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Tungsten Oxide Thin Film for Supercapacitor Application

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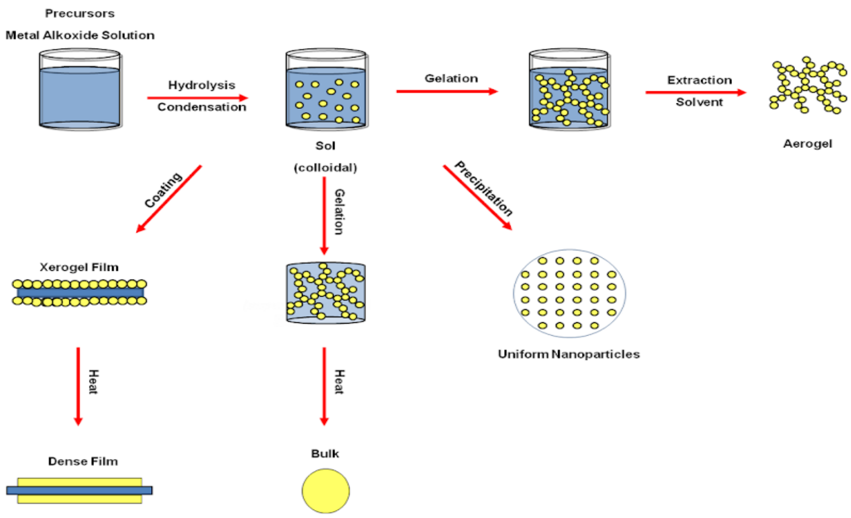
ABSTRACT

Supercapacitor required high conductivity and capacitance and equivalent series resistance when compared with carbon based electrode materials ,low cost and easy to production, thus in this the WO_3 is good materials for supercapacitor. tungsten oxide (WO_3) is one of the stable n type semiconductor having anionic vacancies, which possesses hexagonal structure. Numerous fascinating properties such as existence of multiple oxidation states of W, electrochromic characteristic, high packing density, high energy. Porous films of WO_3 shows drastically different morphologies. With A band gap in the range of 2.6-3.1 eV, depending on its crystal structure. Although the low cost and easy to production it is highly stable and has the ability to survive harsh and corrosive environments such as exposure to strong acids. WO_3 also has been shown to have higher carrier mobility than TIO_2 and has therefore received significant attention from A range of fields from optics, to electronics, aerospace. WO_3 can be synthesized into A wide range of nanostructures such as nanotubes, nanorods, nanowalls, nanoparticles and nanocolumns with high surface to volume ratio makes this A very interesting material for electrochromic devices, photocatalysis, gas sensing, and DSSC. Hence in this we study the thin films of transitional metal's (WO_3) there application as supercapacitor and so on.

SYNTHESIS METHODS

Sol-gel technique

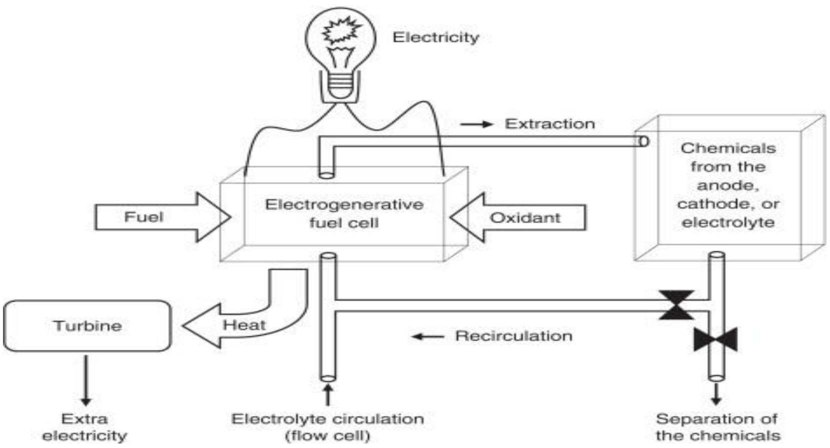
It is one of the famous wet-chemical methods and widely used for the synthesis of transition metal oxide It requires lesser-temperature and provides improved homogeneity for multi-component materials. The process involves the construction of a colloidal suspension and converting to viscous gels or solid materials. This method involves alkoxides where the hydrolysis of alkoxy group results in macromolecular oxide network followed by polycondensation reactions takes place. Deposition of thin films from sol can be achieved by the following methods: (i) Dip coating (ii) Spin Coating (iii) Spraying



