

Chapter 5

Summary

In the present thesis, our prime focus is to fabricate efficient photoanodes with significant light harvesting and reduced recombination losses for DSSC application. With this aim in mind, mesoporous silica which can act as a dual functional material, scatterer or light harvester (for enhancement in dye absorption) as well as recombination inhibitor (for reduction in back electron transfer from TiO_2 to electrolyte) without affecting dye loading, was synthesized and characterized for DSSC application. Further the effect of crystalline and different anisotropic shaped silver nanoparticles on the absorption cross-section of N719 dye has been studied by synthesizing silver nanoparticles under different experimental conditions using chemical reduction method. The results obtained from work done are briefly described as given below.

Mesoporous silica was successfully synthesized using tetraethyl orthosilicate and polyethylene block polymer and was further characterized by XRD, XPS, BET, SEM, HRTEM and SAED. XRD investigations confirm the amorphous nature of mesoporous silica. Pore size of mesoporous silica was calculated by using BET and found to be around 8 nm. Two peaks around 103.3 eV (Si 2p) and 532.4 eV (O 1s) were observed in the XPS spectra of mesoporous silica, confirmed 4+ oxidation state of Si and presence of chemisorbed oxygen. Morphology of mesoporous silica was confirmed using SEM and TEM and was found to be rice shaped with the size in the dimensions of 370 nm \times 1.2 μm . HRTEM image indicates the straight and parallel channels in mesoporous silica with pore size around 8.33 nm, which matches well with the BET results. The presence of fuzzy rings in SAED confirms the amorphous nature of mesoporous silica, which was consistent with the XRD results.

5. SUMMARY

Optimization of morphology of photoanode for the incorporation of mesoporous silica in DSSCs was done by fabricating DSSCs in two different approaches: single layer approach and double layer approach. In single layer approach, photoanode consists of single layer of TiO_2 mixed with mesoporous silica while in double layer, first layer consists of TiO_2 whereas second layer with TiO_2 mixed with mesoporous silica. As we shift from double layer to single layer approach, J_{sc} increases by 16%, V_{oc} remains almost same, FF increases by 13.4% while enhancement in device performance was found to be 30%. Out of these approaches, single layer approach was found to be more effective as compared to double layer approach. Further, mechanism behind the improvement was confirmed by using UV-Vis spectroscopy, dark current measurement and EIS. UV-Vis spectroscopy of photoanodes prepared in single as well as double layer approach confirms the improvement in absorption spectra of N719 dye, with more enhancement in case of photoanode prepared using single layer approach, which is due to uniform mixing of mesoporous silica throughout the photoanode. EIS analysis shows that recombination resistance was found to be more in case of single layer approach as compared to double layer approach, which was consistent with dark current measurement where dark current onset potential is more in the case of single layer. Lesser recombination resistance in double layer approach is due to the presence of recombination losses at interface between two layers. Thus improvement in device performance was found to be more in single layer approach as compared to double layer approach due to increase in light harvesting (as observed by UV-Vis) as well as suppression of recombination of charge carriers (as observed by EIS and dark current measurements).

For the optimization of wt% in single layer approach, three wt% were selected (0.5 wt% , 0.75wt% and 1 wt%). From the J-V characteristics, J_{sc} was found to increase by 25.6%, 42.4% and 54%, V_{oc} remains almost same, FF increases by 3.42%, 4.75% and then decreases by 9% whereas power conversion efficiency was found to increase by 26%, 50% and 40% in case of 0.5 wt%, 0.75% and 1 wt% respectively. Thus, 0.75wt% corresponds to optimized wt% of mesoporous silica. Dye loading was calculated using Beer-Lambert's law and was estimated as 274×10^{-7} mole/cm², 270×10^{-7} mole/cm², 276×10^{-7} mole/cm² and 272×10^{-7} mole/cm² in case of 0 wt%, 0.5 wt% , 0.75wt% and 1 wt% respectively. Thus, it was concluded that the dye loading was not affected by the incorporation of mesoporous silica. This was due to the larger pore size of mesoporous silica as compared to that of N719 dye, through which sites of TiO_2 become available for dye loading which were not available, in case of solid structures. The mechanism

behind the improvement was explained using UV-Vis and EIS measurements. UV-Vis spectra of photoanodes fabricated at different wt% confirmed the scattering nature of mesoporous silica as absorption of N719 dye was estimated from area under UV-Vis curves and found to increase by 6.6 %, 26.59 % and 39 % in case of 0.5 wt%, 0.75 wt% and 1 wt% respectively. While the role of mesoporous silica as recombination inhibitor was reflected from EIS analysis. Recombination resistance was calculated by fitting the experimental data obtained from EIS with R(QR)(QR) model and are found to be 7.04 ohm cm², 11.78 ohm cm², 13.44 ohm cm² and 10.94 ohm cm² at 0 wt%, 0.5 wt% , 0.75wt% and 1 wt% respectively. In addition to this, life time of charge carriers calculated from bode plots follows the same trend and comes out to be 11.47 ms, 16.48 ms, 23.66 ms and 16.48 ms for 0 wt%, 0.5 wt% , 0.75wt% and 1 wt% respectively. Thus mesoporous silica can serve the dual role both scatterer as well as back recombination inhibitor without affecting the dye loading and optimized wt% was estimated to be 0.75wt%.

