Rev.* **2005**, *105*, 1547–1562.
- (9) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; VCH: Weinheim, Germany, 1997.
- (10) Aguilar-Guerrero, V.; Gates, B. Kinetics of CO Oxidation Catalyzed by Supported Gold: A Tabular Summary of the Literature. *Catal. Lett.* **2009**, *130*, 108–120.
- (11) Deng, W.; Frenkel, A. I.; Si, R.; Flytzani-Stephanopoulos, M. Reaction-Relevant Gold Structures in the Low Temperature Water-Gas Shift Reaction on Au-CeO₂. *J. Phys. Chem. C* **2008**, *112*, 12834–12840.
- (12) Rodriguez, J. A.; Liu, P.; Hrbek, J.; Evans, J.; Pérez, M. Water Gas Shift Reaction on Cu and Au Nanoparticles Supported on CeO₂(111) and ZnO(0001): Intrinsic Activity and Importance of Support Interactions. *Angew. Chem., Int. Ed.* **2007**, *46*, 1329–1332.
- (13) Wittstock, A.; Zielasek, V.; Biener, J.; Friend, C. M.; Bäumer, M. Nanoporous Gold Catalysts for Selective Gas-Phase Oxidative Coupling of Methanol at Low Temperature. *Science* **2010**, *327*, 319–322.
- (14) Simões, M.; Baranton, S.; Coutanceau, C. Electro-Oxidation of Glycerol at Pd Based Nano-Catalysts for an Application in Alkaline Fuel Cells for Chemicals and Energy Cogeneration. *Appl. Catal., B* **2010**, *93*, 354–362.
- (15) Lopez, N.; Janssens, T. V. W.; Clausen, B. S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Nørskov, J. K. On the Origin of the Catalytic Activity of Gold Nanoparticles for Low-Temperature CO Oxidation. *J. Catal.* **2004**, *223*, 232–235.
- (16) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* **2007**, *316*, 732–735.
- (17) Venezia, A. M.; Parola, V. L.; Deganello, G.; Pawelec, B.; Fierro, J. L. G. Synergetic Effect of Gold in Au/Pd Catalysts during Hydrodesulfurization Reactions of Model Compounds. *J. Catal.* **2003**, *215*, 317–325.
- (18) Dimitratos, N.; Villa, A.; Wang, D.; Porta, F.; Su, D.; Prati, L. Pd and Pt Catalysts Modified by Alloying with Au in the Selective Oxidation of Alcohols. *J. Catal.* **2006**, *244*, 113–121.
- (19) Wang, D.; Villa, A.; Porta, F.; Prati, L.; Su, D. Bimetallic Gold/Palladium Catalysts: Correlation between Nanostructure and Synergistic Effects. *J. Phys. Chem. C* **2008**, *112*, 8617–8622.
- (20) Dhital, R. N.; Kamonsatikul, C.; Somsook, E.; Bobuatong, K.; Ehara, M.; Karanjit, S.; Sakurai, H. Low-Temperature Carbon–Chlorine Bond Activation by Bimetallic Gold/Palladium Alloy Nanoclusters: An Application to Ullmann Coupling. *J. Am. Chem. Soc.* **2012**, *134*, 20250–20253.
- (21) Edwards, J. K.; Solsona, B.; Landon, P.; Carley, A. F.; Herzing, A.; Watanabe, M.; Kiely, C. J.; Hutchings, G. J. Direct Synthesis of Hydrogen Peroxide from H₂ and O₂ Using Au-Pd/Fe₂O₃ Catalysts. *J. Mater. Chem.* **2005**, *15*, 4595–4600.
- (22) Edwards, J. K.; Ntainjua, N. E.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. Direct Synthesis of H₂O₂ from H₂ and O₂ over Gold, Palladium, and Gold–Palladium Catalysts Supported on Acid-Pretreated TiO₂. *Angew. Chem., Int. Ed.* **2009**, *48*, 8512–8515.
- (23) Liu, J.-H.; Wang, A.-Q.; Chi, Y.-S.; Lin, H.-P.; Mou, C.-Y. Synergistic Effect in an Au–Ag Alloy Nanocatalyst: CO Oxidation. *J. Phys. Chem. B* **2005**, *109*, 40–43.
- (24) Bönemann, H.; Richards, R. M. Nanoscopic Metal Particles – Synthetic Methods and Potential Applications. *Eur. J. Inorg. Chem.* **2001**, *2001*, 2455–2480.
- (25) Roucoux, A.; Schulz, J.; Patin, H. Reduced Transition Metal Colloids: A Novel Family of Reusable Catalysts? *Chem. Rev.* **2002**, *102*, 3757–3778.

- (26) Dash, P.; Dehm, N. A.; Scott, R. W. J. Bimetallic PdAu Nanoparticles as Hydrogenation Catalysts in Imidazolium Ionic Liquids. *J. Mol. Catal. A: Chem.* **2008**, *286* (1–2), 114–119.
- (27) Li, Y.; El-Sayed, M. A. The Effect of Stabilizers on the Catalytic Activity and Stability of Pd Colloidal Nanoparticles in the Suzuki Reactions in Aqueous Solution. *J. Phys. Chem. B* **2001**, *105*, 8938–8943.
