
بسم الله الرحمن الرحيم
Gateway to Knowledge

NANOSTRUCTURED METAL/MIXED METAL OXIDE THIN FILMS: SYHTHESIS, CHARACTERIZATION AND APPLICATIONS

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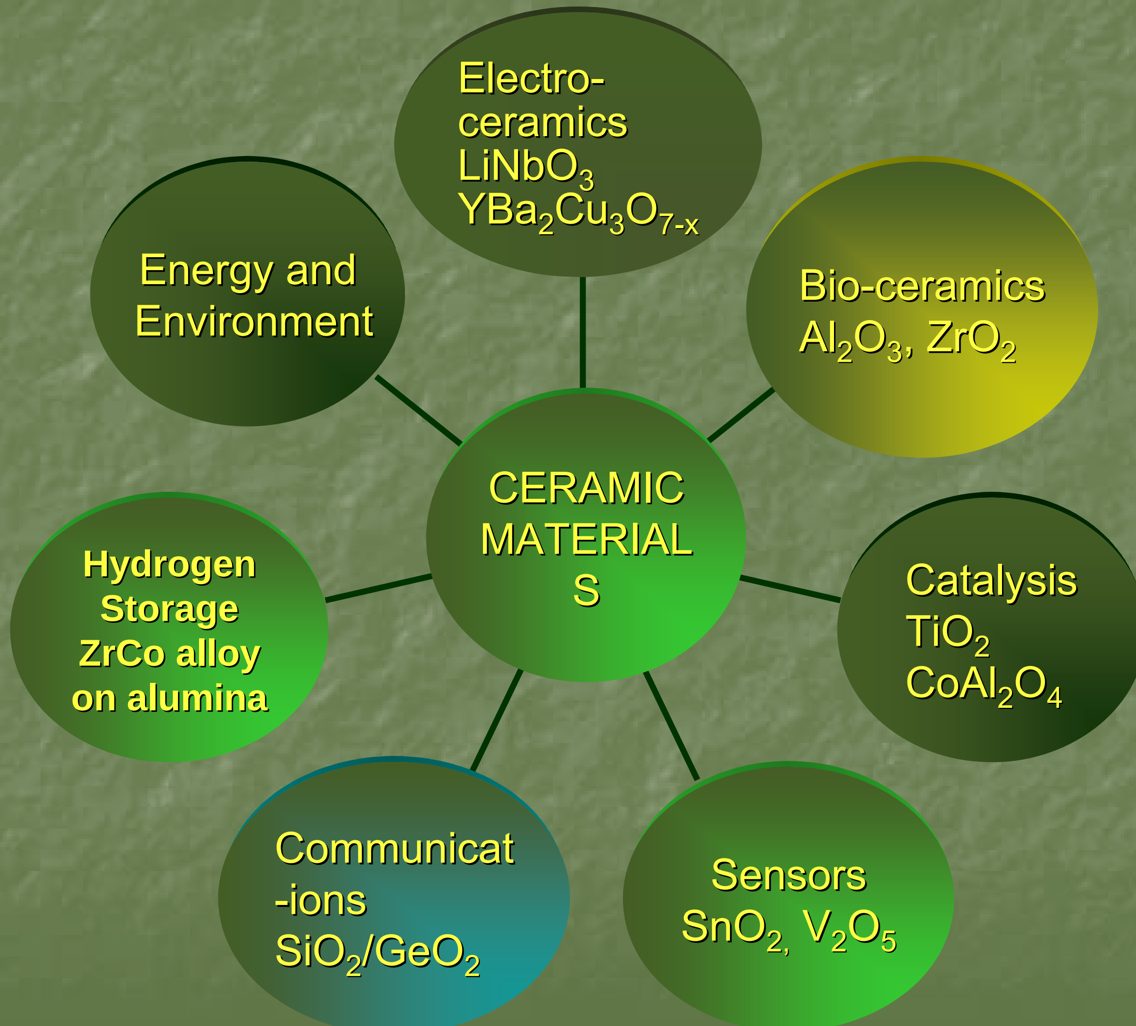
OFF THE RECORD

It is indeed a matter of great pleasure to be with the young scientific community who are going to set future trends of scientific and technological research in Pakistan. Although some improvements have taken place during a period of last 4-5 years, yet it is still a long way to go. The encouraging thing is that people have hope and required potential to act, the discouraging thing is that they lack proper guidance and planning in view of future needs.

We need to develop new efficient catalysts, to invent smart materials, to discover new drugs and ways to synthesize them, to open up the area of nano-science and to solve problems of energy, environment, molecular modeling, computational chemistry (theoretical chemistry) and simulation.

Applications of Ceramic Materials



What are nanomaterials?

Any Solid material that has a nanometer dimension

Building Blocks

- 0 D
  Quantum Dots
- 1 D
  Nanorods
- 2 D
  Sheets, Films
- 3 D
  Nanoparticle

Synthesis of Inorganic Materials

1. Solid State Reactions:
   - Low yield
   - No control over stiochiometery and Particle size
   - Phase purity
   - Laborious method-need several heat cycles etc. > 900^0C
   - Mechanical grinding
   - >100nm

2. Sol-Gel Method
   - Metal ions are precipitated in the presence of gelling agents c.a. citric acid, ethanediol or to form a gel which is heated after removal of water to form complex oxide.
   - Generally temperature is lower than 900^0C used in solid state reactions
   - Purity not so good

3. Gas-Phase Techniques

$$\left(\text{Suitable Precursor}\right) \xrightarrow[\text{Gas phase}]{\Delta} \left(\begin{array}{c}\text{Metal Oxide}\\ \text{(nm)}\end{array}\right)$$

General Properties of Precursors

- Adequate volatility
- Sufficient large temp “window” between evaporation and thermal decomposition
- Clean decomposition without incorporation of impurities
- Good compatibility with co-precursor
- Long shelf life, stable in solution
- Readily available at low cost
- Low hazard

Types of Precursors

- Metal Alkoxides – derivatives of alcohols & aminoalcohols
- Metal β-Diketonates – derivatives of β-diketones
- Metal Carboxylates – derivatives of carboxylic acids

Synthetic Methods

1- Synthesis of Monometallic Alkoxides

- Direct reaction of metal with alcohols

$$M + nROH \longrightarrow M(OR)_n + n/2\ H_2$$

- Treatment of metal salt with alcohol in presence of base e.g.

$$SnCl_2 + 2CH_3OH + 2Et_3N \longrightarrow Sn(OCH_3)_2 + 2Et_3NHCl$$

- Reaction between metal halide and alkali metal alkoxide e.g.

$$MX_n + nM'OR \longrightarrow MX_{n-y}(OR)_y\ /\ M(OR)_n + nM'X$$

- Metal alkoxides exist as oligomeric clusters $[M(OR)_x]_n$. Oligomerization can be suppressed by introduction of bulky alkoxide groups e.g.

