Advanced Nanosensors for Continuous Monitoring of Heavy Metals

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Metal Polymer Nanocomposites

- Applications
  - Sensors
  - Catalysis
  - Nanoelectronics
    - Magnetic recording and information storage
    - MRI enhancement and medical diagnostics
Polyamic Acid

\[
\begin{align*}
\text{Polyamic Acid} & \quad \text{Structure}
\end{align*}
\]
Objectives

- To synthesize Au nanoparticles in organic medium using a short, simple and convenient method.

- To study the potential of the PAA-metal nanoparticle films for the analysis and removal of heavy metals from aqueous medium.
PAA Synthesis and Chemistry

Pyromellitic dianhydride - PMDA

4,4'-Oxydianiline - ODA

MeCN, rt
Stir, 1 hr, filter

Mw = 10,000 (by GPC)
One Pot Synthesis of Stable NPs

PAA-capped Gold nanoparticles-Single phase, stable and monodispersed

Synthesis

PAA was dissolved in DMF and solid AuCl$_3$ was added to it. The reaction was allowed to proceed at room temperature.
Characterization

- UV/Visible Spectroscopy
- SEM
- TEM
- Electrochemical (conductivity, electroactivity)
- EDS (elemental composition)
Absorption Spectrum

Peak at 530 nm is typical of Au nanoparticles of less than 10 nm
Time-dependent UV-VIS spectrum after the addition of 1.5 mg AuCl₃ to a 4 mL dimethylformamide solution containing 1 mg of PAA to form PAA-capped gold nanoparticles: a) 1 min b) 5 min c) 10 min d) 15 min e) 20 min f) 25 min g) 30 min h) 35 min i) 40 min j) 45 min k) 50 min.
PAA Characterization
Infrared

Amide Vibes

COOH Vibes

Pyromellitic dianhydride - PMDA

4,4’-Oxydianiline - ODA

Poly(amic acid) - PAA
$^1$HNMR of PAA

PAA in DMSO at 360 MHz 03/01/2004

Diagram of PAA structure with NMR peaks indicated.
NMR of PAA oxidized by Au Nanoparticles
**Particle Size and Distribution**

TEM of the well dispersed Au nanoparticles from reduction of 1.5 mg AuCl₃ by 6mL of 0.16 mg/mL PAA in DMF

Average particle size: $5.11 \pm 0.89$ nm (from 200 particles)
TEM and SEM Images

TEM of the Au nanoparticles agglomerates from reduction of 10 mg AuCl₃ by 2mL of 10 mg/mL PAA in DMF and diluted to 100 mL

SEM Images of Au Nanoparticle agglomerates on PAA film deposited on GCE x 600
SEM and Elemental Analysis

CV of PAA before and after Au incorporation.
Medium: 0.1M PBS pH 6.19. Scan rate = 50 mV/s

Energy dispersive spectrum of the Au Nanoparticles on PAA film deposited on GCE
Ag Nanoparticles

CV of PAA before and after Ag incorporation.
Medium: 0.1 M PBS pH 6.19

Energy dispersive spectrum of the Ag Nanoparticles on PAA film deposited on RVC
Pd Nanoparticles

Energy dispersive spectrum of the Au Nanoparticles on PAA film deposited on GCE
Co Nanoparticles

Energy dispersive spectrum of the Ag Nanoparticles on PAA film deposited on RVC
Preliminary Environmental Application

[Cysteine]

Acetate Buffer pH 4

[Cysteine]

Cu^{2+}

[Cu^{2+} with Cysteine]

N\_2 \_ S \_ S

OHOC

COOH

Cysteine
Metal Sensing

CV of PAA-Au-Cyst-Cu in Acet Buffer pH 4. Accumulation time = 20 min in 1ppm Cu in buffer. Scan Rate = 50 mV/s

DPASV of PAA-AuNP-Cys-Cu in acetate buffer pH 4. Accumulation time = 20 min in acetate buffer. Voltammetric conditions: reduction potential = -1 V, scan rate = 50 mV/s
Screen-Printed Electrodes

SPE 6% PAA-Cyst-Cu (1ppm) in Acetate Buffer.
Scan rate = 50 mV/s

DPASV of SPE 6% PAA-Cyst-Cu (1ppm) in acetate buffer pH 4. Acc time = 20 min in acetate buffer. Voltammetric conditions: reduction pot = -1V, scan rate = 50 mV/s

PAA Modified Screen Printed Electrode
Selective Removal of Copper

$$\text{H}_2\text{AuCl}_4 + \text{H}_2\text{O}_2 \rightarrow \text{NH}_2$$

HCl, aqueous

Au Nanoparticle + polyaniline composite

Cu Removal

P Buffer pH 5

Cysteine modified Au Nanoparticle + Polymer composite
## Selective Removal of Copper

<table>
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<tr>
<th>PGN oxidation</th>
<th>% Cu Removed</th>
<th>RSD</th>
<th>Other Metals removed</th>
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<tr>
<td>10s</td>
<td>34.72</td>
<td>10.46</td>
<td>Mn</td>
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<tr>
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<td>Zn</td>
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<tr>
<td>500s</td>
<td>99.7±0.3</td>
<td>0.003%</td>
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Biosensing Applications

\[ \text{NH}_2-\text{Ar}_2 \text{CONH}_-\text{ENZYMES} \]

2HN-PROTEINS

\[ \text{HOOC-ANTIBODIES} \]

2HN-ENZYMES

\[ \text{CONH-ENZYMES} \]

\[ \text{CONH-PROTEINS} \]

\[ \text{HNOC-ANTIBODIES} \]
Summary

- Rapid, simple and convenient method of synthesizing Au nanoparticles in organic medium by the use of PAA which acts both as a reducing and a capping agent.
- The process takes about 30 min and the gold particles are stable and can be well dispersed or agglomerated depending on the concentration of the reactants.
- The potential of the PAA-metal nanoparticle films in the analysis and removal of heavy metals from aqueous medium is demonstrated.
- Other metals salts of Co(II), Pd(II) and Ag(I) can also form metal nanoparticles on reduction with PAA and applied potential.
- Preliminary applications for metal testing evaluated.
Further Work

- Investigate the reduction of other metal salts with PAA
- Investigate the use of these metal nanoparticles in environmental and other applications
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