Gum Acacia a Versatile Medium for Biomineralization – Metal Carbonates and Synthesis - Metal Nanoparticles

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Synthesis, Characterization and Applications of

Role of Gum Acacia – Crystal growth modifier

PANi- As Heterogeneous Catalyst

Gum Acacia-Stabilized Silver Nanoparticles

Gum-Acacia supported Pd nanoparticles

Gum Acacia Stabilized Pt Nanoparticles

for various organic transformations
X-ray Photoelectron Spectroscopy

Small Area Detection

X-ray penetration depth ~1 μm. Electrons can be excited in this entire volume.

Electrons are extracted only from a narrow solid angle.

X-ray excitation area ~1 cm². Electrons are emitted from this entire area.
XPS may involve the concurrent emission of both Photoelectrons and Auger electrons.
Auger Electron

L23

L1

K
XPS probes the first ≈ 5-10 nm of a surface and provides the following information:

- Identification of all elements (except H and He) present at concentrations >0.1 atomic %
- Semi-quantitative information (±5%)
- Molecular environment (oxidation states, bonding atoms)
- Surface sensitivity from 5 to 75 angstroms
- Conducting and insulating materials
- Lateral variations in surface composition
- Non-destructive elemental depth profiles and surface heterogeneity (10 nm)
- Destructive elemental Depth profiles (1 μm)
- Spactial resolution for surface mapping from > 10 mm
Surface analysis by XPS requires irradiating a solid in an Ultra-high Vacuum (UHV) chamber with monoenergetic soft X-rays and analyzing the energies of the emitted electrons.

<table>
<thead>
<tr>
<th>Degree of Vacuum</th>
<th>Pressure Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Vacuum</td>
<td>$10^2$</td>
</tr>
<tr>
<td>Medium Vacuum</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>High Vacuum</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Ultra-High Vacuum</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-11}$</td>
</tr>
</tbody>
</table>

- **Remove adsorbed gases from the sample.**
- **Eliminate adsorption of contaminants on the sample.**
- **Prevent arcing and high voltage breakdown.**
- **Increase the mean free path for electrons, ions and photons.**
The Photoelectron Spectrum

- Both photoemission and Auger peaks observed in a spectrum.
- Peaks are superimposed on a rising background, due to inelastically scattered photoelectrons.
XPS Spectra showing the Chemical State of Si

Thin SiO₂ layer on Si

Thick SiO₂ layer on Si

300 W Mg Ka excited spectra
Quantitative Surface Analysis of Poly(ethylene tetraphthalate) - PET

C_{1s} region

C_{1s} region

O_{1s} region

---

Experimental theory

C(1) 65 at% 60 at%
C(2) 23 at% 20 at%
C(3) 12 at% 20 at%
O(1) 51 at% 50 at%
O(2) 49 at% 50 at%

180 W Mg Kα excited spectra
XPS spectra of Pd-PVA films: with Pd/PVA = 0.09 (a) before heating, (b) heated at 130 °C for 30 min, (c) heated at 130 °C for 120 min, and (d) with Pd/PVA = 0.015 heated at 130 °C for 60 min; deconvolution of each spectrum is indicated (ref. 34. © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).
**Typical binding energies for C 1s photoemission peaks from organic materials**

<table>
<thead>
<tr>
<th>functional group</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbon</td>
<td>C-H, C-C 285.0</td>
</tr>
<tr>
<td>amine</td>
<td>C-N 286.0</td>
</tr>
<tr>
<td>alcohol, ether</td>
<td>C-O-H, C-O-C 286.5</td>
</tr>
<tr>
<td>fluorocarbon</td>
<td>C-F 287.8</td>
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<tr>
<td>carbonyl</td>
<td>C=O 288.0</td>
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<tr>
<td>2F bound to a carbon</td>
<td>-CH₂CF₂⁻ 290.6</td>
</tr>
<tr>
<td>3F bound to a carbon</td>
<td>-CF₃ 293-294</td>
</tr>
</tbody>
</table>

