ABSTRACT

Dye Sensitized Solar Cells (DSSCs) based on nanostructured photo anode material have been the subject of vivid interest in recent years due to their high efficiency, low fabrication cost, eco-friendly, and simple processing technique. Over the past few decades, Titanium dioxide (TiO_2) has attracted tremendous attention due to its distinctive properties with enormous potential applications. The design and growth of inorganic semiconductor nanostructures with well controlled sizes and morphologies as a photoanode in DSSCs has been the focus of intense research in recent years. The present study aims at developing TiO_2 based photoanode material employing various nanostructures such as zero dimensional (0D), one dimensional (1D) and three dimensional (3D) structures and examining its morphological persuade on photovoltaic performance. Nanocomposites are being developed and utilized for superior device performance with their unique properties and can achieve synergetic functions beyond the capability of each component when treated independently. Thus we attempted to improve the properties of TiO_2 photoanode by forming nanocomposites with the addition of tin dioxide (SnO_2) which acts as an electron transport layer and also incorporated Copper (Cu) plasmons for better light harvesting phenomenon. Prototype DSSCs were fabricated using cost-effective organic dyes namely Safranin O and

Eosin Y and their efficiencies were evaluated through J-V characterization aiming for low-cost DSSCs with good efficiencies. TiO_2 nanoparticles and TiO_2/SnO_2-Cu nanocomposites were synthesized via a facile sol-gel route whereas 1D and 3D bare and composite nanorod and nanoflower morphologies were developed directly on Indium Tin Oxide (ITO) substrates without using any surfactants and additives by hydrothermal method. FESEM investigations revealed the nanoparticle morphology for bare and TiO_2 nanocomposites and further doping with plasmon activated SnO_2, the particle sizes were reduced paving way for higher surface area which would ensure better dye absorption. Nanorod and nanoflower architecture on ITO substrates were confirmed with dimensions in nano scale. Composite layer formation over the 1D and 3D nanostructures in the case of TiO_2/SnO_2-Cu nanocomposite was verified in FESEM images and all the morphological analysis were additionally established using microstructural HRTEM characterization. The elemental constituents of all the synthesized samples were detected through EDAX analysis and the samples evidenced high levels of purity. The XRD pattern of TiO_2 confirms the formation of anatase phase and the results are in good agreement with a standard reference pattern of titanium dioxide. It was observed that after the introduction of SnO_2 nanoparticle in the pure TiO_2 system, the anatase phase was replaced with

rutile phase making the nanocomposites more suitable for photovoltaic applications. 1D and 3D bare and composite nanostructures possessed rutile phase. The average crystallite sizes were calculated using Scherrer's equation and indicated that the nanorods showcased highest crystallite size followed by nanoflowers and nanoparticles as well, and similar results were observed in nanocomposite architectures implying that morphology plays a significant role in the crystallite nucleation. XPS measurements were performed to analyze the surface composition and chemical structure of the synthesized samples and shifts could be seen in the binding energies of the as-synthesized samples owing to their variant nanostructures. BET analysis indicated that all the synthesized samples exhibited type IV isotherm patterns with distinct hysteresis loop confirming the presence of mesopores in the samples according to the IUPAC nomenclature. Among the multidimensional structures, nanoparticulate structure possessed higher surface area of about 37 m^2 /g than nanorods and nanoflowers, however the surface area was amplified on forming nanocomposite multidimensional structures which shows that nanocomposite architectures exhibit good surface conduction and photovoltaic performance than the bare ones due to their augmented surface area. The optical response of the as-synthesized samples was determined using UV- Diffuse Reflectance spectroscopy. The absorption edge of TiO_2

sample was found below the UV region and it was also seen that Cu doping in SnO_2 resulted in superior absorption across the visible spectrum indicating enhanced photon absorption due to the SPR effect. Also the addition of SnO_2 to TiO_2 could have resulted in an increased probability of electron transition. From Kubelka –Munk plots, the band gap values are evaluated and it was also established that band gap narrowing occurrs and therefore the probability of charge carrier generation and transportation is found to be higher in the composite architectures. This result was further confirmed by field dependent dark and photocurrent studies. In all cases, the photo currents were observed to be more compared to dark currents evidencing the photo responsive phenomenon which is essential for photovoltaic applications. Among the multidimensional TiO_2 nanostructures, nanoflower morphology exhibited better photoconductivity than the nanorod and nanoparticle architectures. For a fixed field of say 100 V/cm, 3D nanocomposite sample showed ~38 folds increase in photo currents and ~145 folds increase in dark currents when compared to bare nanoflower structures. A ~ 14 fold increase in photo current and ~ 12 folds increase in dark current was observed in the case when it is compared to 1D nanocomposite and similarly ~ 23 fold and ~ 18 fold enhancements on comparison with nanoparticle composite. The enriched output of the composite nanoflower structure could be attributed to light

