Effects of particle size and plasmon excitation on the photochemistry of $(\text{NO})_2$ adsorbed on alumina supported Ag nanoparticles

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Introduction

Atoms / Molecules

Metal nanoparticles

Size dependent

- Optical properties
- Electronic properties
- Chemical properties

Bulk materials
Evolution of Electronic Structure

- Formation of metallic band from atomic orbital
- Shift of core and valence bands
Can plasmonic electrons drive photochemistry?

\[ \text{Plasmon Lifetime} < \sim 10 \text{ fs} \]
Ag NPs on thin alumina film

- Particle density ~ $4 \times 10^{11}$ cm$^{-2}$
- Standard deviation of the size distribution ~ 20 to 30 %

Plasmon on Ag NPs

Excitation of (1,0) mode of Mie plasmon at ~ 3.6 eV

Experimental setup -1

For photon induced desorption (PID) and MS-TOF measurements

- Sample: Ag / Al$_2$O$_3$ / NiAl(110) 40 K
- Nd:YAG (2.3, 3.5, 4.7 eV)
- UHV chamber
- QMS Head
- Preamplifier
- Discriminator
- Pulse doser (NO)
- LN$_2$ cooling
- Multichannel scaler (MCS)
  - Fast MCS for MS-TOF (0.8 µs)
  - MCS for PID (2 ms)

Time-of-flight (µs)
Counts
Irradiance [x10$^{15}$ photons/cm$^2$]
MS TOF PID data analysis

Sample | Ionizer | Quadrupole | Detector

Time resolution = 0.8 µs

Data acquisition time : 2ms

Shifted Maxwell-Boltzmann distribution:

\[ f(t) = \frac{a_1}{t^\frac{3}{2}} \exp\left(-b_1\left(\frac{t}{t_1} - v_1\right)^\frac{3}{2}\right) + \frac{a_2}{t^\frac{3}{2}} \exp\left(-b_2\left(\frac{t}{t_1} - v_2\right)^\frac{3}{2}\right) \]

\[ T = \langle E_{\text{trans}} \rangle / 2k_B \]

Fitted by single exponential (until 50%):

\[ y = y_0 + A_1 \cdot \exp\left(-\frac{(x-x_0)}{t_1}\right) \]

\[ \sigma = \frac{1}{t_1 \cdot Ph \cdot f} \]
Thermal reactions of NO dimer

TPD from Ag NPs (10 nm) dosed with NO at 75 K

\[(\text{NO})_2 \rightarrow 2 \text{ NO}\]
\[(\text{NO})_2 \rightarrow \text{N}_2\text{O} + \text{O}\]

m/e = 30
m/e = 44
TPD: NO from Ag NPs

Size dependence

(a) QMS Signal at m/e=30 (arb. units)

(b) Diameter (nm)

$D (\text{nm})$

$\text{Ag(111)}$

$\text{NO}$

$\text{N}_2\text{O}$

Temperature (K)

TPD Peak Temperature (K)

$\frac{1}{\text{Radius (nm}^{-1})}$

$\infty$

TPD: NO from Ag NPs

- Possible origins of the size dependent adsorption energy of NO
  - Dispersion force (van der Waals force) \( \propto \) total number of Ag atoms
  - Electronic structure of Ag NPs
    - eg. \( d \)-band shift,
      - change of electron population near \( E_F \)
  - Surface structure of Ag NPs
    - eg. contraction of lattice parameters \( \propto 1/R \)
Photodesorption cross section

Size and photon energy dependence

Photon energy
- 2.3 eV $p$-pol.
- 4.7 eV $p$-pol.

Cross section, $\sigma \times 10^{-17}$ [cm$^2$]

Mean diameter [nm]

@ 2.3 eV and 4.7 eV
Linear increase of $\sigma$ with $1/R$
Photodesorption cross section

![Diagram of photodesorption process]

- **Confinement effect**
  - Particle size \( \leq \) mean free path of \( e^- \)
  - Enhanced cross-section \( (\sigma) \)

- **Surface to volume ratio**
  - Rate of collision with the surface \( \propto \frac{S}{V} = \frac{1}{R} \)
  - \( \sigma \propto \frac{S}{V} = \frac{1}{R} \)
Photodesorption cross section

Size and photon energy dependence

<table>
<thead>
<tr>
<th>Photon energy</th>
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<tbody>
<tr>
<td>2.3 eV p-pol.</td>
<td>X 10</td>
</tr>
<tr>
<td>3.5 eV p-pol.</td>
<td>X 10</td>
</tr>
<tr>
<td>4.7 eV p-pol.</td>
<td>X 10</td>
</tr>
</tbody>
</table>

Mean diameter [nm]

@ 3.5 eV in p-pol

Excitation of (1,0) mode

Mie plasmon

~3.5 eV

Effects of plasmon

Plasmon decay channels

- Landau Damping
- Radiation Damping

Particle Diameter [nm]

1 4 20

Landau Damping + Radiation Damping

e-h pair - Photon - Photochemistry

Plasmon oscillator strength

$\propto$ number of conduction electrons
Effects of plasmon

Photon energy

Mean diameter [nm]

Cross section, $\sigma \times 10^{-17}$ [cm$^2$]

1/R [nm$^{-1}$]

Ag(111)

Oscillator strength

Landau damping
Translational temperature

Size and photon energy dependence

Mean Diameter (nm)

