



Methods for Characterization and Preparation of Semiconductor Photo- catalysts

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Abstract

Characterization and Preparation Methods of Semiconductor Photocatalysts" could outline the fundamental aspects of semiconductor photocatalysts, their significance in various applications, and the methodologies employed for their characterization and preparation. It might discuss the principles behind semiconductor photocatalysis, highlight key characterization techniques such as spectroscopy and microscopy, and summarize various preparation methods including sol-gel synthesis, chemical vapor deposition, and electro deposition. Additionally, the abstract could touch upon the importance of understanding the structural and chemical properties of semiconductor photocatalysts for optimizing their performance in photocatalytic applications such as water purification, air treatment, and renewable energy generation

Keywords:

1. Introduction

The co-doped semiconductor photocatalysts like SnO₂, ZnO-SnO₂, CdS and ZnO supported on active carbon were synthesized using conventional as well as new preparation methods. The precipitation, co-precipitation, sol-gel and hydrothermal methods were used for the synthesis. It is always be a



challenge for researchers to use the specific method which give high yield, low toxic byproducts and low cost^[1-2]. It is also known that the morphology, size and properties of prepared photocatalysts depend on the method used^[3-4]. The search of different co-doped semiconductor materials supported on active carbon has encompassed us to use various chemicals, solvents and instruments. The synthesized materials further analyzed by different chemical and physical methods.

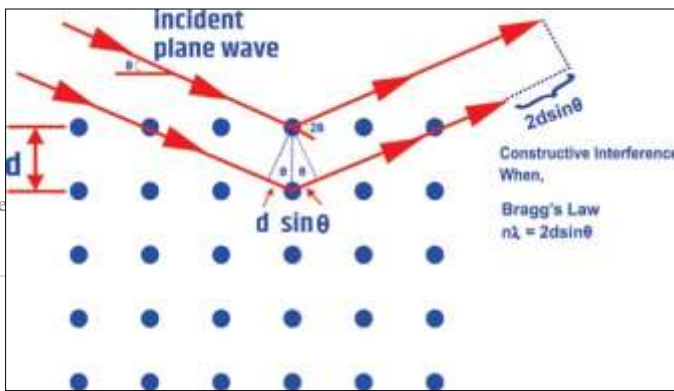
2. Physico-chemical characterization methods

X-ray powder diffraction (XRD)

X-ray powder diffraction is a rapid, non-destructive analytical technique used to investigate the structure of a crystal. Each crystal structure has its characteristic XRD pattern with different intensities and position of diffraction peaks^[5]. This gives very important information about its crystalline phases and structure. The relative concentration of each phase can also be studied by XRD pattern^[6]. When X-ray radiation with wavelength λ constructively interfaces the crystal, XRD pattern is formulated after satisfying bragg's condition:

$$n\lambda = 2d \sin\theta; n = 1, 2, 3, \dots (2.1)$$

Where d is the d -spacing (distance between adjacent planes), θ is the angle of incident and n denotes the layer of plane. In a typical experimental procedure the powder sample is pressed into a sample holder to make a flat surface. When X-ray radiation hits on the atoms in the sample the electrons present in the atom starts to oscillate with similar frequency of X-ray radiation. This process generates constructive or destructive interfaces. The planes which having high electron density shows strong reflection and





intensity^[7]. On the other hand the planes with less electron density show less reflection and low intensity. Accordingly, the XRD diffraction technique is useful for identification and characterization of polycrystalline phases of the sample

Fig 1: Bragg's law

Average crystalline size of nanocrystals can be calculated from wavelength, peak position and its full width at half maxima (FWHM) using scherrer's equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D is the crystalline size, λ is the wavelength of the X-ray radiations (1.542 Å), θ is the scattering angle of the diffraction peak and β is the FWHM. X-ray powder diffraction pattern of prepared sampled were carried out on Bruker D8 Advanced diffractometer using Cu K α radiation source at 40 kV, 30 mA over 2 θ range of 20-80°.

