Supporting Information

The Contradicting Influences of Silica and Titania Supports on the Properties of Au^0 Nanoparticles as Catalysts for Reductions by borohydride

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1. Materials

All the chemicals used in this study were of analytic grade, commercially available, and used without further purification. Water purified with a Milli-Q system with a resistivity > 15 MΩ·cm was used throughout the experiments. Pure argon of 99.996% from oxygen & Argon Works was used for de-aeration. Chloro-auric acid ($HAuCl_4$), titanium tetrachloride ($TiCl_4$), sodium borodeuteride ($NaBD_4$, 98% D), and tetraethyl-orthosilicate

(TEOS) were purchased from Sigma-Aldrich. (3-Aminopropyl) trimethoxysilane (APS) from Alfa Aesar and Sodium borohydride ($NaBH_4$) from STREM.

2. Characterization methods

A Cary 50 Varian UV-visible spectrophotometer was used to measure UV-visible spectra. Transmission Electron Microscopy (TEM) analysis was conducted using a JEOL, JEM-2100F (UHR) instrument equipped with EDX. Powder X-ray diffraction (PXRD) measurements were carried out using a Rigaku SmartLab SE X-ray diffractometer using Cu-Kα (1.54 Å) radiation operated at 40 kV and 30 mA. TEM samples were prepared by drop-casting nanoparticle suspension on a carbon film-coated 300 mesh Cu grid. The samples were dried well before analysis.

3. Synthesis of SiO_2-Au^0-NPs

Monodispersed spherical SiO_2-NPs were synthesized using Stöber's method.[1] A solution of tetra-ethyl-orthosilicate (3 ml) was added to a mixture of NH_4OH (29%, 2 ml) and ethanol (45 ml) to obtain 0.28 M TEOS. Subsequently, the obtained SiO_2-NPs were functionalized with bridging 3-aminopropyltrimethoxysilane, APS (147 mM). The suspension was stirred for 2 hours, then refluxed for an hour. After that, 0.10 M $HAuCl_4$ solution was added dropwise to 0.26 M functionalized (147 mM APS) SiO_2-NPs (in ethanol and NH_3) to produce 5.0 mM of Au^{III} in the suspension. Solid $NaBH_4$ (30 mM) was added to reduce the Au^{III} in the suspension. During the synthesis, the color changed from milky white to dark purple. The mixture was then stirred overnight to ensure the completion of the reaction. The precipitated SiO_2-Au^0-NPs were washed and redispersed in pH 10 water (using NaOH). The obtained aqueous SiO_2-Au^0-NPs suspension was diluted to the required concentrations of nanoparticles.

4. Synthesis of TiO_2-Au^0-NPs

Colloidal TiO_2 suspensions were prepared by modifying the method developed by Rabani et al.[2,3] by hydrolyzing titanium tetrachloride ($TiCl_4$).[4] An ice-cold liquid $TiCl_4$ was added dropwise into an aqueous HCl (0.10 M) solution along with a stream of argon with vigorous stirring. The obtained optically transparent colloidal suspension was dialyzed as fast as possible against a pH of 2.5 aqueous HCl using a Spectra/Por Dialysis membrane tubing (MWCO: 6–8 kD). According to Rabani et al., the resulting Titania suspension has an average diameter of about 1 nm. Larger and more stable particles were achieved by heating the suspension at 55 °C for five days.

Gold NPs attachment to the TiO_2 was performed as follows:[5] an aqueous solution of $HAuCl_4$ (8.0 mL) was added dropwise into the obtained 0.20 M TiO_2 suspension (2.0 mL, pH 1.5) to produce 4.0 mM of Au^{III} in the suspension. The suspension was stirred for 60 minutes to ensure the attachment of Au^{III} onto the TiO_2 surface. The reduction of gold was performed by quickly adding an ice-cold solution of $NaBH_4$ (10 mL, 40 mM) into the TiO_2-Au^{III} suspension. The stirring was continued for eight hours, followed by centrifugation to wash and remove excessive borohydride and borate. The obtained NPs were redispersed in water, followed by sonication to obtain well-dispersed stable TiO_2-Au^0-NPs. The pH of the suspension was adjusted to 10.0 using NaOH solution. The final concentration of gold in the suspensions was 2.0 mM. A blank titania solution at pH 9.0 was prepared by adding borate buffer and NaOH to the acidic titania suspension, followed by sonication for proper dispersion. The obtained titania-gold suspension was diluted to the required nanoparticle concentrations.