SOL GEL CNR-IFN Trento.com(2014)

Electrochemical synthesis -

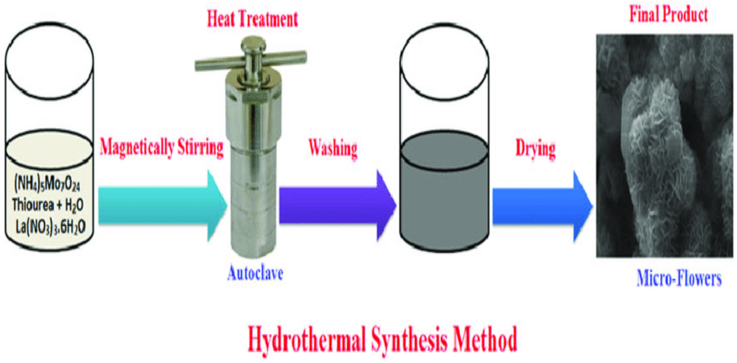
The electrochemical synthesis of thin films is a cost-effective method because it doesn't require expensive instrumentation to form thin films with large surface area to volume ratios. have reviewed the synthesis and photo electrocatalytic water oxidation of WO_3 thin films. WO_3 thin films were widely synthesized with electrochemical syntheses like electrochemical anodization and cathodic electrodeposition. /



Electrochemical synthesis-science direct,2009

Hydrothermal method

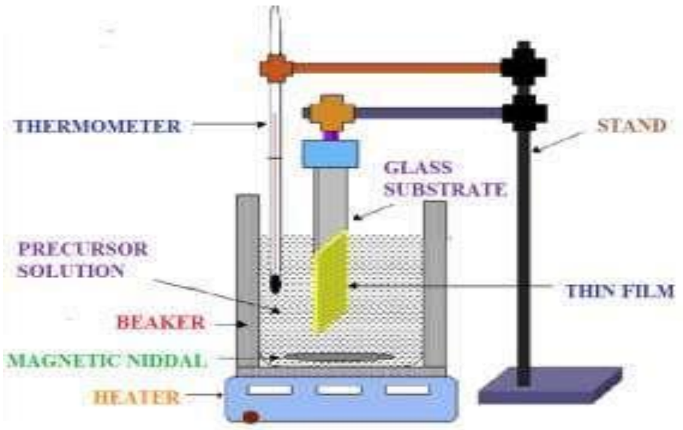
Hydrothermal method is one of the versatile methods for the synthesis of nanomaterials. The advantage of the hydrothermal method which uses the relatively low-temperature crystalline structures is deposited at a relatively high rate than compared to other methods. However, it is very difficult to control the chemical composition. Hence this method is less commonly used for the thin film synthesis.



Hydrothermal SYTHESIS – link.springer.com2016

Chemical bath deposition technique

Thin films deposition from physical methods is expensive and require a large amount of target although produces enhanced quality thin films. Chemical deposition techniques are widely used and cost-effective methods to produce high-quality thin films. The film deposition depends on pH value, solution chemistry, and viscosity. The general chemical deposition processes are chemical vapor deposition (CVD), electrodeposition, sol-gel, spray pyrolysis technique and chemical bath deposition.



Chemical bath deposition(2018)- scientific.Reseach.gate.com

Characterization techniques

TEM- Transmission Electron Microscopes

TEM is used to study specimen morphology and composition. It has advantages of high depth resolution with 0.2 nm resolution, electron diffraction patterns and compositional information. Here a focused beam of electron produced by electron gun are accelerated towards the specimen using a positive electric potential. The beam is then focused by suing metal aperture and magnetic lenses in to a thin focused beam which then strikes the specimen and part of it gets transmitted. This is again focused using projector lens on fluorescent screen to observe the image of sample. Sample preparation: 0.1 to 0.5 mg of sample added with sample and drop casted on copper grid after proper sonication.