3. Surface area (BET) measurement

Measurement of surface area is very important in the study of powder sample. The Brunauer, Emmett and Teller developed an important method to study the textural characterizations like surface area, pore volume and pore size using N₂ gas as an adsorbent gas^[8-9]. In this study these textural properties were studied by N₂ adsorption isotherm measurement using Micrometrics ASAP 2020 Brunaur Emmett Teller surface area analyzer. This study is known as an extension to the multilayer adsorption of the Langmuir model. In this process the chemisorptions is restricted to the monolayer adsorption at the surface. The volume of the adsorbed gas (generally N₂) on the surface of particles is recorded at boiling temperature of nitrogen (-196°C).



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Where V is the adsorbed gas volume at relative pressure P , V_m is the volume of gas adsorbed from monolayer of surface coverage, C is the BET constant and P_0 is saturation pressure. To calculate V_m and C , the BET equation is plotted as an adsorption isotherm between 0.05-0.35 relative pressure. The V_m is found from gradient and then surface area can be obtained using the molecular cross-sectional area.

4. Scanning electron microscopy (SEM)

The Scanning electron microscopy is one of the important type of electron microscope that produce high resolution images with good depth of field of sample by rastering a high energetic electron beam on a fine scale and detecting secondary and back scattered electron signals under vacuum [10-11].

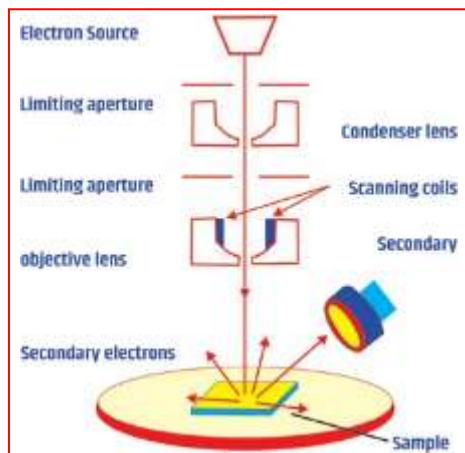


Fig 2: Schematic diagram of scanning electron microscope (SEM)

Fig. 2. shows that the highly energetic electron beam is travel through scan coils and objective lens. Further this beam is get deflect vertically as well as horizontally. Commonly, during the SEM analysis the atoms are excited by the high energy electron beam which gives emission of secondary electrons. These secondary electrons are further detected by detector. After scanning the sample and analyzing the secondary or back scattered electrons, an image is obtained which shows the topology of the surface of sample. In addition to this the elemental analysis of sample is another application of this microscopy known as Energy Dispersive X-ray microanalysis (EDX). The irradiation of electrons of the sample results in the vacancy of electron which is occupied by other electron from higher energy orbital^[12]. To balance the difference in energy levels between the two electrons the X-ray radiations emitted. The analysis of X-ray radiations emitted versus the energy of electrons gives EDX spectra. SEM analysis gives images which have

resolution higher than 1 nm. In the present study SEM images were obtained from FEI Nova NanoSEM 450.

5. UV-visible diffuse reflectance spectroscopy (UV-vis DRS)

UV-vis DRS spectroscopy provides us information about structure of the molecules^[13]. The absorption of UV and visible light by many molecules causes electronic excitations which move electrons from ground state to excited state^[14]. The absorbed light is reflected in all directions. The small fraction of this light is scattered within the sample and then come to its surface is known as diffuse reflection. After amplifying the signal to noise ratio of the collected reflected radiations give UV-vis DRS spectra. The absorption of light energy by molecules is governed and formulated by Beer-Lamberts law as:

$$A = \varepsilon \cdot c \cdot l$$

Where A, ε , C and l are absorbance, absorptivity, concentration and length of the cell respectively. Moreover; the absorbance is also depend on size of molecules, and type of sample. If the size of molecule is much higher than wavelength of absorbed light then scattering and reflection is observed. Therefore for powder samples the UV-vis DRS analysis is based on Kubelka-Monk equation:

$$F(R) = \frac{(1-R)^2}{2R}$$

Where F(R) is equivalent to absorption coefficient and R is diffuse reflectance at front face. The bandgap energy was calculated by using following equation:

$$\alpha(h\nu) = A(h\nu - E_g)^n$$



Where α , h , ν , A and E_g are the absorption coefficient, planck's constant, frequency of absorbed light and bandgap energy. n is obtained from type of semiconductor used.