5. Synthesis of Au^0-NPs

Gold nanoparticles were prepared using a modified Creighton's procedure.[6] Briefly, a freshly prepared (30 mL, 2.0 mM) ice-cold solution of $NaBH_4$ was added to an aqueous solution of 1.0 mM $HAuCl_4$ under vigorous stirring. The nanoparticle suspensions prepared were at pH 9.20.

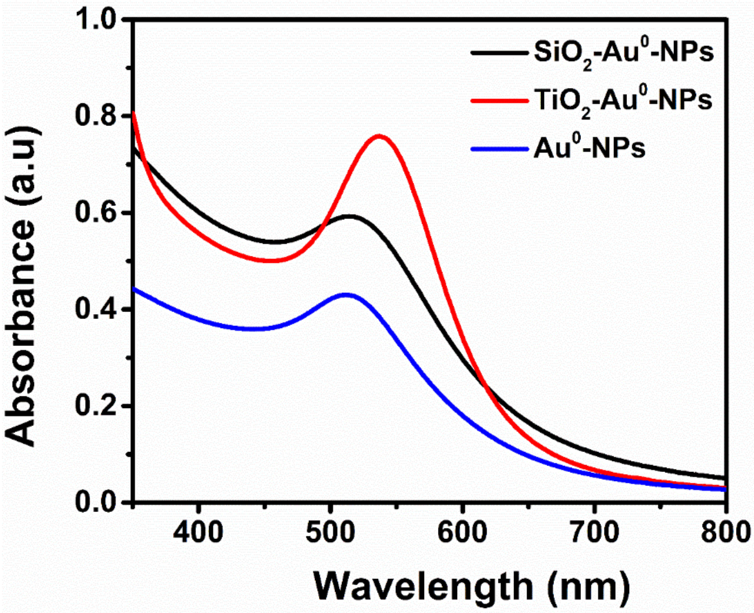

Figure S1. UV-visible spectra of Au^0-NPs (blue), SiO_2-Au^0-NPs (black), and TiO_2-Au^0-NPs (red). The concentration of gold in all suspensions is 0.20 mM.

