MATERIALS AND METHODS

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METHODS AND MATERIALS

The ability to fabricate nanomaterials (often in the form of nanoparticles) with strictly controlled size, shape, and crystalline structure, has inspired the application of nanochemistry to numerous fields, including catalysis, optics, and electronics. The use of nanomaterials in such applications also requires the development of methods for nanoparticle assembly or dispersion in various media. Although much progress has been realized during the last decades in the development of highly advanced analytical tools enabling the characterization of nanostructures and an understanding of their physical properties. The synthesis of well-defined nanoparticles has resulted in several prominent milestones in the progress of nanoscience, including the discovery of semiconducting nanoparticles.

In this chapter, the experimental works on preparation of semiconducting nanomaterials are described in detail. The methods used for the preparation of semiconducting nanomaterials are solid-state mechanochemical processing method and sol gel method. The initial stage involved the preparation of metal oxide semiconducting nanomaterials, followed by the addition of dopant. The sensitization of metal oxide nanoparticles has been done using the dyes such as eosin B, fast sulphon black F and solochrome black T [1].

3.1 MATERIALS

Anhydrous zinc chloride (ZnCl₂) and sodium hydroxide (NaOH) were procured from Merck (Mumbai, India). Titanium isopropoxide (Ti(OC(CH₃)₂)₄) was procured from
HIMEDIA, Mumbai. Copper dichloride (CuCl₂), cadmium chloride hemipentahydrate (CdCl₂. 2\frac{1}{2} H₂O) and polyethylene glycol 400 (H-(O-CH2-CH2)₉-OH) were procured from s. d. fine-CHEM Ltd. (Mumbai, India). All the chemicals were of analytical grade and used as received for the experiments. Double distilled water was used throughout the experiments.

### 3.2 SYNTHESIS OF SEMICONDUCTING NANOMATERIALS

#### 3.2.1 Synthesis of ZnO, CdO and CuO nanoparticles

While synthesizing semiconducting nanoparticles, the concentration of ZnCl₂, NaOH and PEG 400 can alter the gelation, which affects the particle size. In a typical synthesis, 5 g of ZnCl₂ and 3 g of NaOH were ground separately for 5 min in an agate mortar. Thus obtained fine powder of ZnCl₂ and NaOH were mixed with 6 mL of PEG 400 and subjected to further grinding for 30 min. The resultant paste was washed in an ultrasonic bath several times with double distilled water and ethyl alcohol to remove the PEG 400. Finally, the product was dried at 70 °C in an oven and the resultant solid was subsequently annealed at 350 °C for 3 h. The similar procedure has been followed for the preparation of CuO and CdO nanoparticles at different temperature.

#### 3.2.2 Synthesis of Cu-ZnO, Cd-ZnO and Cu-CdO nanoparticles

A 5 g of ZnCl₂, 3 g of NaOH and 80 mg (1.6% w/w) of CuCl₂ were ground separately for 5 min in an agate mortar. The obtained fine powders were ground together with PEG 400 for further 30 min. Then the resultant paste was washed in an ultrasonic bath several times with double distilled water and ethyl alcohol to remove PEG. Finally, the product was dried at 70 °C in an oven. The resultant solid was annealed at different temperatures...
for 3 h. The similar procedure has been undertaken for the preparation of Cu-CdO and Cd-ZnO nanoparticles.

### 3.2.3 Preparation of anatase TiO$_2$ and Cu-TiO$_2$ nanoparticles

In a typical synthetic procedure, 4 mL of titanium isopropoxide (HIMEDIA, Mumbai) was dissolved in 30 mL of isopropanol (Merck), which was added dropwise (16 drops/min) to a round bottomed flask containing 4 mL of glacial acetic acid (s. d. fine-CHEM Limited, Mumbai) under stirring. The resulting clear sol was left undisturbed for 24 h. Then the sol was diluted by the dropwise (16 drops/min) addition of 30 mL double distilled water under stirring. The homogeneous clear gel was collected and kept under stirring for 15 h. The resultant gel was kept in an ultrasonic bath for 30 min. Thus obtained gel was washed several times with water and ethanol and then subjected to drying at 70 °C for 1 h in an oven. The complete dehydration of agglomerated powder was accomplished by simple distillation, using 50 mL of dry benzene in a 250 mL round bottom flask, equipped with a simple distillation unit. The resultant solid was subsequently annealed at 550 °C for 2 h. Similar procedure was followed for the preparation of anatase Cu-TiO$_2$ semiconducting nanoparticles by the dropwise (16 drops/min) addition of 30 mL aqueous CuCl$_2$ (80 mg) solution to the clear sol of titanium isopropoxide.