**Typical chemical shifts for O 1s photoemission peaks from organic materials**

<table>
<thead>
<tr>
<th>functional group</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonyl</td>
<td>-C=O, O-C=O 532.2</td>
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<tr>
<td>alcohol, ether</td>
<td>-O-H, O-C-O 532.8</td>
</tr>
<tr>
<td>ester</td>
<td>C-O-C=O 533.7</td>
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</table>

*Figure 3.* C1s spectra derived from X-ray photoelectron spectroscopy of teak heartwood, showing an unextracted section with percentage of C1 (C-C and C-H) at 73, of C2 (C-OH) at 17, C3 (O-C-O or C=O) at 7, and C4 (O-C=O) at 3 (Fig. 3a), and a section extracted with acetone and chloroform in which the percentage of C1, C2, C3, and C4 measured 42, 35, 19, and 4, respectively (Figure 3b).
Biomineralization

- The process by which mineral crystals are deposited in an organized fashion in the matrix (either cellular or extracellular) of living organisms” (Boskey, 1998).

- The study of the formation, structure and properties of inorganic solids deposited in biological system.

Components of Biominerals

**Organic materials**: protein, glycoprotein, polysaccharide, etc

**Inorganic materials**: silica, calcium carbonate, hydroxyapatite, etc
Biologically induced biomineralization
- Biologically controlled biomineralization
- Site-directed biomineralization
- Control mechanism

Biomineralization is a new type of chemistry

New type of chemistry

Synthesis

Construction

(Hard and Soft Matter)

Design of functionalized inorganic-organic materials
(Small and large)
Biomineralization: a new chemistry

Biomineralization has shifted towards a chemical perspective

Bioinorganic Chemistry
Biomimetic Materials Chemistry

- Structural and compositional characterization of biominerals,
- Understanding the functional properties of biominerals
- Elucidation of the processes through which organic macromolecules and organic structures
- Control the synthesis, construction and organization of inorganic mineral-based materials.
- Supramolecular chemistry
- Organized matter chemistry
General Biomineralization Mechanism

1.) **Nucleation**
   - Specific (anionic) protein nucleators that provide a template or sequester the ions and direct the ions in an ordered orientation to form the initial crystal structure

2.) **Crystal expansion**
   - Ions add onto specific sites on the initial crystals
   - Crystals aggregate

3.) **“Other” molecules (ex. matrix proteins) regulate crystal expansion**
   - Can bind to the crystals to inhibit or shape crystal formation
   - Can transport or sequester ions
General principles

- uniform particle sizes
- well-defined structures and compositions
- high levels of spatial organization
- complex morphologies
- controlled aggregation and texture
- preferential crystallographic orientation
- higher-order assembly
- hierarchical structures
Outline of the talk

Impact of natural Gum Acacia material as crystal growth modifier on the crystallization of $\text{BaCO}_3$ & $\text{SrCO}_3$ superstructures

Green synthesis of metal nanoparticles in aqueous medium using Gum Acacia a natural biopolymer as reducing, stabilizing and templating agent
Highly branched polysaccharide consisting of β-(1-3) galactose backbone with linked branches of arabinose and rhamnose, which terminate in glucuronic acid.

About 10 wt % - arabinogalactan–protein complex (GAGP–GA glycoprotein), arabinogalactan chains are covalently linked to a protein chain through serine and hydroxyproline groups.

Glycoprotein – About ~1% - Highest protein content (~50 wt %) Differs in its amino acids composition from that of the GAGP complex.

The functional group (-OH) present in Arabinose and rhamnose and (-COOH) of gluconic acids play a crucial role in the growth and formation metal carbonates and metal nanoparticles.