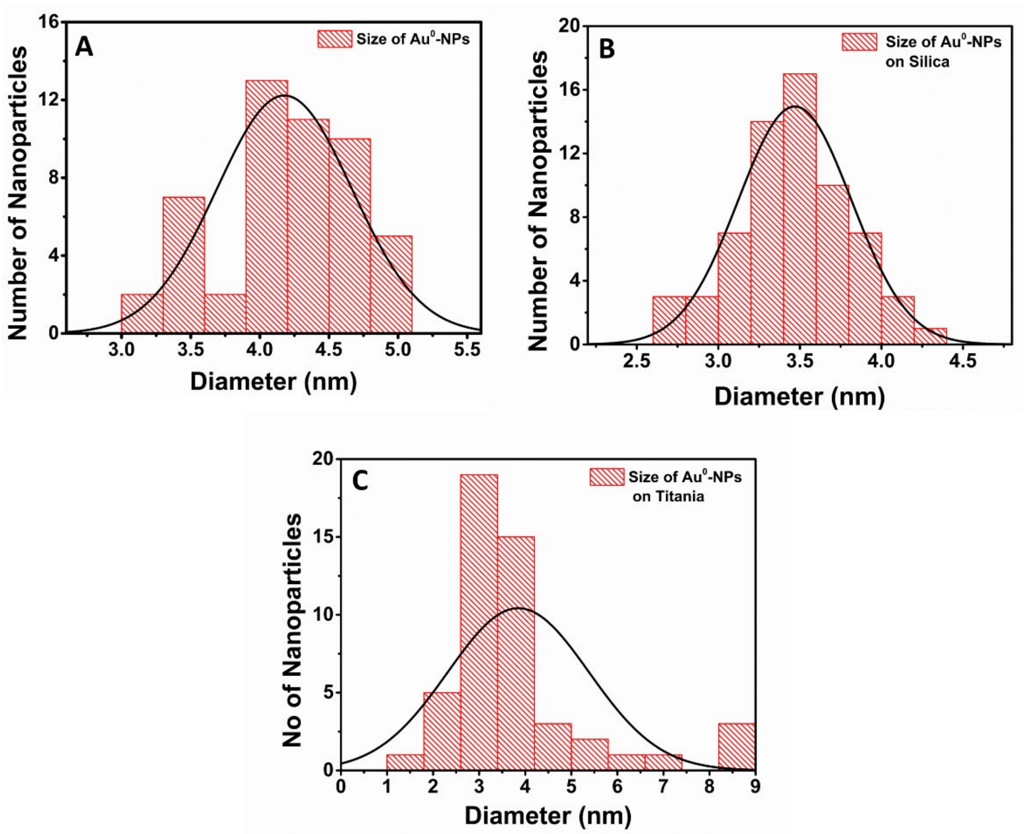

Figure S2: Size distribution curves of Au^0-NPs (A), SiO_2-Au^0-NPs (B), and TiO_2-Au^0-NPs (C).

Table S1. Atomic % of the elements obtained from EDX.

Catalyst	Element	Atomic %
Au^0-NPs	Au	100
	Si	40.87

SiO_2-Au^0-NPs	O	56.66
	Au	2.46
TiO_2-Au^0-NPs	Ti	23.57
	O	73.84
	Au	2.59

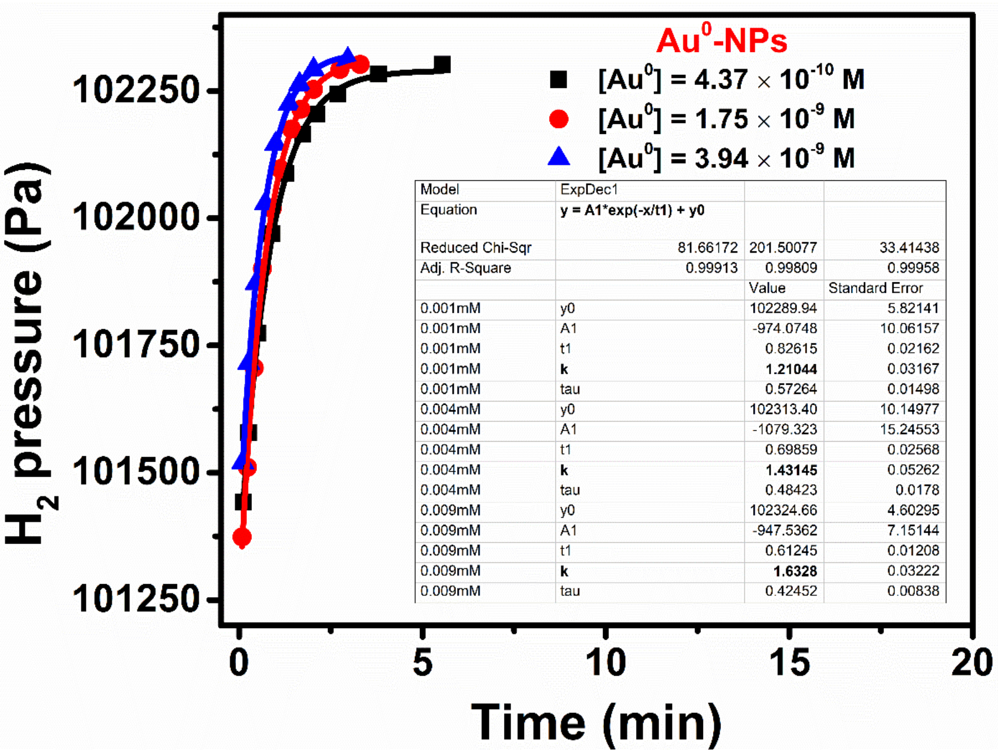

Figure S3. Kinetic plots of hydrogen formation in the hydrolysis of BH_4^- in the presence of Au^0 -NPs at pH 9.0. $[BH_4^-]$ = 0.50 mM. (Note $[Au^0]$ is the Au^{III} used to prepare the NPs).