6. Transmission electron microscopy (TEM)

Transmission electron microscopy is an important analytical technique for directly imaging nanomaterials to obtain quantitative measures of particles, grain size, size distribution and morphology ^[15]. In this technique a high energy electron beam is transmitted through a very thin sample. After interaction of electron and atoms of molecule show scattering of electrons. Further, these scattered electrons projected onto a fluorescent screen and gives crystal structures, grain boundaries and dislocation of atoms. TEM spectroscopy has ability to give high resolution images compared to other microscopes ^[16]. The shape, size, quality of sample, density of quantum walls and dots can be examined through high resolution images. In addition to this the finest details of internal structure of molecules can also be studied by transmission electron microscopy. The electron density variations as well as analog images may be obtained using CCD camera. In this study, TEM and HRTEM images were obtained from FEI Tecnai F30 operated at 300kV.

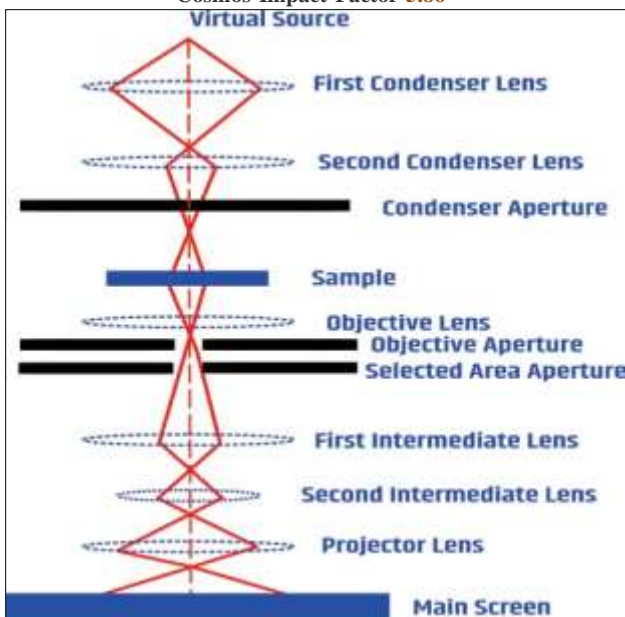


Fig 3: Diagram of transmission electron microscope (TEM)

7. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of sample provides good deal of information about structure of synthesized metal oxides ^[17]. In this spectroscopy, when sample is exposed to IR radiations, the molecule absorbs energy of IR radiation and gets excited to higher vibration energy level. The type of IR wavelengths absorbed by the molecule depends on the type of atoms and chemical bonds in the molecule. The IR spectrum consists of number of peaks; each peak is due to a particular vibration excitation of the molecule ^[18]. The IR spectrums in the present study were recorded using avatar-330 spectrophotometer at room temperature in the range of 400-4000 cm^{-1} .

i. Photoluminescence (PL) spectroscopy

Photoluminescence is a non-destructive technique used to probe the efficiency of charge carriers trapping and e/h pair recombination during

photocatalysis of the sample ^[19]. Photoluminescence spectroscopy is based on the emission of the light by sample after the absorption of electromagnetic radiations. Absorption of these electromagnetic radiations results photoexcitation of electrons. The excited electrons return to their ground state, the excess energy is released out in the form of emission of light. It is well known that more the PL intensity, the lower e/h pair recombination and lower charge carriers separation efficiency. Photoluminescence (PL) emission spectra of prepared photocatalysts at room temperature were obtained using SCINCO FluoroMate FS-2.

ii. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic technique with high surface sensitivity ^[20]. This technique is used to study the empirical formula, chemical states and elemental composition of the sample. A monochromatic beam of aluminum and magnesium X-ray is allowed to irradiate the sample. The electrons from core levels of atoms get excited and ejected. These ejected electrons from the 1-10 nm top layer having kinetic energy and it is analyzed by hemispherical electron energy analyzer.