XRD (X - Ray powder diffraction)

XRD is non-destructive rapid analytical technique used for phase identification and provide information on unit cell dimensions. Diffraction is based on constructive interference of monochromatic x-rays and a crystalline sample. Main components include x-ray tube, sample holder and detector. When high velocity electrons generated from crt containing tungsten filament are bombarded on sample then it dislodges the inner shell electrons of target i.e. Sample. This produces characteristic spectra containing several components most common are $k\alpha$ and $k\beta$. This technique is applicable to only crystalline solids and the crystal lattice planes act as diffraction grating. It is based on bragg’s law $n\lambda = 2d\sin\theta$, where by scanning sample through range of 2θangles, all possible diffractions of the lattice should be attained due to random orientation of powder material. Conversion of diffraction peaks to d spacing allows identification of phase by comparing with standard data. In demonstration part how to load sample, staring up of instrument and applying parameters were nicely explained

Cyclic voltammetry –

Is rarely used for quantitative determinations, but it is widely used for the study of redox processes , for understanding reaction intermediates and for obtaining stability of reaction . A volumetric cell consists of three micro electrode , they are working electrode are of various geometries and materials, ranging from small hg drop to flag Pt disks, . Mercury : it displays wide negative potential range .) It surface is readily regenerated by producing a new drop or film , and many metal ions can be reversibly reduced into it . . The auxiliary electrode (counter) : passes all the current needed to balance the current observed at the working electrode . The reference electrode : the reference electrode should provide a reversible half-reaction with nernstian behaviour. It's only role is to act as reference is measuring and controlling the working electrodes potential. The most commonly used reference electrodes for aqueous solution are the calomel electrode. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace .

Optical absorption

absorption spectroscopy is useful in chemical analysis because of its specificity and its quantitative nature. The specificity of absorption spectra allows compounds to be distinguished from one another in a mixture, making absorption spectroscopy useful in wide variety of applications. An absorption spectrum can be quantitatively related to the amount of material present using the beer-lambert law. Determining the absolute concentration of a compound requires knowledge of the compound's absorption coefficient. The absorption coefficient for some compounds is available from reference sources, and it can also be determined by measuring the spectrum of a calibration standard with a known concentration of the target.

Field emission scanning electron microscopy (FESEM)

FESEM works on electron as source and can be used for studying surface topography, morphology and elemental composition of different samples. It has advantages of high depth resolution, 3d imaging. In principle ‘electrons are liberated from field emission source and accelerated in a high electric field gradient within high vacuum column. These so called primary electrons are focused and deflected by some electronic lenses and scan coils to produce narrow scan beam that bombards object, as a result, secondary electrons are emitted from the object. The angle and velocity of these electrons related to surface structure of objects and detector catches the secondary electrons and produces an electronic signal which is amplified and transformed to image scanner to generate image. In the sample preparation, sample must be moisture free, for solid powdered samples proper grinding is required and for biological samples it should be chemically fixed.

Literature Review On WO_3 Thin Films For Supercapacitor Application

The advance economic development has stimulated wide range of significant global challenges including the immense demand for the sustainable and clean energy sources. In the past two decades rapid headway in the field of new reliable energy storage and conversion devices like supercapacitors have been the better than ever power option due to their presently promising features as high power capability, rapid charging/discharging ability and long cycling stability ;The low energy density of electrochemical double layer capacitor (charge storage occurs due to ion adsorption), electrodes fabricated basically from carbon based material however limits the technology. Greater specific capacitance and energy density can be realized from pseudocapacitive (charge storage occurs from the surface redox faradic reactions) electrodes based on transition metal oxides are the emerging as commendable materials for high performance supercapacitor electrodes.