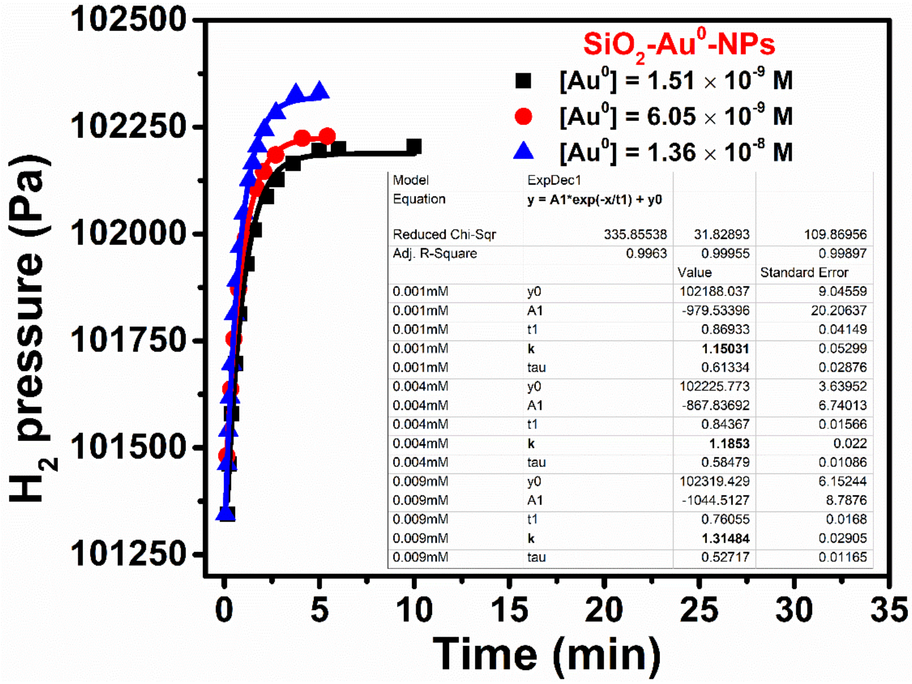

Figure S4: Kinetic plots of hydrogen formation in the hydrolysis of BH_4^- in the presence of SiO_2-Au^0 -NPs at pH 9.0. [BH_4^-] = 0.50 mM. (Note [Au^0] is the Au^{III} used to prepare the NPs).

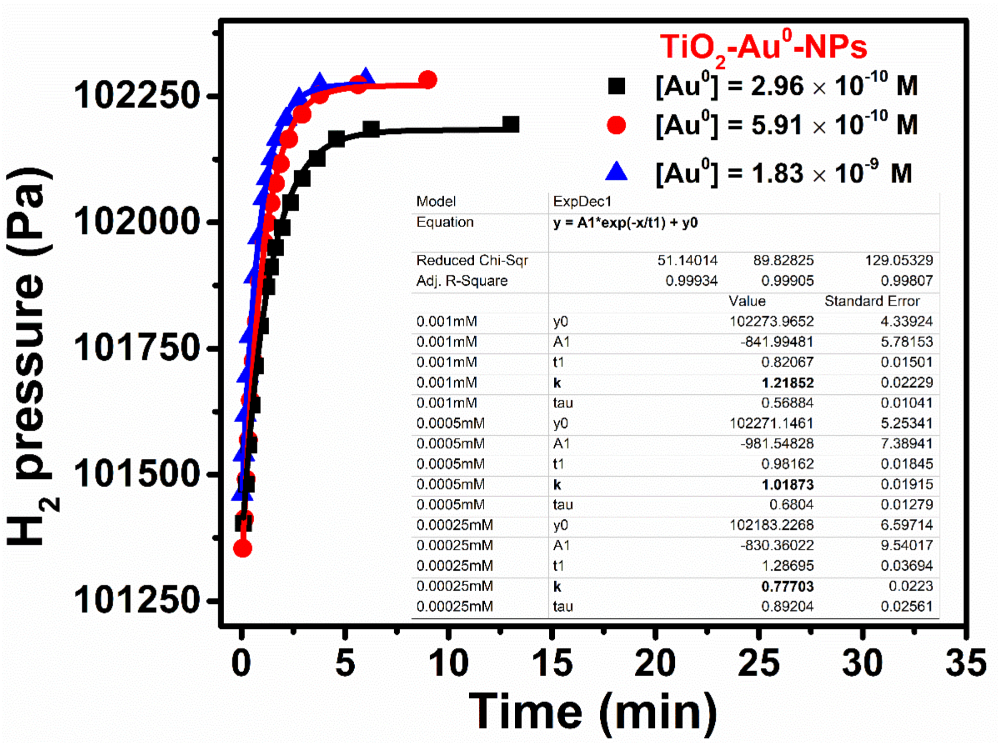

Figure S5. Kinetic plots of hydrogen formation in the hydrolysis of BH_4^- in the presence of TiO_2-Au^0 -NPs at pH 9.0. [BH_4^-] = 0.50 mM. (Note [Au^0] is the Au^{III} used to prepare the NPs).