The binding energy given in the XPS spectrum is the elemental fingerprint ^[21]. This gives useful information about surface elemental composition of sample. In addition to this the chemical environment around atoms, charge and ionic state information can also be obtained.

The B.E. of ejected electrons is calculated by following equation: Where, prepared photocatalysts.

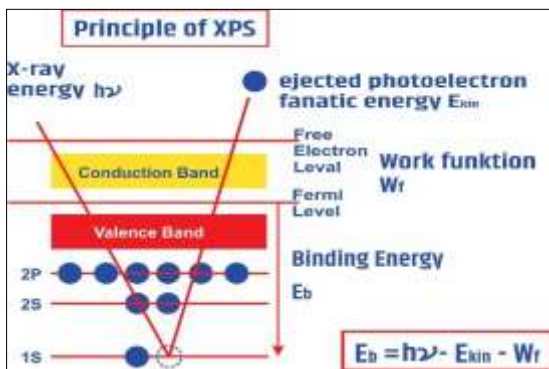


Fig 4: Schematic representation of principle of X-ray photoelectron spectrometer (XPS)

iii. Raman spectroscopy

Raman spectroscopy is commonly used in chemistry to study the structural fingerprint of the molecules by which molecule can be identified [22]. The principal of Raman spectroscopy is based on the probing of inelastic scattering of the irradiated monochromatic light after its interaction with sample. The peaks observed in Raman spectra are due to vibration, rotational and low frequency modes in the system [23]. The size of the nanocrystals can also be investigated using phonon confinement effect. Those molecular vibrations of the sample which are polarizable can produce Raman shifted photons, so this method is also known as complimentary to IR spectroscopy. Raman spectroscopy is a useful technique to study the structural phases as well as binding configurations of sample. In this study, Raman spectra were recorded on Renishaw InVia Raman spectrometer at room temperature.

8. Methods for the synthesis of photocatalysts

i. Precipitation method

The formation of solid compound in solution during a chemical process is known as precipitation method [26]. When the reaction is carried out in liquid solution, the solid is get settled at bottom called as precipitate and the rest liquid part is known as supernatant. During the process the formed solid compound in solution is get settle at bottom due to gravitational force or centrifugation. The precipitation occurs only if generated insoluble material has higher density. It is well known that when the material is present in solution is above its solubility limit lead to precipitate. This method is very useful to synthesize the nanoparticles of various photocatalysts. Nucleation is also an important step during precipitation. The generation of solid particles at interface requires relative surface energy. The reaction shows supersaturation without this energy.