Metal tungsten oxide (WO_3) is one of the stable n type semiconductor having anionic vacancies, which possesses hexagonal structure. Numerous fascinating properties such as existence of multiple oxidation states of W, electrochromic characteristic, high packing density, high energy density, large pseudo capacitance etc. have led to enormous applications in the field of lithium ion batteries [1&8]gas sensing,[2]photocatalysis[3-4]solarcells,[5] electrocatalysis, and electrochromic devices including electrochemical devices. Most recently, transition metal oxides such as Fe_2O_3, TiO_2, MnO_2, ZnO, V_2O_5, and WO_3 have been given prominence to be efficient for portable and flexible supercapacitor electrode material, Specifically, significant attention has been devoted to WO_3 as a worthy electrode material for supercapacitor [6-7] due to their superior electrochemical property. In particular WO_3 possesses high intrinsic density (> 7 gcm-3), high theoretical capacity (~700 mAh/g), high energy density, good cycling stability, excellent rate Plus performance as well as good crystalline phase.[8-9], WO_3 also used in application of perovskite solar cells , WO_3 thin films were successfully prepared by spin coating-pyrolysis methods using the ammonium meta tungstate DMF/water solution as the precursor solution, and are demonstrated as efficient compact layers for the planar perovskite solar cells[10] with the WO_3 nanoparticles, WO_3 nanorods and WO_3 nanosheets as the scaffold layer have achieved photovoltaic conversion efficiency of 2.14%, 3.27% and 3.80%.[11] The planar perovskite solar cell with 15 nm WO_3 compact layer gave a 9.69% average and 10.14% maximum photoelectric conversion efficiency, whereas the planar perovskite solar cell with 60 nm TiO_2 compact layer achieved a 11.79% average and 12.64% maximum photoelectric conversion efficiency[12]. , organic-inorganic composite as hole transport layer consisting of water-free PEDOT:PSS and tungsten oxide (WO_3) nanoparticles, which enhanced the power conversion efficiency of normal-structure perovskite solar cells (PSCs)[13]; WO_3-rGO nanoflower composite formed by coating positive charge WO3 on negatively charged GO reported for the supercapacitor application[14-15], the supercapacitor electrodes based on graphene-WO_3 hybrids prepared by hydrothermal method and WO_3/graphene nanoplates prepared by microwave method, demonstrating good electrochemical properties[16]; Most recently, the attractive properties of WO_3-based materials have increased their consideration for application dye-sensitized solar cells (DSSC) technology[17], nano or microstructures within the non-electrode elements of DSSCs such as electrolytes can enhance the light-harvesting characteristic of the cells avoiding charge recombination, and hence increase their solar energy performance, and used as application of supercapacitor.[18] table 1 shows , compile data of use of transitional metal oxide for different energy savings and energy conversion applications in nanomaterial's form.

Table No:1 Shows Literature Survey On Application Of Transitional Metal Oxides

SR. NO.	MATERIALS	METHOD OF SYNTHESIS	OPTICAL BAND GAP	CRYSTAL STRUCTURE BY XRD	MORPHOLOGY	APPLICATIONS
1.	TIO_2, WO_3 **(18)**	Spin -Coating	WO_3 > -4.15 eV TiO_2 >-4.0 eV	Nano-particle Tetragonal	cross-sectional and surface morphology SEM	Perovskite solar cells.
2.	TIO_2 **(19)**	Chemical bath deposition	3.35 and 3.48 eV	Thin film ,Cross sectional monoclinic	TEM, AFM, SEAD,	Smart - supercapacitor
3.	Tio_2 , WO_3 **(5)**	The atomic layer deposition (ALD) technology	3.32 and 2.97 eV	Monoclinic Nano-particles	(FESEM, Hitachi, SU8010)	Planar Perovskite Solar Cell with Efficiency Exceeding 20%
4.	WO_3	Hydrothermal	2.3eV -	Hexagonal	Kelvin – Probe	supercapacitor