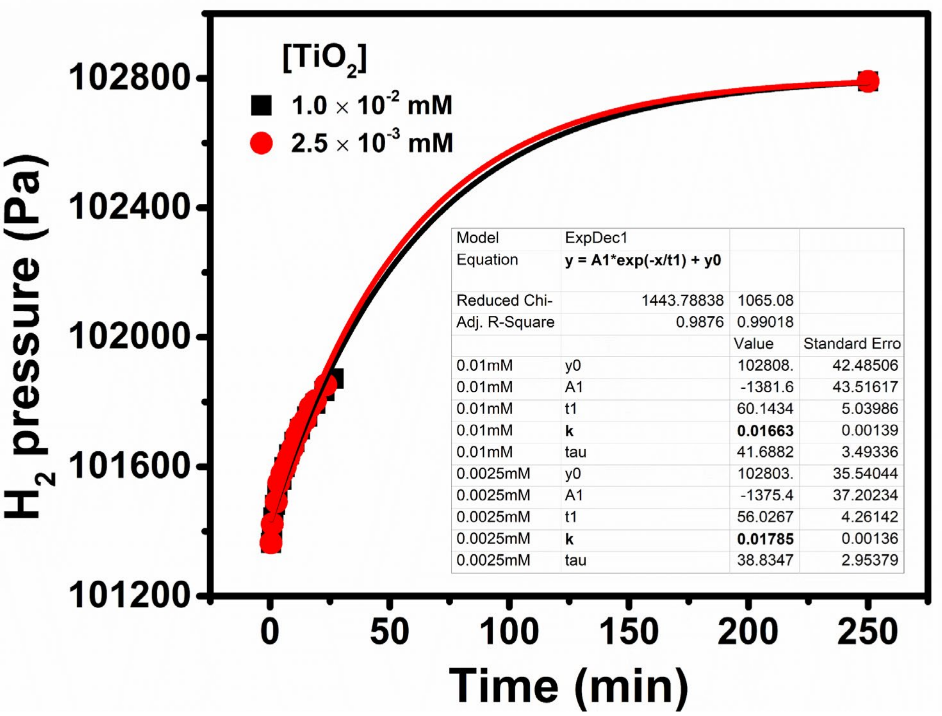

Figure S6. Kinetic plots of hydrogen formation in the hydrolysis of BH_4^- in the presence of TiO_2-NPs at pH 9.0. $[BH_4^-]$ = 0.50 mM. (Note $[TiO_2]$ is the $TiCl_4$ used to prepare the NPs).