$Zr(OC_2H_5)_4$ $Zr(O\text{-}ipr)_4$ $Zr(O\text{-}t\text{-}But)_4$

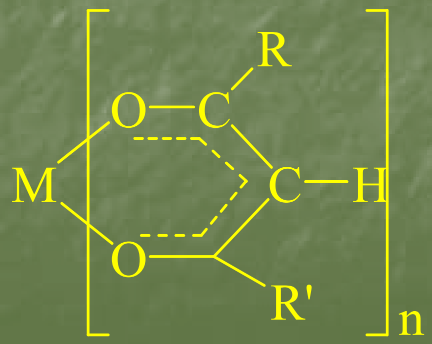
or use of other bidentate ligands such as N, N-dimethyl aminoalcohols

2 - Synthesis of Metal β-Diketonates

Most widely used precursors.

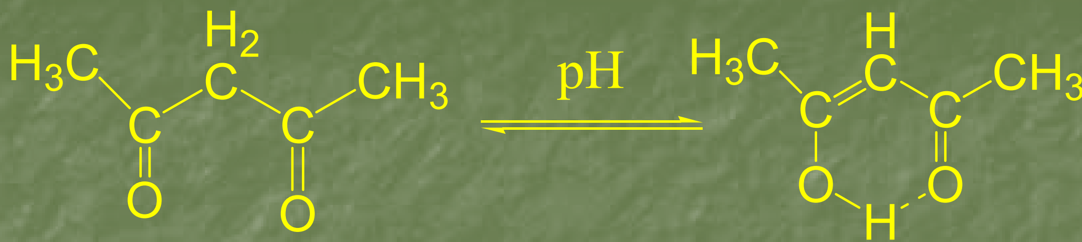
Properties can be tailored to suite process parameters:

- Evaporation temperature
- Deposition temperature
- Layer parity and uniformity
- Volatility : $Zr(acac)_4 < Zr(tfac)_4 < Zr(hfac)_4$



$R = R' = CH_3$ (acac)
$R = CH_3$, $R' = CF_3$ (tfac)
$R = R' = CF_3$ (hfac)

They are easily prepared as follows:



Keto Enol

$$MX_n + n(acacH) \xrightarrow{\text{pH Control}} M(acac)_n + nHX$$

Sono-chemical method:

$$M(NO_3)_n + n\ acacH \xrightarrow{))))} M(acac)_n$$

3- Synthesis of Heterobimetallic Precursors

- Bridging between two different metal alkoxides *e.g.

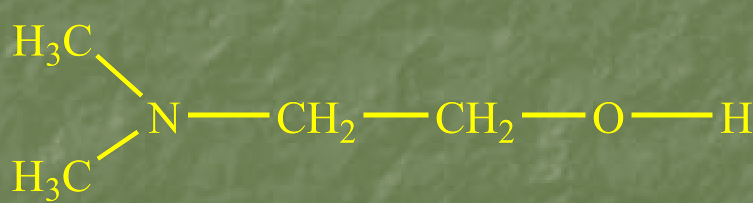
  $Mg[Nb(OEt)_6]_2.2C_2H_5OH$

  $Sr[Ta(OPr)_6]_2.2ProH$

  Commonly used alkoxides are:

  ethoxides, isopropoxide (most effective), t-butoxide

  Aminoalkoxides are also used to increase possibility of bridging e.g. $SrNb(OEt)_5(dmae)_2(EtOH)_2$**



(dmaeH)

* D. C. Bradley, R. C. Mehrotra, “Metal Alkoxides”, Academic press, New York, 1978.

A. C. Jones et al. *J. Matt. Chem.* **2004, 14, 887-894.

- Reaction between aminoalkoxide and metal β-diketonate

  e.g.

  $Ba_2Co(acac)_4(dmae)_3(dmaeH)$ *

  $Ni_2Cu_4(acac)_2(\mu\text{-}OH)_2(dmae)_4Cl_4$

  $Co_2Cu_4(acac)_2(\mu\text{-}OH)_2(dmae)_4Cl_4$

  $[TlNi(acac)_2(dmae)]_2$

- Reaction between aminoalkoxide and metal carboxylates

  e.g.

  $Zn_7Cu_5(OAc)_{10}(\mu\text{-}OH)_6(dmae)_4Cl_4$

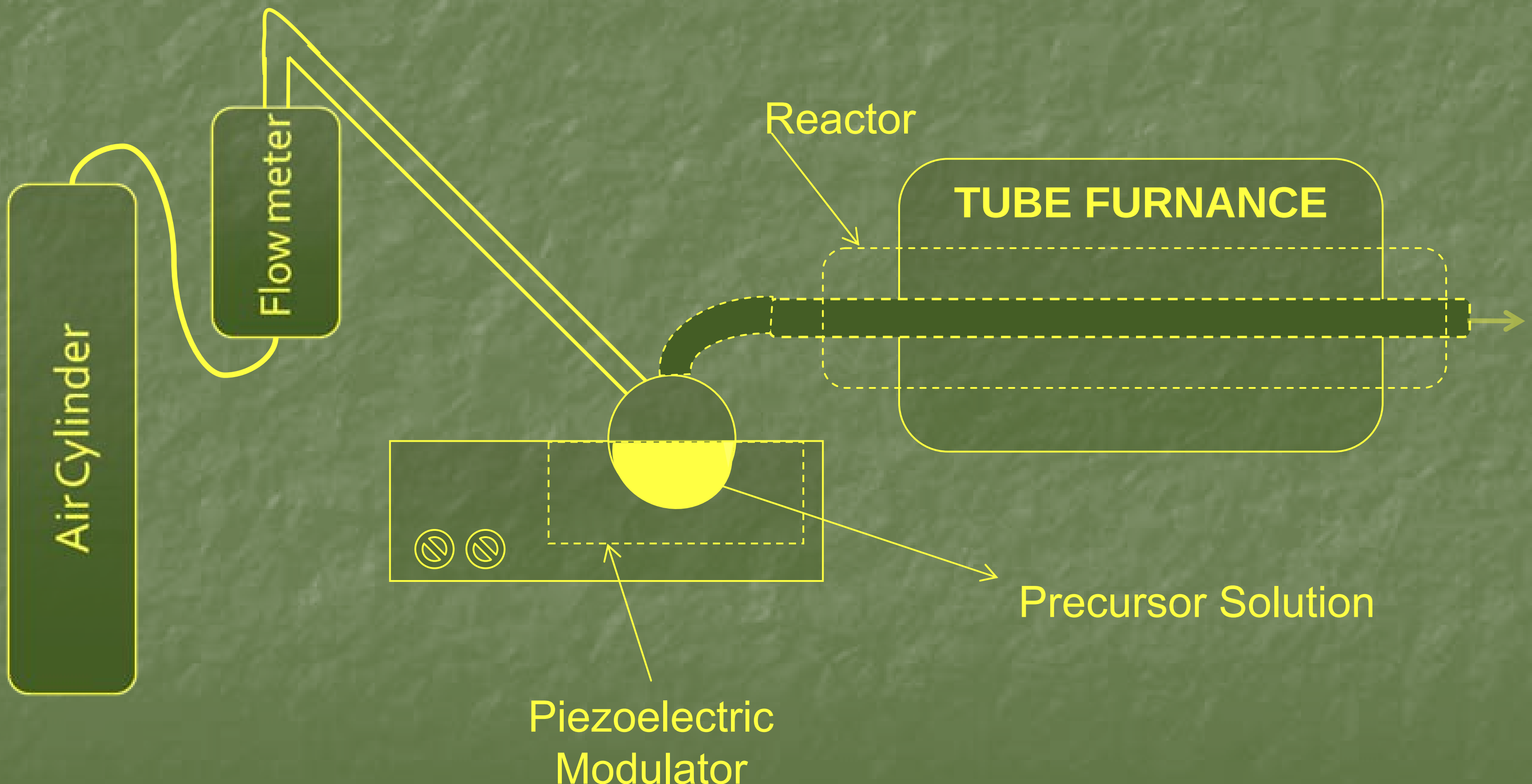
  $Ti_4Cu_6(dmae)_6(\mu\text{-}O)_6(\mu\text{-}OH)(OAc)_9.H_2O$