Photon energy
- 2.3 eV p-pol.
- 3.5 eV p-pol.

\[
\frac{\langle E_t \rangle}{2k_B} \text{[K]}
\]

Ag(111)

@ 2.3 and 3.5 eV

- \( T_t \) is constant at \( \sim 700 \) K
- No plasmon effect on \( T_t \)

\[ \sim 3.5 \text{ eV} \]
\[ \sim 2.4 \text{ eV} \]
Translational temperature

Size and photon energy dependence

- $T_t$ is constant at ~700 K
- No plasmon effect on $T_t$ at 4.7 eV
- $T_t$ increases at small $D$ at 2.3 and 3.5 eV

Photon energy

- 2.3 eV $p$-pol.
- 3.5 eV $p$-pol.
- 4.7 eV $p$-pol.

Mean Diameter (nm)

Mean Diameter (nm)

$\langle E_t \rangle/2k_B$ [K]

$1/R$ [nm$^{-1}$]

Ag(111)

$\sim 3.5 \text{ eV}$

$\sim 2.4 \text{ eV}$
Translational temperature

Size and photon energy dependence

Mean Diameter (nm)

Photon energy

- 2.3 eV p-pol.
- 3.5 eV p-pol.
- 4.7 eV p-pol.

Ag(111)

<Et>/2kB [K]

1/R [nm⁻¹]

Time of Flight (μs)

State resolved study of photodesorbed NO via REMPI
Experimental setup - 2

State resolved detection of NO via (1+1) REMPI

(1+1) REMPI principle

**Experimental setup**

- **Sample**
- **Repeller**
- **Pump laser**
- **Probe laser**
- **To MCP**

**Ion detection**

**REMPI - TOF**

\[ v = 0, J^* = 3.5, \Omega = 1/2 \]

**REMPI spectrum**

\[ A^2 \Sigma_{1/2} \rightarrow X^2 \Pi_{1/2} \]

\[ A^2 \Sigma_{3/2} \rightarrow X^2 \Pi_{3/2} \]
Rotational temperature

8-nm Ag NPs /Al₂O₃/NiAl(110)  @ 3.5 eV in p-pol.

REMPI - Spectrum

\[ \nu = 0 \]

Pump-probe delay = 29 µs

Boltzmann Plot

\[ \nu = 0, \, \Omega = 1/2 \text{ and } 3/2, \]

\[ T_{\text{rot}} = 465 + 50 \text{ K} \]
Rotational temperature

Size and photon energy dependence

v = 950 m/s  
v = 1500 m/s
Vibrational temperature

Size and photon energy dependence

\[ v = 950 \text{ m/s} \quad v = 1500 \text{ m/s} \]

Vibrational Temperature (K)

Particle Diameter (nm)

NO\(^+\) Signal intensity [a.u.]

Photon Energy (eV)

8 nm Ag NPs

4 nm Ag NPs

Pump-probe delay [\mu s]
State resolved TOF spectra
NO ($v = 0$, $\Omega = 1/2$), $h\nu = 2.3$ eV

$J'' = 28.5$

$J'' = 16.5$

$J'' = 3.5$

Positive T - R correlation

[Graph showing the relationship between $E_{\text{rot}}$ (cm$^{-1}$) and $<E_t>/2K_B$ (K) for different Ag NPs diameters: 4 nm, 8 nm, 11 nm, and Ag(111)]
Photodesorption Dynamics

Desorption via transient ion state

Antoniewicz Model

$E_K'$

$E_K$

$E_k$

$D_0$

$M+A^-$ or $M+A^+$

$M+A$

Photoexcitation mechanisms

Photon energy dependence

@ 2.3 and 3.5 eV
Desorption via transient negative ion (TNI) state

@ 4.7 eV
Desorption via TNI or transient positive ion (TPI) state
Photodesorption Dynamics

TNI versus TPI
Photodesorption Dynamics

Rotational excitation
(Impulsive model)

✓ Ground PES (neutral state)

\[ L = P \times l \sin \alpha \]

Common excitation mechanism for T and R

Positive T – R correlation
Photodesorption Dynamics

Vibrational excitation

✓ Excited PES (Transient ion state)

\((\text{NO}_2)^-\) \hspace{1cm} (\text{NO}_2)^+\)
Summary

**Confinement** of electrons can result in an increase of the desorption cross section ($\sigma$) with the surface to volume ratio ($1/R$) of the NPs.

**Plasmon** excitation can result in additional enhancement of $\sigma$ which has maximum at an intermediate size.

**Confinement** of electrons and **plasmon** excitation do **not** alter the individual desorption dynamics of NO, at least for $h\nu \leq 3.5$ eV.

At sufficiently high $h\nu$ (4.7 eV) to form **hot holes** in the adsorbate a **new desorption mechanism** is found, which results in more energetic desorbates. It is probably proceeds via **TPI** (Transient positive ions).
Confinement & plasmon excitation

**MNPs**

- **Confinement**: Electron dynamics, Transport property
- **Optical property**: Mie plasmon $\rightarrow$ field enhancement

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**Diagram:**
- Metal Substrate
- Adsorbate
- Hot electrons
- MNP
- Dielectric Substrate
- Metal Substrate
- Plasmon field enhancement
- Mie plasmon $\rightarrow$ field enhancement