### 3.3 EFFECT OF DOPANT

Undoped semiconductors are active only under ultraviolet (UV) light because of their wide band gap rendering it inactive under visible light, which causes most of the solar spectrum to go unabsorbed. Extending the optical absorption of semiconductors to the visible region, therefore, doping is one of the important subjects for the increased utility
of semiconductors in the field of solar cells. Impurities doping induces substantial modifications in electrical and optical properties of semiconductor materials. By doping with different impurities, the structural properties of semiconductors can be modified, and consequently its optical constants and absorption spectra. Some studies have suggested that observed enhancement of the photo conversion efficiency was due to electron trapping by the copper ions leading to the prevention of electron-hole recombination [1-3].

3.3.1 EFFECT OF ANNEALING TEMPERATURE

One of the other sensitive factors that affect the crystal quality, oxygen defect and local structure of semiconductor oxides during sample preparation process, is annealing temperature. The samples were annealed at different temperatures. The resistivity of samples decreases as the annealing temperature increases [4].

3.3.2 EFFECT OF LATTICE PARAMETERS FOR DOPED SAMPLES

The lattice constant or lattice parameter refers to the constant distance between the unit cells in a crystal. Lattices in three dimensions generally have three lattice constants, referred as $a$, $b$, and $c$. However, in the special case of cubic crystal structures, all of the constants are equal and referred as $a$. Similarly, in hexagonal crystal structures, the $a$ and $b$ constants are equal, and referred as $a$ and $c$ constants. A group of lattice constants could be referred to as lattice parameters. However, the full set of lattice parameters consist of three lattice constants and the three angles between them.

The lattice parameters for all the undoped and doped semiconductors were calculated through XRD data $(h k l)$ using the following formula:

For Cubic:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$
For Tetragonal: \( \frac{1}{d_{hkl}^2} = \left[ h^2 + k^2 + l^2 \left( \frac{a}{c} \right)^2 \right] \frac{1}{a^2} \)

For Hexagonal: \( \frac{1}{d_{hkl}^2} = \left[ \frac{4}{3} \left( h^2 + k^2 + \frac{1}{2} c \right) + l^2 \left( \frac{a}{c} \right)^2 \right] \)

When dopant is introduced into the lattice, dopant ion lodges into the position of semiconductors, which leads to a decrease or increase in the lattice constants [5, 6].

3.3.3 Calculation of optical band gap \( (E_g) \)

The optical band gap \( (E_g) \) of the undoped and doped semiconducting nanomaterials was calculated by using the formula:

\[
E_g = \frac{hc}{\lambda}
\]

where \( h \) is Planck’s constant, \( c \) is velocity of light, and \( \lambda \) is wavelength.

Debye-Scherrer Equation for calculation of particles size 

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Where \( \lambda \), \( \theta \) and \( \beta \) are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and line width at half maximum, respectively.

3.4 CHARACTERIZATION TECHNIQUES

Crystallinity of nanoparticles were carried out on a X-Ray diffractometer using Cu-K\( \alpha \) radiation (\( \lambda = 0.15406 \) nm). The patterns were recorded in the range of 10° to 80° (2\( \theta \)). The crystallite size and morphology of the samples were analyzed using Field emission scanning electron microscope (FESEM) fitted with an Energy-dispersive X-ray spectroscopy (EDAX) [Model: Nova Nano SEM600- FEI, Japan]. High resolution transmission electron microscopic (HRTEM) analysis of the sample has been carried out to investigate the morphology of synthesized material, using JEOL microscope (Model: JEM 3010) operating at an accelerating voltage of 300 kV. The absorbance for undoped and doped nanomaterials was measured through UV-Vis spectrophotometer (Model:...
USB 4000, Ocean Optics, USA). FT-IR spectrum was recorded using Thermo Nicolet 5700 FTIR Spectrophotometer with KBr pallets.

3.4.1 X-RAY DIFFRACTION STUDIES

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Crystallinity of all the nanoparticles were carried out on a X-Ray diffractrometer using Cu-Kα radiation (\(\lambda = 0.15406 \text{ nm}\)). The patterns were recorded in the range of 10° to 80° (2θ). When a monochromatic X-ray beam with wavelength \(\lambda\) is projected onto a crystalline material at an angle \(\theta\), diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number \(n\) of wavelengths. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material can be obtained. X-Ray diffractometers fall broadly into two classes: single-crystal and powder. Single-crystal diffractometers are most often used to determine the molecular structure of new materials. Powder diffractometer are routinely used for phase identification and quantitative phase analysis and can be configured for many applications, including variable-temperature studies, texture and stress analysis and grazing incidence diffraction [7].