* Asif A. Tahir, Kieran C. Molloy, Muhammad Mazhar, Gabriele Kociok-Kohn, Mazhar Hamid, Sarim Dastgir, Inorg. Chem. 2005, 44, 9207-9212.

Notable Features

- Coordinatively saturate each metal centre by use of chelating ligands i.e. β-diketonate, carboxylates and functionalized alcohols.
- Application of multidentate ligands to force oligomeric complex into a more strictly molecular regime, generally reducing the possibility of interaction between monomeric units.
- Covering the metal oxide core by organic surroundings making the complex soluble in organic solvents.

How to make thin films? Apparatus for AACVD



Particle Size Control

Ultrasonic Nebulizer for Generating Nanoparticles

Particle size can be approximately controlled by controlling parameters.

$$d_h = 0.73 \sqrt[3]{\frac{T}{\rho f}}$$

T = surface tension of solvent

ρ = density of the solvent

f = frequency

For water

T = 0.0729 N/m

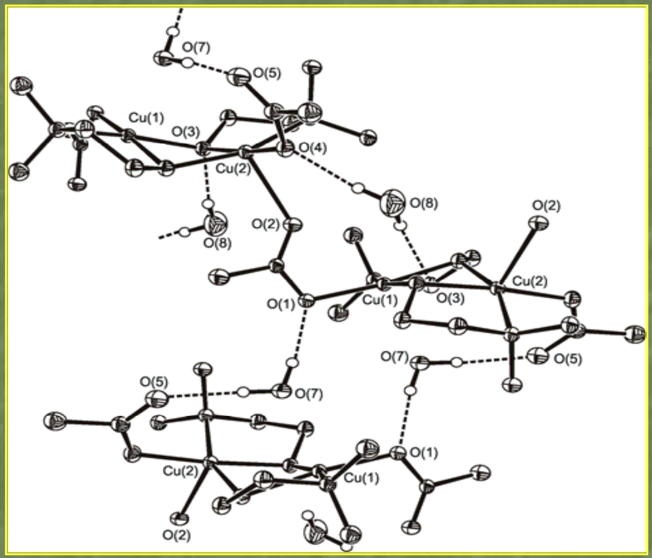
ρ = 1000 Kg/m3

f = 2.4 mHz

The size of the particles generated is approximately around 1.7 μ.

APPLICATIONS

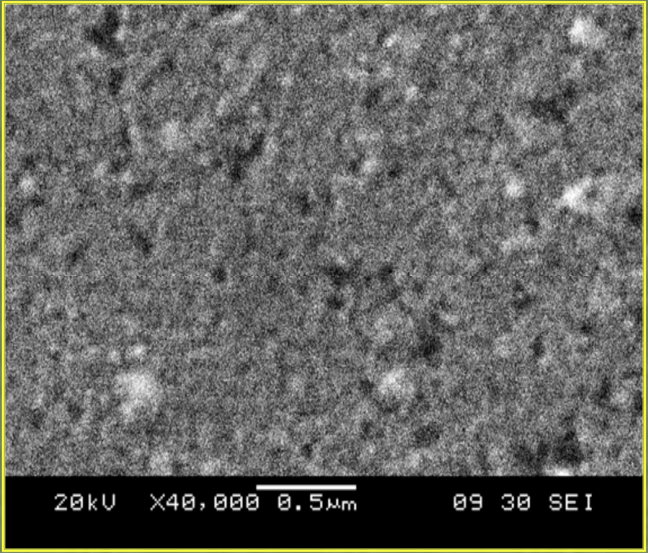
Metal coating



$[Cu(dmae)(OCOCH_3).H_2O]_n$

AACVD

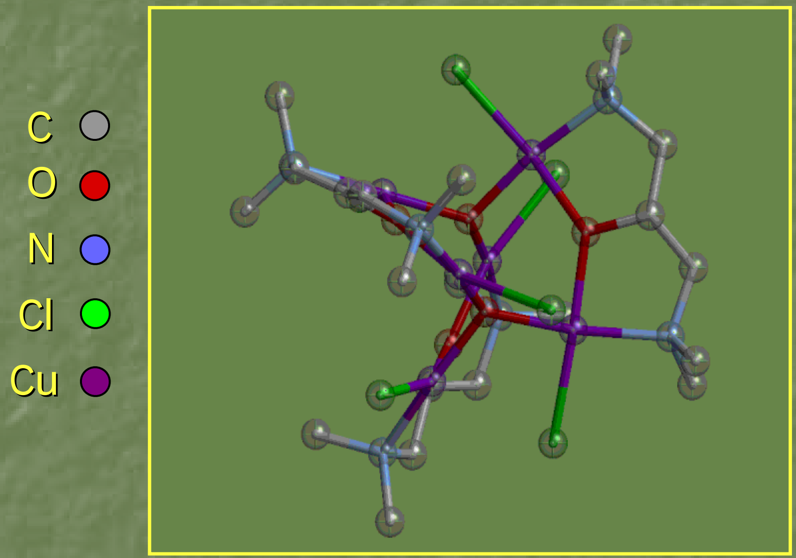
300 ° C / N_2



Cu (40-80nm)

$[Cu(dmae)(OCOCH_3).H_2O]_n$ (dmaeH = N, N-dimethylaminoethanol) was synthesized by the reaction of copper(II) acetate monohydrate $[Cu(OCOCH_3)_2.H_2O]$ and dmaeH in toluene. The complex undergoes facile decomposition at 300°C to form thin films of Cu on metallic and non metallic substrates.