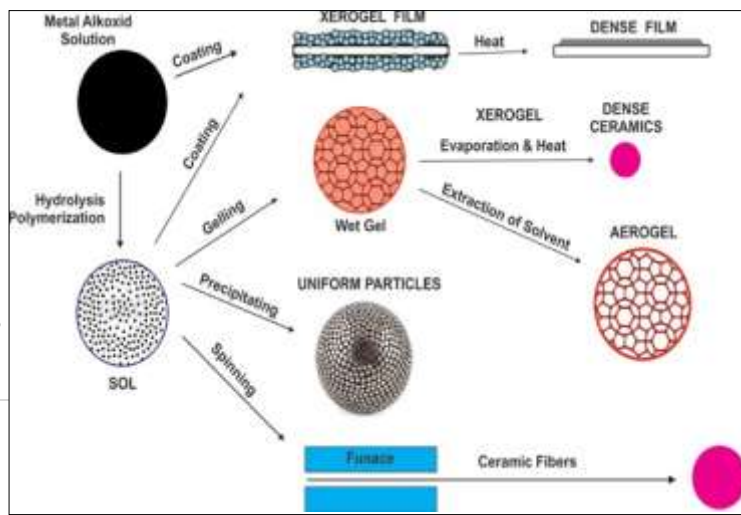
ii. Hydrothermal method

Hydrothermal is one of the important technique used to synthesize the

good quality nanocrystals. The size of synthesized crystal is depends on the solubility of minerals in high temperature and pressure of water ^[27]. This process is generally carried out in teflon lined stainless steel autoclave containing aqueous solution at high temperature and pressure. Further the temperature is increased above the boiling point of solution to get the pressure of vapor saturation. Water is acts as solvent in the recrystallization. The solid material is synthesized during this process. Size, morphology and surface properties of prepared solids can be easily controlled through monitoring the solvent, pressure and temperature during the process. The crystalline phases which are unstable at the melting point as well as those which have high vapor pressure, can be synthesized using hydrothermal method.

iii. Sol-gel method

Variety of nanosized semiconductor photocatalysts can be prepared by sol-gel method. The morphological as well as chemical properties can be easily controlled by this method ^[28]. Several oxides in the form of thin films, porous membrane, powders can be synthesized by sol-gel method. The sol-gel method is commonly used to synthesize semiconductor photocatalyst with high surface area which is difficult to obtain by conventional methods. In addition to this the mixing level of ingredients is retained in the synthesized compound. This method is also found successful in the production of stained glass. The composition of product can be easily controlled through cheap and low temperature sol-gel method. Even very small quantity of dopant can be uniformly introduced using this method. In the general sol-gel method colloidal suspension i.e. sol is formed from





hydrolysis and polymerization process. Metal alkoxides and metal salts are used as a precursor to prepare sol.

Fig 6: Schematic drawing of sol-gel method

This sol can be used to make dense films, ceramics, ceramic fibers etc ^[29]. After transfer of sol into mold it gives gel. Further drying and heating gives glass and ceramic materials. The obtained products from sol-gel method have various applications in thin films, coating materials, nanoscale

powders etc.

iv. Co-precipitation method

The carrying down by a precipitate of material, which is soluble under the reaction conditions, is called as co-precipitation method ^[30].

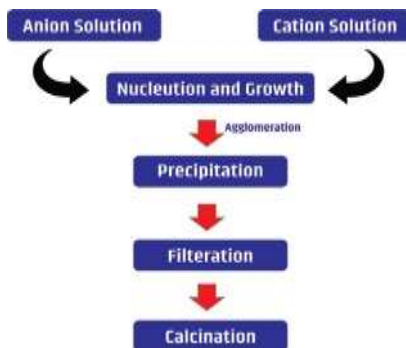


Fig 7: Schematic representation of co-precipitation method

It is well known that separation of a crystalline precipitation from the solution is difficult task as it may contain some impurities from mother liquor. The digestion of the solution is found as a solution to mitigate this problem. Generally, there are three different mechanisms of co-precipitation method i.e. inclusion, occlusion and adsorption. There are several applications of co-precipitation method apart from chemical analysis i.e. wastewater demineralization, radionuclide migration etc.

Conclusion

The conclusion of a paper on "Characterization and Preparation Methods of Semiconductor Photocatalysts" would likely summarize the key findings and insights obtained from the study. It might emphasize the importance of thorough characterization techniques in understanding the structural, chemical, and optical properties of semiconductor photocatalysts. Additionally, the conclusion could highlight the significance of various preparation methods in tailoring the properties of photocatalysts to enhance their performance in photocatalytic

applications. Furthermore, the conclusion might discuss the current challenges and future directions in the field of semiconductor photocatalysis. This could include advancements in material design, novel characterization techniques, and strategies for improving the efficiency and stability of photocatalysts. Overall, the conclusion should provide a comprehensive overview of the research conducted and its implications for the broader scientific community interested in semiconductor photocatalysis.