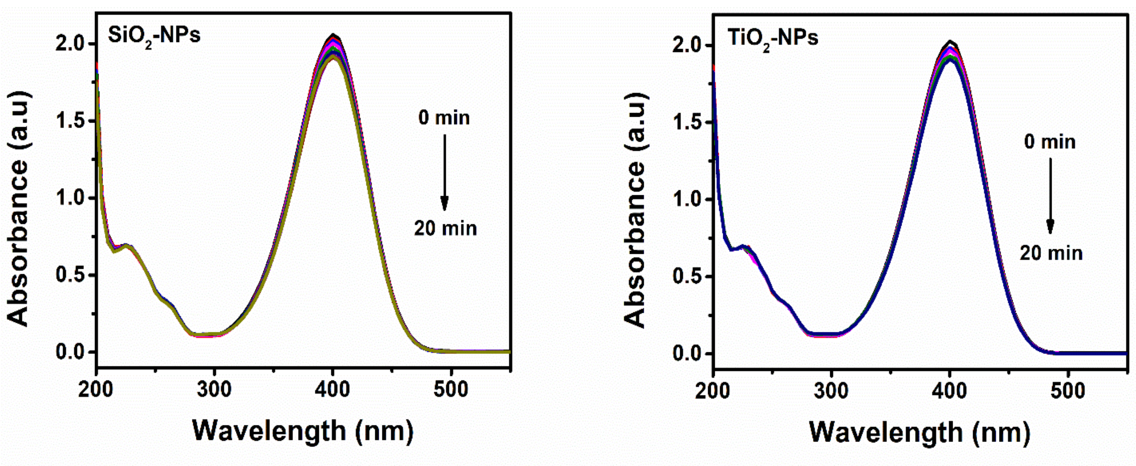

Figure S7. Time-dependent UV-visible spectra of the catalytic reduction of 4-nitrophenol using SiO_2-NPs and TiO_2-NPs, at pH 9.0.

6. Concentration of Gold Nanoparticles

(I) SiO_2- Au^0-NPs

$[Au^0\text{-NP}] = C/n$ (n = the average number of Au^0 atoms in one nanoparticle)

C = [Au]

$n = (volume \times NA \times \rho)/M_w$

Assuming that on silica, the gold nanoparticles are half balls and are not balls due to contact with the silica surface:

$[Au^0\text{-NP}] = 2(C/n)$

Average radius gold in SiO_2-Au^0-NPs = 1.75×10^{-7} cm

$n = (volume \times NA \times \rho)/M_w = (4/3\times \pi \times (1.75 \times 10^{-7})^3 \times 6.022 \times 10^{23} \times 19.3)/196.97$

$= 1.323 \times 10^3$ Au^0 atoms/Au^0-NP

1. C= 9.0×10^{-6} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (9.0 \times 10^{-6}\ M / 1.323 \times 10^3) =$ **1.36×10^{-8} M**

2. C= 4.0×10^{-6} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (4.0 \times 10^{-6}\ M / 1.323 \times 10^3) =$ **6.05×10^{-9} M**

3. C= 1.0×10^{-6} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (1.0 \times 10^{-6}\ M / 1.323 \times 10^3) =$ **1.51×10^{-9} M**

(II) TiO_2-Au^0-NPs

Average radius of gold in TiO_2-Au^0-NPs = 1.9×10^{-7} cm

Assuming that on titania, the gold nanoparticles are half balls and are not balls due to contact with the titania surface:

$n = (volume \times NA \times \rho)/M_w = (4/3 \times \pi \times (1.9 \times 10^{-7})^3 \times 6.022 \times 10^{23} \times 19.3)/196.97$

$= 1.69 \times 10^3$ Au^0 atoms/Au^0-NP

1. C= 1.0×10^{-6} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (1.0 \times 10^{-6}\ M / 1.69 \times 10^3) =$ **1.83×10^{-9} M**

2. C= 5.0×10^{-7} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (5.0 \times 10^{-7}\ M / 1.69 \times 10^3) =$ **5.91×10^{-10} M**

3. C= 2.5×10^{-7} M

$[Au^0\text{-}NP] = 2(C/n) = 2\ (2.5 \times 10^{-7}\ M / 1.69 \times 10^3) =$ **2.96×10^{-10} M**

(III) Bare Au^0-NPs

$[Au^0\text{-}NP] = C/n$ (n = the average number of Au^0 atoms in one nanoparticle)

C = [Au]

$n = (volume \times NA \times \rho)/Mw$

$[Au^0\text{-}NP] = C/n$

Average radius of gold = 2.1×10^{-7} cm

$n = (volume \times NA \times \rho)/M_w = (4/3 \times \pi \times (2.1 \times 10^{-7})^3 \times 6.022 \times 10^{23} \times 19.3)/196.97$

$= 2.287 \times 10^3$ Au^0 atoms/Au^0-NP

1. C= 9.0×10^{-6} M

$[Au^0\text{-}NP] = C/n = 9.0 \times 10^{-6}\ M / 2.287 \times 10^3 =$ **3.94×10^{-9} M**

2. C= 4.0×10^{-6} M

$[Au^0\text{-}NP] = C/n = 4.0 \times 10^{-6}\ M / 2.287 \times 10^3 =$ **1.75×10^{-9} M**

3. C= 1.0×10^{-6} M

$[Au^0\text{-}NP] = C/n = 1.0 \times 10^{-6}\ M / 2.287 \times 10^3 =$ **4.37×10^{-10} M**

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