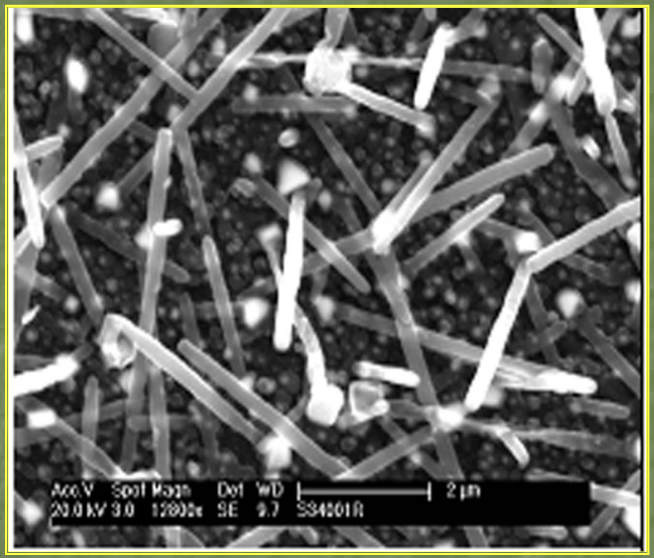
Copper nano-rods



$Cu_6(ddmap)_6Cl_6$

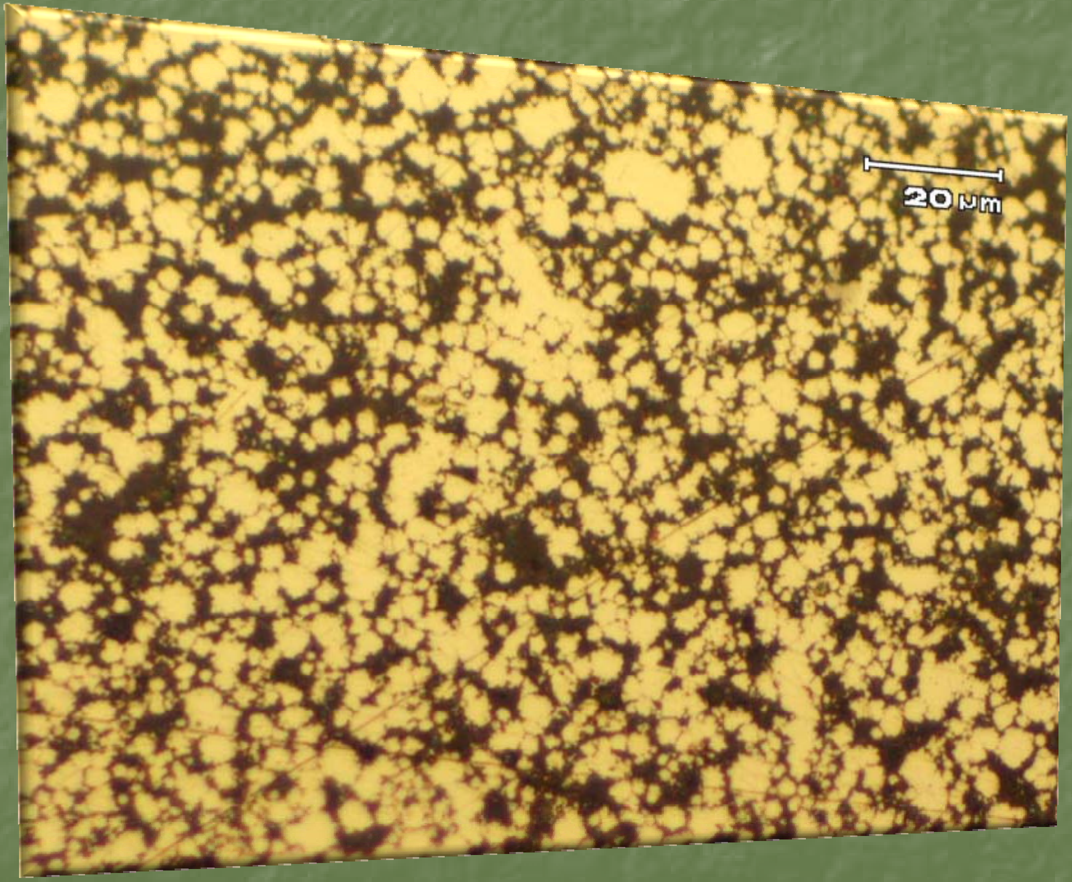
AACVD

300 °C / N_2



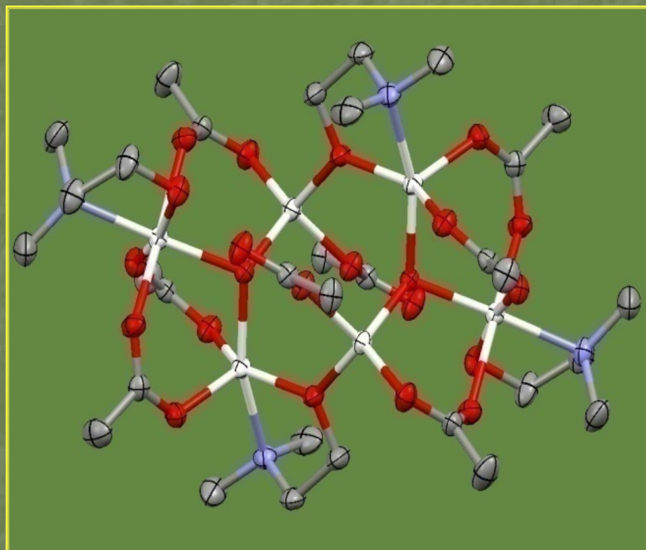
Cu nanorods

- Deposition of gold on nickel



Gas/ethanol vapor sensor

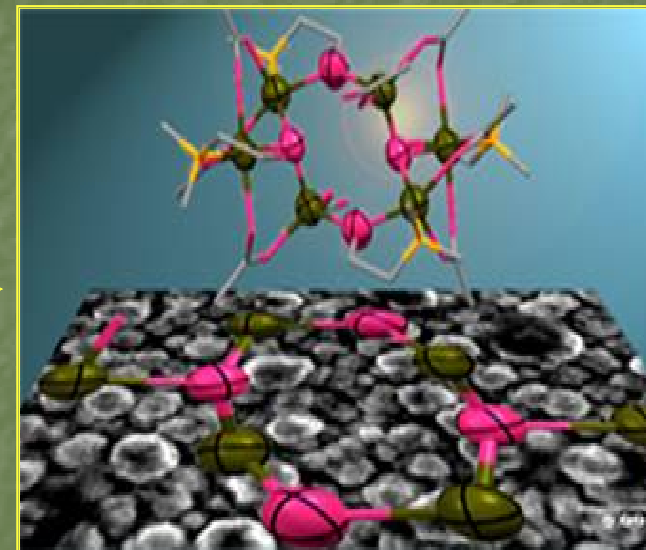
C
O
N
Zn



$Zn_6(OAc)_8(\mu\text{-}OH)_2(dmae)_2$

AACVD

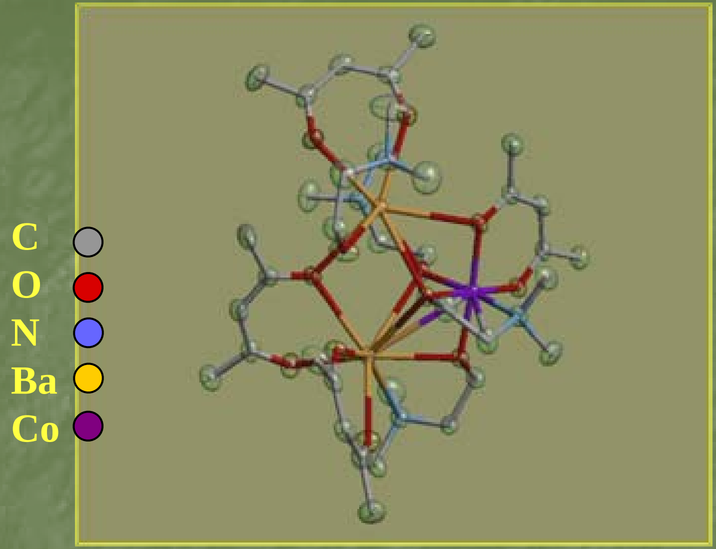
300 ° C / N_2



ZnO

* Mazhar Hamid, Asif A. Tahir, Muhammad Mazhar, Fiaz Ahmad, Kieran C. Molloy, Gabriele Kociok-Kohn. *Inorganica Chimica Acta* 2008, 361, 188–194.