- (28) Okumura, M.; Kitagawa, Y.; Kawakami, T.; Haruta, M. Theoretical Investigation of the Hetero-Junction Effect in PVP-Stabilized Au₁₃ Clusters. The Role of PVP in Their Catalytic Activities. *Chem. Phys. Lett.* **2008**, *459*, 133–136.
- (29) Boekfa, B.; Pahl, E.; Gaston, N.; Sakurai, H.; Limtrakul, J.; Ehara, M. C–Cl Bond Activation on Au/Pd Bimetallic Nanocatalysts Studied by Density Functional Theory and Genetic Algorithm Calculations. *J. Phys. Chem. C* **2014**, *118*, 22188–22196.
- (30) Mdluli, P. S.; Sosibo, N. M.; Revaprasadu, N.; Karamanis, P.; Leszczynski, J. Surface Enhanced Raman Spectroscopy (SERS) and Density Functional Theory (DFT) Study for Understanding the Regioselective Adsorption of Pyrrolidinone on the Surface of Silver and Gold Colloids. *J. Mol. Struct.* **2009**, *935*, 32–38.
- (31) Abdelghany, A. M.; Mekhail, M. S.; Abdelrazek, E. M.; Aboud, M. M. Combined DFT/FTIR Structural Studies of Monodispersed PVP/Gold and Silver Nano Particles. *J. Alloys Compd.* **2015**, *646*, 326–332.
- (32) Mdluli, P. S.; Sosibo, N. M.; Mashazi, P. N.; Nyokong, T.; Tshikhudo, R. T.; Skepu, A.; van der Lingen, E. Selective Adsorption of PVP on the Surface of Silver Nanoparticles: A Molecular Dynamics Study. *J. Mol. Struct.* **2011**, *1004*, 131–137.
- (33) Smith, J. S.; Bedrov, D.; Smith, G. D. A Molecular Dynamics Simulation Study of Nanoparticle Interactions in a Model Polymer-Nanoparticle Composite. *Compos. Sci. Technol.* **2003**, *63*, 1599–1605.
- (34) Kyrychenko, A. NANOGOLD Decorated by pHLP Peptide: Comparative Force Field Study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12648–12660.
- (35) Kyrychenko, A.; Korsun, O. M.; Gubin, I. I.; Kovalenko, S. M.; Kalugin, O. N. Atomistic Simulations of Coating of Silver Nanoparticles with Poly(vinylpyrrolidone) Oligomers: Effect of Oligomer Chain Length. *J. Phys. Chem. C* **2015**, *119*, 7888–7899.
- (36) Jiménez, A.; Sarsa, A.; Blázquez, M.; Pineda, T. A Molecular Dynamics Study of the Surfactant Surface Density of Alkanethiol Self-Assembled Monolayers on Gold Nanoparticles as a Function of the Radius. *J. Phys. Chem. C* **2010**, *114*, 21309–21314.
- (37) Henz, B. J.; Chung, P. W.; Andzelm, J. W.; Chantawansri, T. L.; Lenhart, J. L.; Beyer, F. L. Determination of Binding Energy and Solubility Parameters for Functionalized Gold Nanoparticles by Molecular Dynamics Simulation. *Langmuir* **2011**, *27*, 7836–7842.
- (38) Heikkilä, E.; Gurtovenko, A. A.; Martinez-Seara, H.; Häkkinen, H.; Vattulainen, I.; Akola, J. Atomistic Simulations of Functional Au₁₄₄(SR)₆₀ Gold Nanoparticles in Aqueous Environment. *J. Phys. Chem. C* **2012**, *116*, 9805–9815.
- (39) Mandal, T.; Dasgupta, C.; Maiti, P. K. Engineering Gold Nanoparticle Interaction by PAMAM Dendrimer. *J. Phys. Chem. C* **2013**, *117*, 13627–13636.
- (40) Logsdail, A. J.; Curley, B. C.; Roberts, C.; Johnston, R. L. *Birmingham Cluster Genetic Algorithm (BCGA-2010)*; University of Birmingham: U.K., 2010.
- (41) Johnston, R. L. Evolving Better Nanoparticles: Genetic Algorithms for Optimising Cluster Geometries. *Dalton Trans.* **2003**, 4193–4207.
- (42) Pittaway, F.; Paz-Borbón, L. O.; Johnston, R. L.; Arslan, H.; Ferrando, R.; Mottet, C.; Barcaro, G.; Fortunelli, A. Theoretical Studies of Palladium–Gold Nanoclusters: Pd–Au Clusters with up to 50 Atoms. *J. Phys. Chem. C* **2009**, *113*, 9141–9152.
- (43) Bruma, A.; Ismail, R.; Paz-Borbón, L. O.; Arslan, H.; Barcaro, G.; Fortunelli, A.; Li, Z.; Johnston, R. L. DFT Study of the Structures and Energetics of 98-Atom AuPd Clusters. *Nanoscale* **2013**, *5*, 646–652.
- (44) Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kalé, L.; Schulten, K. Scalable Molecular Dynamics with NAMD. *J. Comput. Chem.* **2005**, *26*, 1781–1802.