The proteinaceous core with amino acids stabilize the formed metal carbonates and metal nanoparticles.
Role of Gum Acacia – Crystal growth modifier – Metal reducing agent

Highly branched polysaccharide

\textbf{β-(1-3) galactose} backbone with linked branches of \textbf{arabinose} and \textbf{rhamnose}, which terminate in \textbf{glucuronic acid}

\textbf{10 wt % - arabinogalactan–protein complex} (GAGP–GA) \textbf{glycoprotein}

\textbf{Arabinogalactan chains} are covalently linked to a protein chain through \textbf{serine} and \textbf{hydroxyproline} groups

\textbf{Glycoprotein} – About \textbf{~1\%}

Highest protein content \textbf{(\textasciitilde 50 wt \%)}

Differs in its amino acids composition from that of the GAGP complex

The functional group \textbf{(-OH)} present in \textbf{arabinose} and \textbf{rhamnose} and \textbf{(-COOH)} of \textbf{gluconic acids} play a crucial role in the growth and formation metal carbonates and metal nanoparticles

The \textbf{proteinaceous core} with \textbf{amino acids} stabilize the formed metal carbonates and metal nanoparticles.
Flow chart for the synthesis of $\text{BaCO}_3$ and $\text{SrCO}_3$ clusters

$\text{BaCl}_2/$$\text{SrCl}_2$ (1 mmol)

$\downarrow$

0.5% wt GA /1.0% wt GA

$\downarrow$ stirring for 0.5h

Clear solution

$\downarrow$

$\text{NaHCO}_3$

$\downarrow$ stirring for 0.5 h

24 hrs crystallization

$\downarrow$

Filtered, dried at room temperature

$\downarrow$

Product for characterization

(XRD, SEM-EDAX, TGA-MS, FTIR, and TEM)
SEM images of BaCO$_3$ superstructures

(a) Dendrimeric structures in the absence of additive.
(b) & (c) Room temp reaction process at 0.5% & 1.0% GA
(d) & (e) Hydrothermal (90°) reaction process at 0.5% & 1.0% GA
SEM images of SrCO$_3$ superstructures

(a) Dendrimeric structures in the absence of additive.
(b) & (c) Room temp reaction process at 0.5% & 1.0% GA
(d) & (e) Hydrothermal (90$^\circ$) reaction process at 0.5% & 1.0% GA
Mechanism for the formation rice-like hollow hybrid

Formation of amorphous metal carbonate particles

Aggregation of GA chains

Binding of metal carbonate particles

Polymorph transformation

Mechanism for the formation spherical hybrid

Formation of amorphous metal carbonate particles

Binding of metal carbonate particles

Polymorph transformation

Aggregates of absorbed crystallites
TGA-MS Studies

Gum Acacia

MS – 44 a.m.u

SrCO3

MS – 44 a.m.u
SrCO$_3$ With Gum Acacia

MS – 44 a.m.u

SrCO$_3$ With Gum Acacia Calcined

MS – 44 a.m.u
Preparation of Acacia-Stabilized Silver Nanoparticles: A Green Approach

Schematic illustration of the synthesis of silver nanoparticles with the acacia polymer

UV-Vis spectra of silver nanoparticles with the acacia polymer at different times

UV-Vis spectra of silver nanoparticles in acacia polymer (0.3 wt%) with different concentrations of AgNO₃.

UV-Vis spectra of silver nanoparticles with AgNO₃ concentration of 0.5 wt% and different concentrations of acacia polymer.
TEM images for silver nanoparticles prepared with an AgNO₃ concentration of 0.5 wt % and different concentrations of acacia: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.5 wt %. 
Direct One-Pot Reductive Amination of Aldehydes with Nitroarenes in a Domino Fashion: Catalysis by Gum-Acacia-Stabilized Palladium Nanoparticles

XRD pattern of acacia stabilized Pd nanoparticles

SREEDHAR et. al.
Vol. 121, 1765–1773 (2011)
TEM images and histograms showing the particle size distribution of GA-Pd nanoparticles before (a) and after (b) catalysis observed at 120 kV.
High resolution narrow scans of C 1s for (a) Gum Acacia and (b) Gum Acacia-Pd nanoparticles.