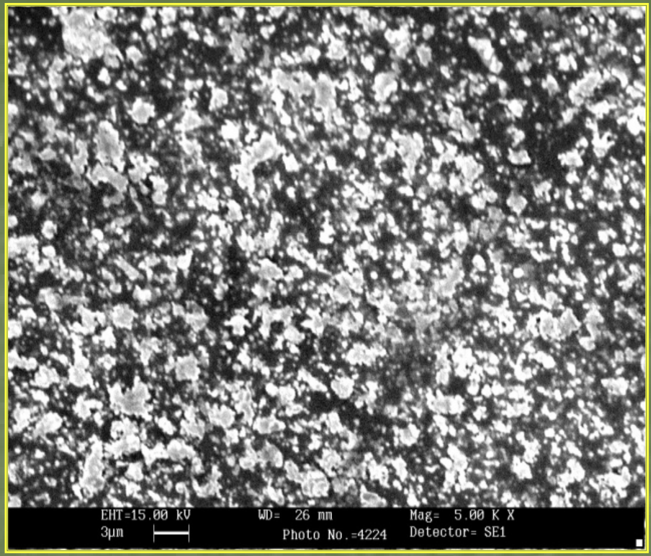
Thin Film of Ba/Co Bimetallic Oxide



$[Ba_2Co(acac)_4(dmae)_3(dmaeH)]$

AACVD

500°C

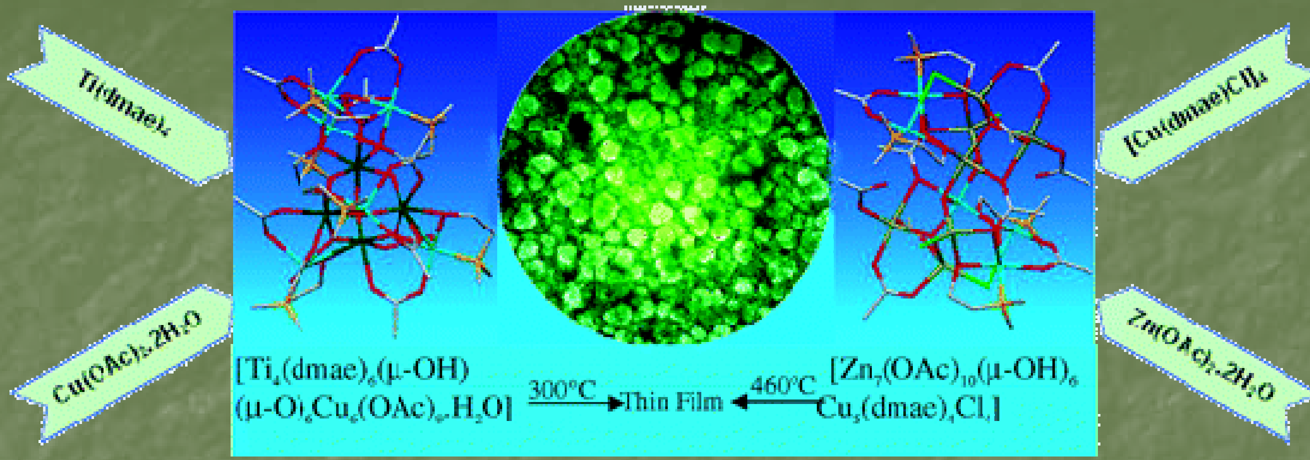


Ba_2CoO_3

Synthesis of single source precursor for chemical vapour deposition of Ba_2CoO_3 thin film from $[Ba_2Co(acac)_4(dmae)_3(dmaeH)]$ (dmaeH = N, N-dimethylaminoethanol) (acac = 2,4-pentanedionate) is being reported in 85% yield. The complex has been characterized by spectroscopic and single crystal X-ray analysis. This heterobimetallic precursor undergoes facile thermal decomposition to produce thin films of bimetal oxide Ba_2CoO_3.

* Asif A. Tahir, Kieran C. Molloy, Muhammad Mazhar, Gabriele Kociok-Kohn, Mazhar Hamid, and Sarim Dastgir. *Inorg. Chem.* 2005, 44, 9207-9212.

Thin film of CuTi/CuZn oxide

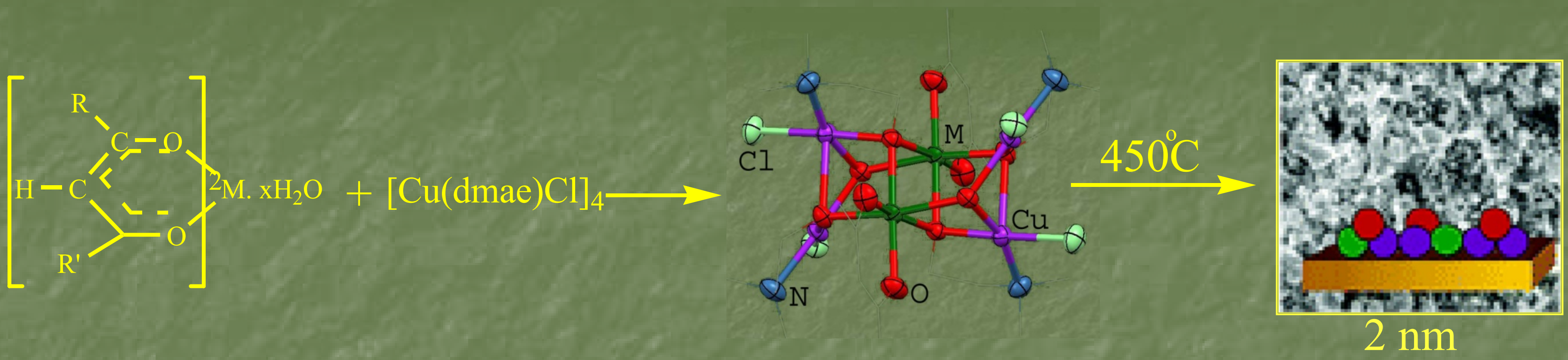


22 nm 26 nm

Heterobimetallic molecular precursors $[Ti_4(dmae)_6(\mu\text{-}OH)(\mu\text{-}O)_6Cu_6(OAc)_9\cdot H_2O]$ (1) and $[Zn_7(OAc)_{10}(\mu\text{-}OH)_6Cu_5(dmae)_4Cl_4]$ (2) for the deposition of metal oxide thin films of $Cu_6Ti_4O_{12}$ (Cu_3TiO_4, TiO_2) and $Cu_5Zn_7O_{12}$ (ZnO, CuO) were prepared and characterized by melting point, elemental analysis, Fourier transform IR, fast atom bombardment mass spectrometry, thermal analysis (TGA), and single-crystal X-ray diffraction. SEM and XRD of the thin films suggest the formation of impurity-free crystallite mixtures of Cu_3TiO_4 and TiO_2, with average crystallite sizes of 22.2 nm from complex 1 and of ZnO and CuO with average crystallite sizes of 26.1 nm from complex 2.