When X-rays interact with atoms in two lattice planes, and the path length difference between rays equals a whole multiple of the wavelength of the radiation, constructive interference occurs. Bragg’s law (\(n\lambda = 2dsin\theta\)) describes the conditions for constructive interference in certain directions and the production of diffracted X-rays.
3.4.2 FIELD-EMISSION SCANNING ELECTRON MICROSCOPIC STUDIES

Scanning Electron Microscope (FESEM) is commonly used to study surfaces, structures, morphologies and forms of materials. A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. The images viewed using FESEM are created by detecting secondary electrons ejected from samples as they are bombarded by focused, high energy electron beams. In order to know the surface morphology and the elements present in the synthesized nanoparticles, the scanning electron microscopic (SEM) studies were carried out. The crystallite size and morphology of the samples were analyzed using Field emission scanning electron microscope (FESEM) fitted with an Energy-dispersive X-ray spectroscopy (EDAX) [Model: Nova Nano SEM600-FEI, Japan]. Energy dispersive X-ray spectroscopy (EDX or EDS) is an analytical tool predominantly used for chemical characterization. High energy electron beams (in an FESEM or TEM) strike the material to be analysed, and X-rays are emitted. These X-rays can be detected by a SiLi detector, calibrated with respect to cobalt metal emission (6.925 keV), and then used to identify and analyze the elemental composition of the specimen surface. Its characterization capabilities are due in large part to the fundamental principle that each element of the Periodic Table has a unique electronic structure and, thus, a unique response to electromagnetic waves [8-10].

3.4.3 UV-Vis SPECTROSCOPIC STUDIES

Ultraviolet visible spectroscopy (UV/Vis) uses light in the visible and adjacent near ultraviolet (UV) ranges. At these wavelengths, molecules undergo electronic transitions.
In this technique, the light passes through the sample to be analyzed, and some of the light is absorbed by the sample. Thus, the sample has to be thick enough such that some of the light is transmitted. Another factor is that the sample must be placed onto a supporting substrate, for example, quartz, that is transparent at the wavelengths of light used. When visible or ultraviolet light is absorbed by the valence electrons of the material, these electrons are promoted from their ground states to higher energy excited states. The energies of the orbitals involved in electronic transitions have fixed values. The difference between the initial and final intensities is recorded and then plotted into a spectrum as wavelength against absorbance [11]. From UV-Vis, it can be seen that the strongest absorption peak of the as-prepared sample appears at around 350 nm. Doped semiconductors have good absorption in visible region. Semiconductor crystallites in the diameter range of a few nanometers show a three dimensional quantum size effect in their electronic structure. These quantum size effects on the band gap absorption energy can be measured by UV-Vis absorption spectroscopy. From the UV study we can calculate the energy band gap. The fundamental absorption, which corresponds to the transmission from valence band to the conduction band, is employed to determine the band gap of the material.

3.4.4 FT-IR SPECTROSCOPIC STUDIES

FT-IR spectral studies of anatase TiO₂ and Cu-TiO₂ nanoparticles were carried out. Infrared (IR) spectroscopy measures the absorption of IR radiation by materials as the atoms vibrate about their bonds. It is primarily used to identify bond types, structures and functional groups in organic and inorganic compounds. When illuminated by IR radiation of the appropriate frequencies, atoms, ions, and functional groups in molecules will
vibrate about their bonds and energy will be absorbed. Each bending and stretching vibrational mode of a molecule or functional group will absorb at a particular frequency. When exposed to appropriate IR frequencies, energy will be absorbed from the incident radiation as vibrational intensities increase. The FT-IR investigations were carried out in the frequency range 4000-400 cm$^{-1}$ (Perkin-Elmar model 1600 FTIR) [12, 13].

3.4.5 X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES

X-ray photoelectron spectroscopic (XPS) study was carried out to elucidate both the titanium structure and the chemical state of Copper particles. XPS study is a commonly used surface sensitive chemical analysis technique that operates under ultra-high-vacuum. When X-rays irradiate a sample surface, electrons will be ejected from valence and core levels of both surface and near surface atoms. The kinetic energies of ejected photoelectrons are not only characteristic of the atoms from which they are emitted, but can also provide information on the chemical states of those atoms [14, 15].

3.5 FABRICATION OF DYE-SENSITIZED NANO METAL OXIDE SEMICONDUCTING FILMS

Doctor blade method

As synthesized metal oxide semiconducting nanoparticles were used to prepare films by doctor blade method. Glass plate of 2 cm x 2 cm dimension was used as support. Metal oxide semiconducting nanoparticles (1g) were dispersed in 1:1 water and ethanol (v/v) system by sonication followed by stirring until gelation occurred (for about 5 min) to obtain a paste of appropriate viscosity. The resultant paste was coated on a transparent glass plate by doctor blade method using scotch tape as the spacer. The paste was
flattened uniformly with a glass rod and then calcinated at 80 °C for 30 min under air to eliminate water and alcohol adsorbed on the semiconductor surface [16-19].

**Dye adsorption on oxide semiconductor films**

Dye solutions of 0.6 and 1.37 mM were prepared using dilute ethanol (20 mL alcohol + 5 mL water). Semiconductor films were immersed into this solution for 1 h to fix the dye on the surface of semiconductor electrodes. After dye adsorption, the color of the films will be changed. The coloured films were kept under sunlight for 30 min. A similar procedure was followed to fix Fast Sulphon Black F (0.25, 0.51 mM) and Solochrome Black T (0.26, 0.43 mM) dyes on semiconductor electrode.
3.6 STRUCTURE OF DYES

Eosin B

Fast Sulphon Black F

Solochrome Black T
REFERENCES