High resolution narrow scans of Pd 3d for (a) Gum Acacia-Pd and (b) Pd nanoparticles.
TEM images of the Pd nanoparticles prepared using palladium precursor and acacia gum in the ratios, a) 1:5.88, b) 1:11.76, c) 1:23.52, and d) 1:29.41.
Atomic force microscopy images of (a) pure acacia gum, (b) acacia gum stabilized Pd nanoparticles after 1 h and (c) 6 h heating at 100 °C
Reductive N-alkylation of Nitroarenes by Hydrogenation

1. Reduction

2. Halogenation

SREEDHAR et al. 2009, 74, 8806
GA-Pd Nanoparticles Catalyzed Reductive Amination of Different Aldehydes with Nitrobenzene under H₂ Atmosphere

<table>
<thead>
<tr>
<th>entry</th>
<th>aldehyde</th>
<th>product</th>
<th>time (h)</th>
<th>yield (%)</th>
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<td>( \text{PhCHO} )</td>
<td>( \text{Ph-NH} )</td>
<td>6</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>( \text{BrPhCHO} )</td>
<td>( \text{BrPh-NH} )</td>
<td>6</td>
<td>85</td>
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<tr>
<td>3</td>
<td>( \text{PhCHO} )</td>
<td>( \text{Ph-NH} )</td>
<td>5</td>
<td>94</td>
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<tr>
<td>4</td>
<td>( \text{H₃C-PhCHO} )</td>
<td>( \text{H₃C-Ph-NH} )</td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>( \text{HO-PhCHO} )</td>
<td>( \text{HO-Ph-NH} )</td>
<td>5</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>( \text{O-PhCHO} )</td>
<td>( \text{O-Ph-NH} )</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>( \text{PhCH₂CHO} )</td>
<td>( \text{PhCH₂-NH} )</td>
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<tr>
<td>8</td>
<td>( \text{CH₃CHO} )</td>
<td>( \text{CH₃-NH} )</td>
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<tr>
<td>9</td>
<td>( \text{CH₃CH₂CHO} )</td>
<td>( \text{CH₃CH₂-NH} )</td>
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<tr>
<td>10</td>
<td>( \text{PhCO} )</td>
<td>( \text{Ph-NH} )</td>
<td>5</td>
<td>94</td>
</tr>
</tbody>
</table>

*aReaction conditions: aldehyde (1 mmol), nitrobenzene (1.2 mmol), methanol (5 mL), and Pd catalyst (1.3 mol %) at room temperature.*
Pd Nanoparticles

$\text{(H}_2\text{ Gas)}$

$\text{C}_3\text{H}_7\text{CHO}$

$\text{C}_6\text{H}_5\text{CHO}$

Yield (%) vs. No. of Cycles

R = Alkyl or Aryl
Gum-Acacia supported Pt nanoparticles: Effective reusable catalyst in aqueous solution for selective hydrogenation of nitroarenes

TEM images of GA-Pt nanoparticles (a) fresh catalyst (b) used catalyst (c) HRTEM of fresh catalyst (d) histogram of fresh and used GA-Pt catalyst and (e) SAED pattern of GA-Pt catalyst.

SREEDHAR et. al.  
Catalysis Communication  
12 (2011) 1009–1014
UV-Vis absorption spectra of GA-Pt nanoparticles dispersed in water heated at 100°C recorded at different time intervals. Inset shows as prepared GA-H$_2$PtCl$_6$ solution (a) before and (b) after heating at 100°C for 24 h.
XRD pattern of GA-Pt nanoparticles
XPS high resolution narrow scans of (a) C 1s and (b) Pt 4f for GA-Pt nanoparticles
Hydrogenation of nitroarenes using colloidal GA-Pt nanoparticles.\textsuperscript{a}

<table>
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<tr>
<th>Entry</th>
<th>Nitroarene</th>
<th>Product</th>
<th>Yield (%)\textsuperscript{b}</th>
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<td></td>
<td>91, 84\textsuperscript{c}</td>
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<td>3</td>
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<td>95, 87\textsuperscript{c}</td>
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<tr>
<td>12</td>
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<td>75</td>
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</table>

\textsuperscript{a}Reaction conditions:
Aromatic nitro compound (1 mmol), GA-Pt colloidal nanoparticles in water (5 mL, 0.24 mol\% of platinum) at room temperature under H\textsubscript{2} atmosphere (1 Atm).

\textsuperscript{b}Isolated yields.