* Mazhar Hamid, Asif A. Tahir, Muhammad Mazhar, Matthias Zeller and Allen D. Hunter. *Inorg. Chem.* 2007, 46, 4120-4127.

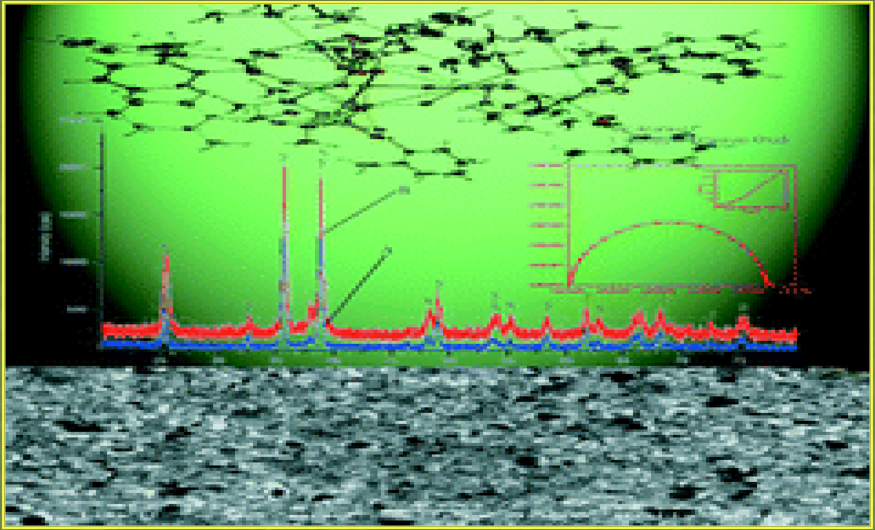
Thin film of CuCo/CuNi oxide



Heterobimetallic molecular precursors $[Co_2(acac)_2(\mu\text{-}OH)_2Cu_4(dmae)_4Cl_4]$ (**2**) and $[Ni_2(acac)_2(\mu\text{-}OH)_2Cu_4(dmae)_4Cl_4]$ (**3**) [dmaeH = *N*,*N*-dimethylaminoethanol and acac = 2,4-pentanedionate] for the deposition of mixed oxide thin films were prepared and characterized by MP, CHN, FT-IR, FABMS, magnetometery and single-crystal X-ray diffraction. TGA study shows that both complexes undergo controlled thermal decomposition at 450°C to give mixed metal oxides. Solid-state FT-IR, SEM, EDX, and XRD analysis were performed to analyze the chemical composition and surface morphology of the deposited oxide thin films. The results obtained indicate the formation of impurity-free crystalline mixed oxide films with particle sizes ranging from 0.55 to 2.0m.

* Mazhar Hamid, Asif A. Tahir, Muhammad Mazhar, Matthias Zeller, Kieran C. Molloy and Allen D. Hunter. *Inorg. Chem*. 2006, 45, 10457-10466.

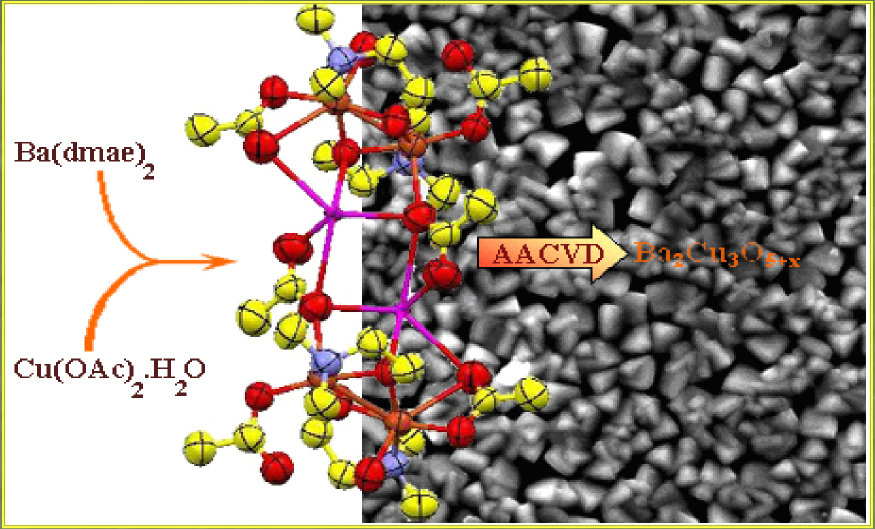
Thin film of Cu/Ti oxide



Heterobimetallic molecular precursors $[Ti_4(dmae)_6(\mu\text{-}OH)(\mu\text{-}O)_6Cu_6(benzoate)_9]$ (**1**) and $[Ti_4(dmae)_6(\mu\text{-}OH)(\mu\text{-}O)_6Cu_6(2\text{-}methylbenzoate)_9]$ (**2**) were prepared and characterized by MP, CHN, FT-IR, TGA and single crystal X-ray analysis. The TGA analysis proves that complexes (**1**) and (**2**) undergo facile thermal decomposition at 550°C to form copper titanium mixed metal oxides. The SEM/EDX and XRD analyses suggest the formation of carbonaceous impurity free good quality thin films of crystalline mixtures of $\alpha\text{-}Cu_3TiO_4$ and TiO_2 for both (**1**) and (**2**), with average grain sizes of 0.29 and 0.74 μm, respectively.

* Asif Ali Tahir, Mazhar Hamid, Muhammad Mazhar, Matthias Zeller, Allen D. Hunter, Muhammad Nadeem and Muhammad Javed Akhtar. Dalton Trans. 2008, 1224–1232.