scattering induced by the nanorods within the nanoflowers, which in turn cause the light to be multiply absorbed during the transporting process. Also upon plasmon activation on the composite samples, the surface conductivity is prone to increase as the plasmon absorption wavelength falls in the visible range. FTIR spectrum analysis confirmed the formation of metal oxide (TiO_2) in the bare material and composite of plasmon supported SnO_2/TiO_2 nanostructured samples. Twelve different prototypes of DSSCs were fabricated using bare TiO_2 multidimensional nanostructures and SnO_2/Cu activated TiO_2 multidimensional nanostructures using Safranine O and Eosin Y dyes. In both cases nanoflower based photoanodes showcased better performance in bare and nanocomposite form. On comparison, Safranin O dye sensitized DSSCs employing TiO_2/SnO_2-Cu nanoflower photoanode were considered to be highly efficient, exhibiting a record efficiency of 0.64% in laboratory conditions and hence emphatically establishing the status of TiO_2/SnO_2-Cu nanoflower as adept photoanode systems in DSSCs. Hence, multifaceted advantages such as wide band gap nature, high transmittance of the SnO_2 and the plasmonic enhancement of the Cu were achieved in the composite film. We anticipate that the reported work would open up a promising possibility for the fabrication of high-efficiency DSSCs, using these systems.

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V. CHANDRAKALA

Contents

LIST OF SYMBOLS AND ABBREVIATIONS

Ω	ohm
μA	microamperes
mA	milliamperes
hυ	photon energy
η	conversion efficiency
λ	wavelength of the X-ray beam
α	Absorption Coefficient
β	Full width half maximum
ºC	degree celsius
μ	mobility of charge carriers
θ	angle of incidence of X-ray beam
σ	electrical conductivity
BET	Brunauett-Emmett-Teller
BJH	Barrett-Joyner-Halenda
Cu	Copper
CdS	Cadmium Sulphide
CdSe	Cadmium Selenide

D	Crystallite Size
D.C	Direct Current
DSSC	Dye Sensitized Solar Cell
Eg	Optical Band gap
eV	electron volt
E1	Eosin Y (0.1mM)
E2	Eosin Y (0.3mM)
E3	Eosin Y (0.5mM)
F	Farad
FTO	Fluorine doped tin oxide
ff	Fill factor
FT-IR	Fourier Transform Infrared
g/mol	gram/mol
gcm^{-3}	gram per centimeter cube
h	Plank constant
HOMO	Highest occupied molecular orbital
HRSEM	High Resolution Scanning Electron Microscope
I	Current
I^-/I_3^-	Iodine and tri-iodide

I_{max}	Maximum Current
ITO	Indium tin oxide
IR	Infra red
I_{sc}	Short circuit current
K	Kelvin
k	Boltzmann Constant
kV	kilovolt
kWh	Kilowatt hour
LUMO	Lowest unoccupied molecular orbital
m	metre
mM	millimolar
Nb_2O_5	Niobium Pentoxide
NH_3	Ammonia
nm	nanometer
P_{dia}	BJH average pore diameter
P_{max}	Maximum Power
ppm	Parts per million
Pt	platinum
R_{sh}	Shunt Resistance

S_{BET}	BET Surface area
SNP	SnO_2 nanoparticles
SCA	SnO_2/Cu (0.5 mol %)
SCB	SnO_2/Cu (1 mol %)
SCC	SnO_2/Cu (5 mol %)
Si	Silicon
SnO_2	Tin dioxide
S1	Safranin O (0.1mM)
S2	Safranin O (0.3mM)
S3	Safranin O (0.5mM)
TCO	Transparent Conducting Oxide substrate
TiO_2	Titanium dioxide
TSC A	TiO_2 (75%)- SnO_2 (25%)/Cu
TSC B	TiO_2 (50%)- SnO_2 (50%)/Cu
TSC C	TiO_2 (25%)- SnO_2 (75%)/Cu
TNP	TiO_2 nanoparticles
TNR	TiO_2 nanorods
TNF	TiO_2 nanoflowers
TRC	TiO_2 nanorod- SnO_2/ Cu composite

TFC	TiO_2 nanoflower- SnO_2/ Cu composite
Triton X-100	Polyoxyethylene (10) octylphenyl ether
UV	Ultra Violet
UV-DRS	Ultra Violet- Diffuse Reflectance Spectroscopy
V	Voltage
V_{max}	Maximum Voltage
V_{oc}	Open circuit voltage
W	Watt
WO_3	Tungsten trioxide
XRD	X-ray diffraction
ZnO	Zinc Oxide
ZrO_2	Zirconium dioxide