\textsuperscript{c}Yield after fifth cycle.
PANi- As Heterogeneous Catalyst

Unique features of PANi as support for heterogeneous catalysis

- inert nature
- insolubility in many organic solvents and water
- high thermal stability as they decompose at around 300 °C
- easy separation of the catalyst by simple filtration.
- easy to handle
- easy reusability


Synthetic Metals 156 (2006) 1139
PANI-Sc (3 mol %)


Org. Lett. 7 (2005) 1971

Org. Lett. 6 (2004) 4821

Tetrahedron 45 (2004) 3561

R = alkyl, aryl; R' = alkyl, aryl, H

Tetrahedron 63 (2007) 8002

Tetraallyltin

TMS

Me

OH

Me

R = alkyl, aryl; R' = alkyl, aryl, H

52-98%
Template free polymerization of aniline using ammonium persulfate as an oxidant in the presence of base under ultrasound irradiation.

Different morphologies (nanospheres, nanorods and nanotubes) were obtained by tuning the ratio of aniline and base in the presence of the oxidant.

\[
\begin{align*}
\text{aniline} + \text{NaOH} & \\
0.15:10 & \\
0.12:10 & \\
0.1:10 & \\
\text{Overnight at } 0^\circ\text{C} & \\
\text{Ammonium persulphate (0°C)} & \\
\text{Filtered, washed, dried} & \\
\text{After 6 h} & \\
\end{align*}
\]
0.01M (NH₄)₂VO₃ in H₂O, rt, 6h stirring
Filtered

Nano PANI dispersed in water

BET Surface area (m²/g)

ICP-AES
Vanadium content

2.16 wt%

2.20 wt%

2.16 wt%
SEM & TEM images of nanoPANI
Sequential formation of PANi nanorods – TEM images

1 h–irregular particulate morphology

6 h–particles growing in length

24 h–uniform rod shaped PANi nanoparticles

12 h–gradual formation of non-uniform rod shaped PANi

Philips TECNAI FEI12
Sequential formation of PANi nanorods – AFM images

Oligomers aggregate to form granules

Granules self assembly to form chains

Chains eventually grow into rods

Veeco Nanoscope IV
Sulfoxidation

Shape versus Reactivity

S\text{Br} + \text{H}_2\text{O}_2

Conversion

30\% \ (0.5\text{h})

90\% \ (0.5\text{h})

100\% \ (0.5\text{h})

SREEDHAR et. al.

copolymers
advanced
technologies
20 (2009) 950-958
**Nano PANi-VO$_3^{2-}$: Catalytic application for Sulfoxidation Reaction**

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst $^a$</th>
<th>Time (h)</th>
<th>Conv. (%) $^b$</th>
<th>Sulfoxide</th>
<th>Sulfone</th>
<th>Selectivity $^b$ (%)</th>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>S</td>
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<tr>
<td>3</td>
<td>R</td>
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<td>T</td>
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<tr>
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<td>7</td>
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<td>0.5</td>
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<td>100 (100)$^c$</td>
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<td>8</td>
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<td>0.5</td>
<td>100 (90)$^c$</td>
<td>100 (100)$^c$</td>
<td>-</td>
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</table>

$^a$ PANI - , S-nanospheres, R-nanorods, T-nanotubes, PANI-V, SV- nanospheres with VO$_3^{2-}$, RV- nanorods with VO$_3^{2-}$, TV- nanotubes with VO$_3^{2-}$

$^b$ Conversions & Selectivities based on $^1$H NMR spectroscopic integrations

$^c$ Conversion after fifth cycle.
**Conclusions**

- Use of natural material, Gum acacia for synthesis of higher ordered superstructures having remarkable effect in control on the nucleation, growth and alignment of metal carbonate particles in the reaction process.

- Gum acacia acts as crystal growth modifier

- A highly facile, simple, cost effective, and green approach has been developed for the synthesis of nearly monodispersed Pd, Pt and Ag nanoparticles via a simple aqueous-phase reaction between metal ions and naturally occurring gum acacia.

- Gum acacia not only acts as a reducing agent but also works as a stabilizer.