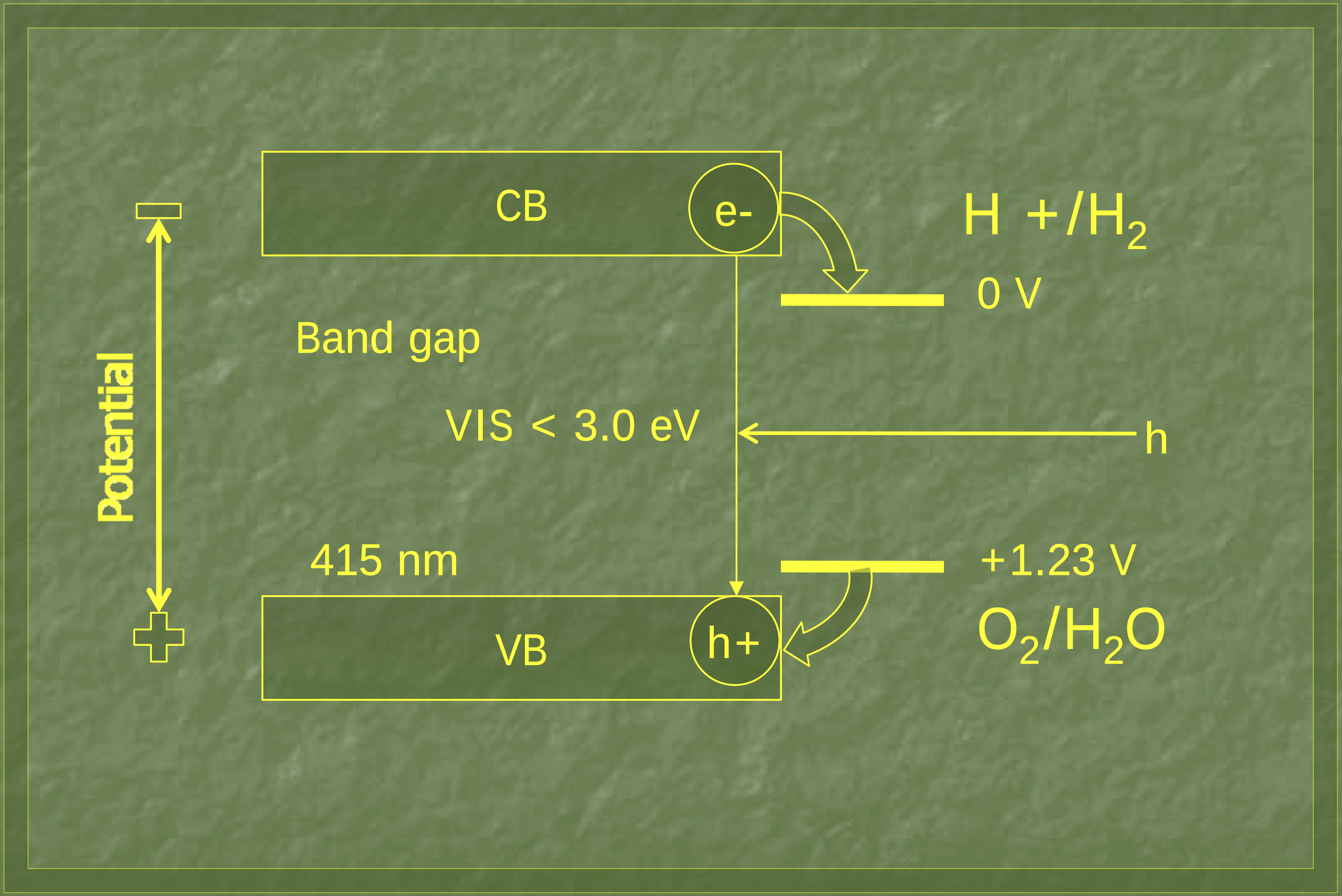
Thin film of $Ba_2Cu_3O_{5+x}$



A new heterobimetallic complex, $Ba_2(\mu\text{-}O\text{-}OAc)_4(OAc)_2Cu_4(\mu\text{-}O\text{-}dmae)_4(OH)_2$ (**1**), synthesized by direct method from $Ba(dmae)_2$ and Cu $(OAc)_2$. H_2O was characterized by melting point, CHNS, FT-IR, TGA, mass spectrometry and single crystal x-ray diffraction. Thin films, deposited by AACVD at 325 ºC from complex (**1**) were characterized by XRPD and SEM.

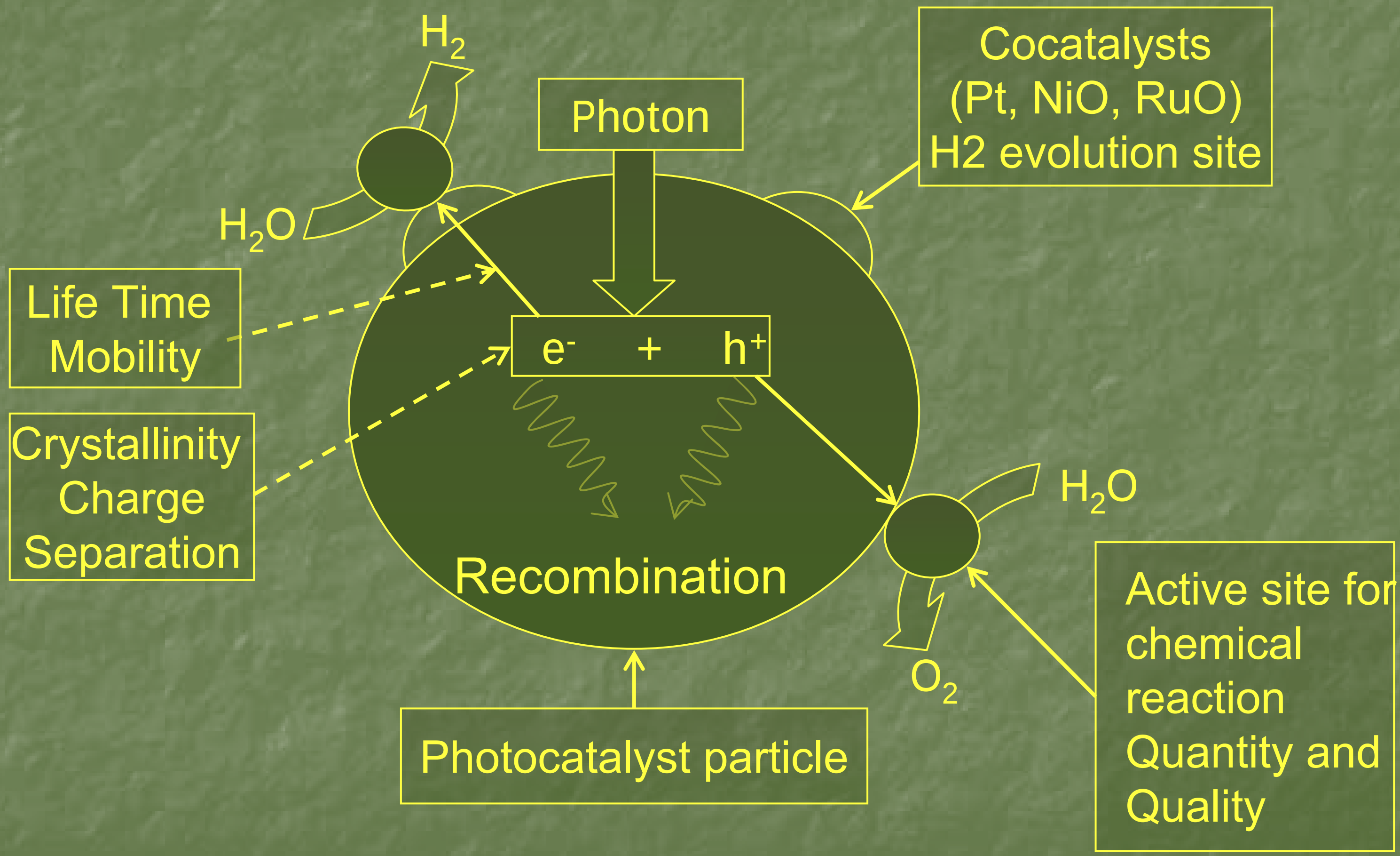
*Submitted: Muhammad Shahid, Muhammad Mazhar, Inorg. Chem. 2008.