- (45) Heinz, H.; Vaia, R. A.; Farmer, B. L.; Naik, R. R. Accurate Simulation of Surfaces and Interfaces of Face-Centered Cubic Metals Using 12–6 and 9–6 Lennard-Jones Potentials. *J. Phys. Chem. C* **2008**, *112*, 17281–17290.
- (46) Zhou, Y.; Saidi, W. A.; Fichthorn, K. A. A Force Field for Describing the Polyvinylpyrrolidone-Mediated Solution-Phase Synthesis of Shape-Selective Ag Nanoparticles. *J. Phys. Chem. C* **2014**, *118*, 3366–3374.
- (47) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. Comparison of Simple Potential Functions for Simulating Liquid Water. *J. Chem. Phys.* **1983**, *79*, 926–935.
- (48) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. Numerical Integration of the Cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of N-Alkanes. *J. Comput. Phys.* **1977**, *23*, 327–341.
- (49) Straatsma, T. P.; Berendsen, H. J. C.; Postma, J. P. M. Free Energy of Hydrophobic Hydration: A Molecular Dynamics Study of Noble Gases in Water. *J. Chem. Phys.* **1986**, *85*, 6720–6727.
- (50) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. CHARMM: A Program for Macromolecular Energy, Minimization, and Dynamics Calculations. *J. Comput. Chem.* **1983**, *4*, 187–217.
- (51) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.
- (52) Vanommeslaeghe, K.; Hatcher, E.; Acharya, C.; Kundu, S.; Zhong, S.; Shim, J.; Darian, E.; Guvench, O.; Lopes, P.; Vorobyov, I.; et al. CHARMM General Force Field: A Force Field for Drug-like Molecules Compatible with the CHARMM All-Atom Additive Biological Force Fields. *J. Comput. Chem.* **2010**, *31*, 671–690.
- (53) Chen, B.; Potoff, J. J.; Siepmann, J. I. Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary, and Tertiary Alcohols. *J. Phys. Chem. B* **2001**, *105*, 3093–3104.
- (54) Maerzke, K. A.; Siepmann, J. I. Monte Carlo Simulations of Binary Mixtures of Nitrotoluene Isomers with N-Decane. *J. Phys. Chem. B* **2009**, *113*, 13752–13760.
- (55) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- (56) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.
- (57) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270–283.
- (58) Binkley, J. S.; Pople, J. A.; Hehre, W. J. Self-Consistent Molecular Orbital Methods. 21. Small Split-Valence Basis Sets for First-Row Elements. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.
- (59) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. 6-31G* Basis Set for Atoms K through Zn. *J. Chem. Phys.* **1998**, *109*, 1223–1229.
- (60) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. 6-31G* Basis Set for Third-Row Atoms. *J. Comput. Chem.* **2001**, *22*, 976–984.
- (61) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent Molecular Orbital Methods. XXIII. A Polarization-type Basis Set for Second-row Elements. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- (62) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.
- (63) Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.

- (64) Sakata, K.; Ato, Y.; Tada, K.; Koga, H.; Yamanaka, S.; Kawakami, T.; Saito, T.; Okumura, M. Theoretical Investigation for Heterojunction Effects in Polymer-Stabilized Au Nanocluster Catalysis: Difference in Catalytic Activity between Au:PVP and Au:PAA. *Chem. Lett.* **2016**, *45*, 344–346.
- (65) Saavedra, J.; Doan, H. A.; Pursell, C. J.; Grabow, L. C.; Chandler, B. D. The Critical Role of Water at the Gold-Titania Interface in Catalytic CO Oxidation. *Science* **2014**, *345*, 1599–1602.
- (66) Meeprasert, J.; Namuangruk, S.; Boekfa, B.; Dhital, R. N.; Sakurai, H.; Ehara, M. Mechanism of Ullmann Coupling Reaction of Chloroarene on Au/Pd Alloy Nanocluster: A DFT Study. *Organometallics* **2016**, *35*, 1192–1201.
- (67) Gurtu, S.; Rai, S.; Ehara, M.; Priyakumar, U. D. Ability of Density Functional Theory Methods to Accurately Model the Reaction Energy Pathways of the Oxidation of CO on Gold Cluster: A Benchmark Study. *Theor. Chem. Acc.* **2016**, *135*, 1–12.
- (68) Rai, S.; Ehara, M.; Deva Priyakumar, U. Nucleobases Tagged to Gold Nanoclusters Cause a Mechanistic Crossover in the Oxidation of CO. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24275–24281.
- (69) Rai, S.; Ranjan, S.; Singh, H.; Priyakumar, U. D. Modulation of Structural, Energetic and Electronic Properties of DNA and Size-Expanded DNA Bases upon Binding to Gold Clusters. *RSC Adv.* **2014**, *4*, 29642–29651.
- (70) Rai, S.; Singh, H.; Priyakumar, U. D. Binding to Gold Nanoclusters Alters the Hydrogen Bonding Interactions and Electronic Properties of Canonical and Size-Expanded DNA Base Pairs. *RSC Adv.* **2015**, *5*, 49408–49419.