	(6)		3.08 eV		Force Microscopy (KPFM), TEM	
5.	WO_3 **(21)**	Spin -coating	ITO 4.9 FTO 4.8	Thin film Monoclinic	TEM, AFM, SEAD,	Printable WO_3 electron transporting layer for perovskite solar cells: Influence on device performance and stability
6.	WO_3-rGO Hybrids **(14)**	Hydrothermal	2.04 eV	Simple cubic , monoclinic hexagonal different materials composition	(FESEM, JEOL JSM-7100F, SEM, TEM)	Mesoporous WO_3-rGO Hybrids for High-Performance Supercapacitor Electrodes
7.	Ammonium Meta tungstate DMF, WO_3 **(10)**	Electrostatic spraying , Solvo thermal tech.	2.6 – 3.6 eV	surface and cross-sectional morphology	TEM, XRD, SEM	To improve efficient compact layers in planar perovskite solar cells
8.	SnO_2 Inverse Opal/WO_3/$BiVO_4$ **(21)**	Drop casting Spin coating WO_3/$Bivo_4$ WO_3: Doctor-blade	0.73 eV and 3.45 eV	Thin film nanograins	TEM, SEM	Solar Water Oxidation: Systematic Development in purification .
9.	Cs_2CO_3/PCBM Buffer Bilayer, WO_3 **(22)**	Hydrothermal	0.6 and 0.75 eV	Nanoparticle or Nanorods monoclinic	TEM, SEM, SEAD,XRD	Buffer Bilayer as Carriers Transporting Materials for Perovskite Solar Cells application and developments
10.	Graphene/ Silicon (Gr/Si)(**23**)	Facile thermal evaporation, Hydrothermal Method	4.3 eV and 5.3 eV,	homogenous thin film with ultra-smooth morphology	(TEM, Hitachi HT7700) , SEM	silicon solar cells using a transition metal oxide interlayer for solar panels application
11	WO_3 **(24)**	Solvothermal method	0.92 eV	Ortho-rhombic	X-ray diffraction (XRD) , TEM, UV visible spectrophotometry	Stable perovskite solar cells application
12	Titanium isopropoxide, 4-tert-butylpyridine,	Hydrothermal process. Solution-casting	0.67 -0.71 eV	Nano-particle or nanorods monoclinic	TEM , SEM	Solar energy conversion from WO_3 Nano and microstructures with

	(LiI), ($Na_2WO_4 \cdot 2H_2O$), ($(NH_4)_2C_2O_4$), **(18)**	method.				charge transportation and light-scattering characteristics
13.	($WO_3 \cdot H_2O$) **(13)**	Hydrothermal	0.9 -2.46 eV	Ortho-rhombic , mono-clinic	Cyclic voltammetry Galvanostatic charge–discharge, SEM,TEM	high performance supercapacitor.
14	g-C_3N_4-WO_3 **(4)**	Ball milling and heat treatment methods	2.7 eV	Thin film nanocrystal	TEM, (XRD), UV–vis diffuse reflection spectroscopy (DRS), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) methods.	Photo-catalyst application
15	, WO_3 **(2)**	Spin coating	0. 24 -2.48 eV	Nano wires	XRD	Investigation of gas chromic properties of WO3 has become more attractive due to its promising application prospect in the field of gas sensing, smart window and display industries
16	$Na_2WO_4 \cdot 2H_2O$ H_2WO_4. H_2O **(25)**	Hydrothermal	3.6 ± 0.2 eV	Poly-crystalline monoclinic, and ortho-rhombic	X-ray photo-electron spectroscopy (XPS),XRD,. TEM	Solution-Processed Mesoporous WO3 As An Interfacial Cathode Buffer Layer For Photovoltaic Applications
17	$BiVO_4$/WO_3/ SnO_2 **(26)**	Sol−gel spin-coating method	SnO_2 3.51 eV WO_3 - 3.04 eV BIO_4-2.38	Nano-structures such as nanowires, nanorods, helix, and	FE-SEM, JSM-7600F, Jeol). Cross-Sectional TEM, STEM, And EDS	Photoelectrochemical (PEC) water splitting, which directly converts sunlight into

			eV	inverse opal structures		hydrogen fuels.
18	WO_3, Li_2SO_4, $(NH_4)_2SO_4$, **(27)**	Hydrothermal	2.06-4.70 eV	Hexagonal ,ortho-rhombic WO_3 nanowire	FESEM, TEM,XRD	WO3 nanowire arrays will also have applications in field-emission devices, gas sensors and photocatalysis.
19	TIO_2, WO_3 **(3)**	Spin coating	-0.23 To 0.6 eV	Nanosheets rough Surface topography	TEM	photocatalytic science and technology towards large-scale energy and environmental applications.
20	PS(Pd)/WO_3 **(2)**	Sol gel methods	2.15 To -1.5 eV	Cross section rough surface nanoarrays	XRD, TEM , FESEM	Low-Temperature Formation of a WO_3 Thin Film by Hydrogen Sensor . Sensor technology.

Conclusions-

The detailed literature studies on supercapacitors and materials used shows, the proposed material i.e. tungsten oxide has scope in this field of application.

Future prospectus-

Tungsten oxide, the stable inorganic metal oxide has metal in variable oxidation state and hence in near future, the suitable method for synthesis will be selected and deposited films will be applied for supercapacitor applications. In this case, the method of deposition, preparative parameters and characterization plays very vital role.

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