Photocatalytic splitting on semiconductor film

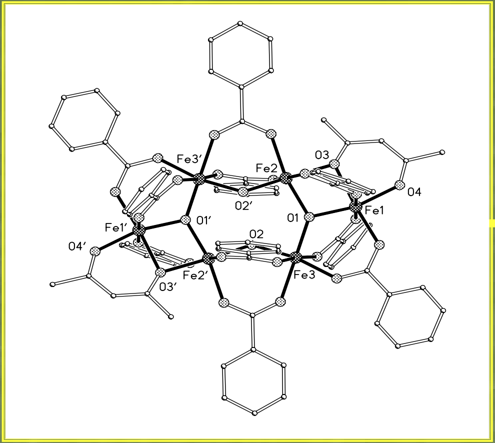


Process for photocatalytic reaction

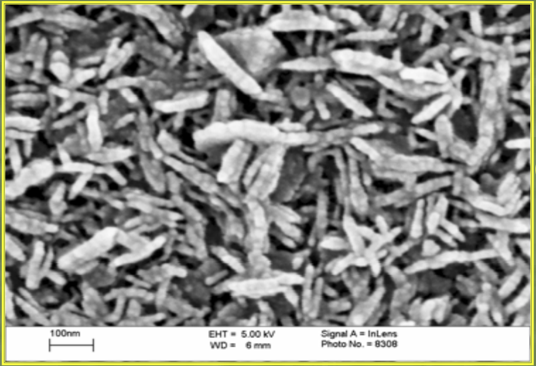
BULK AND SURFACE PROPERTIES



α-Fe_2O_3 for water splitting into H_2 and O



475°C



α-Fe_2O_3

35 nm

Hexanuclear, Iron complex, $[Fe_6(PhCOO)_{10}(acac)_2(O)_2(OH)_2]\cdot 3C_7H_8$ **(1),** (where PhCOO= bezoate and acac = 2,4-Pentanedionate) was synthesized and analyzed by melting point, FTIR, single crystal X-ray analysis and thermal analysis. The TGA analysis prove that complex (**1**) undergo facile thermal decomposition at 475°C to give iron oxide residue. In house designed aerosol assisted chemical vapor deposition technique was used to deposit sticky, high quality thin film on SnO_2 coated conducting glass substrate at 475°C. The photocurrent potential plots indicate that the photocurrent onset is at about 0.75V and the photocurrent density at 1.23V vs RHE is about 0.3mAcm-2 and photocurrent rises steeply and highest photocurrent density of 1.5mAcm-2 at 1.6V with out any dark current.

*Submitted: Asif A. Tahir, K. uG. U Wijayantha, Muhammad Mazhar, Vickie McKee, Sina Serami Yarahmadi. JACS, 2008.

Hydrogen Storage

Hydrogen can be stored as :

- Gas
- Liquid
- Elemental hydrogen
- Hydrides or analates

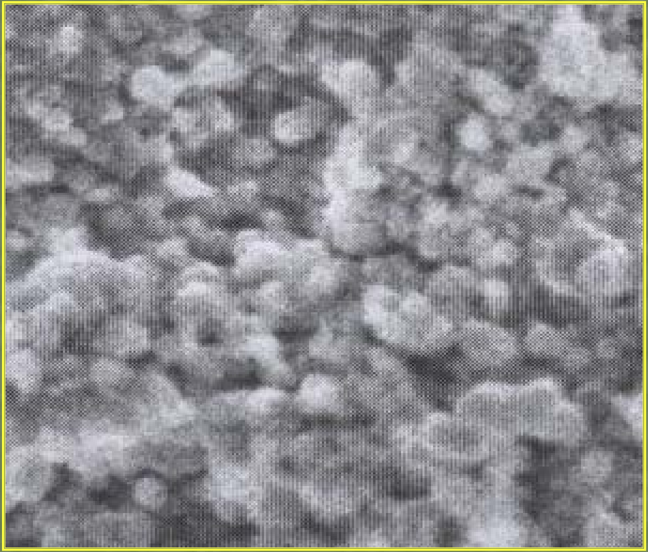
Solid state storage is the safest and most effective way of routinely handling hydrogen gas.

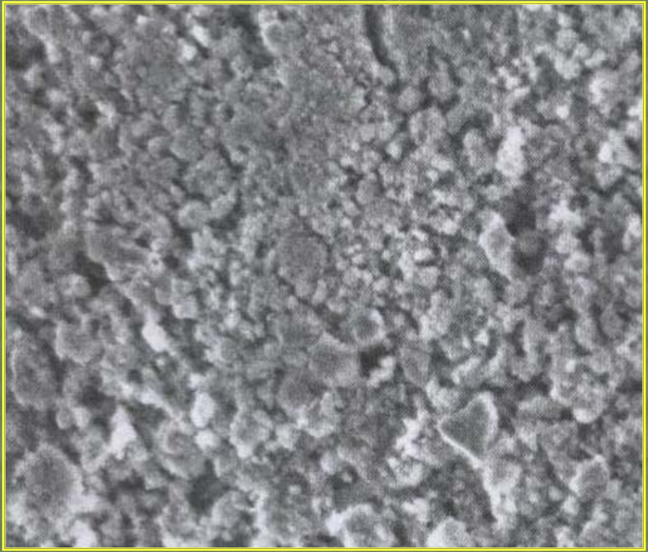
Commandments of Hydrogen Storage Materials

- High storage capacity: minimum of 8% by weight
- Decomposition temperature : 60-120 °C
- Reversibility of thermal absorption and desorption
- Cycle with rapid kinetics
- Low cost
- Non toxic
- Inert towards water and oxygen

i. **SEM of Zr-Ni coated on alumina molecular sieves**

ii. **SEM of Zr-Co coated on alumina granules**





- Synthesis of Multifunctional Materials

  1. Metal/mixed metal sulphides
  2. Metal/metal alloy nanoparticles
  3. Metal nitrides

CONCLUSION

Molecularly designed homo- and hetero-bimetallic precursors of various transition and non transition metals can be easily prepared for Aerosol Assisted Chemical Vapour Deposition (AACVD) of single metal or mixed metal oxide for application as advance materials.

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THANK YOU