References

1. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y, Science. 2001;293:269-275.
2. Begum NS, Ahemad HMF, Hussain OM. Bull. Mater. Sci. 2008;31:741-749.
3. Das D, Mishra HK, Parida KM, Dalai AK. Journal of Molecular Catalysis A. 2002;189:271-279.
4. Gambhire AB, Lande MK, Arbad BR, Rathod SB, Gholap RS, Patil KR. Materials Chemistry and Physics. 2011;125:807-810.
5. Tebby Z, Babot O, Toupance T, Park DH, Campet G., Delville MH, Chem. Mater. 2008;20:7260-7269.
6. Parida KM, Dash SS, Das DP. J. Colloid Interface Sci. 2006;298:787-792.
7. Wachs IE, Roberts CA. Chem. Soc. Rev. 2010;39:5002-5007.
8. Rouquerol J, Llewellyn P, Rouquerol F. Studies in Surface Science and Catalysis. 2007;160:49-54.
9. Hanaor DAH, Ghadiri M, Chrzanowski W, Gan Y. Langmuir, 2014;30:15143.
10. Hortola P. Microscopy and Microanalysis. 2015; 21:1504-1510.
11. Tahmasebi P, Sahimi M, Physical Review E. 2012;85:066709.
12. Klein T, Buhr E, Frase CG, Advances in Imaging and Electron Physics. 2012;171:297-304.



13. Soovali L, Room EI, Kutt A. Accreditation and Quality Assurance. 2006;11:246-254.
14. Ansell S, Tromp RH, Neilson GH. J. Phys.: Condens. Matter., 1995;7:1513-1520.
15. Ross B. Science. 2015;350:1490-1499.
16. Kosasih FU, Ducati C. Nano Energy. 2018;47:243-254.
17. Manor J, Feldblum ES, Arkin IT. The Journal of Physical Chemistry Letters. 2012;3:939-945.
18. Brielle ES, Arkin IT. The Journal of Physical Chemistry Letters, 2018;9:4059-4066.
19. Kaindl RA, Carnahan MA, Hagele D, Lovenich R, Chemla DS. Nature, 2003;423:734-741.
20. Ray S, Shard AG. Analytical Chemistry. 2011;83:8659-8666.
21. Gumerova NI, Rompel A. Journal of Catalysis. 2014;311:369-375.
22. Itoh Y, Hasegawa T. The Journal of Physical Chemistry A. 2012;116:5560.
23. Schlucker S. Journal of Biophotonics. 2011;4:453-461.
24. Silva CG, Wang W, Selvam P, Dapurkar S, Faria JL. Studies in Surface Science and Catalysis. 2006;162:151-160.
25. Amrhein K, Stephan D. Photochem. Photobiol. Sci. 2011;10:338-345.
26. Xu L, Wei B, Liu W, Zhang H, Su C, Che J. Nanoscale Research Letters. 2013;8:536-542.
27. Dhal JP, Mishra BG, Hota G. RSC Adv. 2015;5:58072.
28. Tseng TK, Lin YS, Chen YJ, Chu H. Int. J. Mol. Sci. 2010;11:233-240.
29. Shukla P, Shukla JK. J. Sci.: Adv. Mater. Devi. 2018;3:452-463.
30. El-Shazly AN, Rashad MM, Abdel-Aal EA, Ibrahim IA, El-Shahat MF, Shalan AE. J. Environ. Chem. Eng. 2016;4:317-322.
31. Metcalfe TL, Dillon PJ, Metcalfe CD. Environ. Toxicol. Chem. 2008;27:811-819.



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32. Scott MJ, Jones MN. Biochim. Biophys. Acta. 2000;1508:235-240.