np-Ag_{sc} and np-Ag_{pc} were successfully synthesized by chemical reduction method using AgNO₃ and NaBH₄ without and with CTAB respectively and were further characterized by UV-Vis, HRTEM and SAED. From TEM images, the morphology of Ag nanoparticles was observed to be spherical in both the cases. Their size was estimated from TEM images and comes out to be 5.2 nm and 8.7 nm with standard deviation of 9% and 11% in case of np-Ag_{sc} and np-Ag_{pc} respectively. The presence of (200) and (220) planes corresponding to d-spacings 2.039 Å and 1.457 Å in np-Ag_{pc} while (200) plane corresponding to d-spacing of 2.067 Å in np-Ag_{sc} was confirmed from HRTEM images. In addition to this, from HRTEM images, polycrystalline nature of np-Ag_{pc} was also confirmed because of the presence of different grains as compared to single grain in np-Ag_{sc}. These results matches well with SAED results where presence of ring structure is the indication of polycrystalline nature of np-Ag_{pc} as compared to dotted pattern in np-Ag_{pc}, which is the indication of its single crystalline nature. Further indexing of patterns confirm the presence of (111), (200), (220) and (311) planes in polycrystalline nanoparticles in comparison to (111), (2 $\bar{2}$ 0), (3 $\bar{1}$ 1) and (2 $\bar{2}$ 0) planes in case of single crystalline nanoparticles. The presence of these planes indicates the face centered cubic structure of Ag nanoparticles. The UV-Vis spectra of np-Ag_{sc} and np-Ag_{pc} confirms the plasmonic nature of Ag nanoparticles showing SPR peaks at 405 nm and 407 nm respectively. Further their stability was checked by doing UV-Vis spectroscopy repeatedly for six months. FWHM were estimated from UV-Vis spectra by fitting lorentzian peaks and found to be 0.337 eV and 0.592 eV for np-Ag_{sc} and np-Ag_{pc} respectively. Both the systems are ho-

5. SUMMARY

mogeneous as particles are spherical in shape with the standard deviation in size nearly 10%. Dephasing times were calculated using FWHM and comes out to be 3.9 fs and 2.2 fs in np-Ag_{sc} and np-Ag_{pc} respectively. Further, enhancement in effective absorption cross-section of N719 dye was observed when above synthesized nanoparticles were incorporated in dye solution (solution form) as well as in photoanode (film form). This confirms the plasmonic effect of Ag nanoparticles as enhancement was found to be near to 400 nm where SPR peak had observed. 24.42% and 8.52% improvement in molar extinction coefficient (ϵ) or absorption cross-section (σ) in solution form while in thin film form, 21.01% and 7.97% was estimated in the case of np-Ag_{sc} and np-Ag_{pc} respectively. Thus, effect of crystallinity of Ag nanoparticles on the effective absorption cross-section of N719 dye was demonstrated and concluded that single crystalline Ag nanoparticles have more dephasing time as compared to polycrystalline Ag nanoparticles and can act as interesting candidates in light harvesting enhancement of photoanode in DSSCs. It was also confirmed theoretically that single crystalline Ag nanoparticles are better candidates for enhancement in absorption cross-section of N719 dye as compared to polycrystalline nanoparticles due to the absence of scattering centers in them.

Different anisotropic shaped Ag nanoparticles were synthesized successfully using chemical reduction of AgNO₃ with reducing agent NaBH₄ by varying the concentration of surfactant CTAB as 2 mM, 3 mM and 4 mM. These synthesized nanoparticles were then characterized by UV-Vis, XRD, TEM, NBD and FTIR. XRD of Ag nanoparticles prepared under different experimental conditions indicate peaks at 38.116^o, 44.277^o, 64.426^o and 77.472^o due to (111), (200), (220) and (311) planes respectively. These results are consistent with JCPDS card Number 04-0783, representing face centered cubic structure in all the cases. Attachment of CTAB on the surface of Ag nanoparticles prepared at different CTAB concentrations was confirmed by comparing FTIR of pure CTAB with Ag nanoparticles prepared at different CTAB concentrations. FTIR confirms the attachment of CTAB through its head group. Peaks corresponding to symmetric and asymmetric stretching vibrations (2850 cm⁻¹ and 2917 cm⁻¹) and rocking mode (719 cm⁻¹ and 730 cm⁻¹) of CH₂ in CTAB remains at same positions even in the case of Ag nanoparticles capped with CTAB, which confirms that there is no interaction between tail of CTAB and Ag nanoparticles. On the contrary, reduction in intensity, broadening as well as small shift was observed in the peaks corresponding to scissoring vibrations of C-H (1431 cm⁻¹, 1486 cm⁻¹) and stretching mode of C-N⁺ (960 cm⁻¹) in head group (CH₃-N⁺) of CTAB when compared with FTIR

data of CTAB capped Ag nanoparticles, confirmed the attachment through head group of CTAB. The morphology of Ag nanoparticles was confirmed from TEM images and found that as concentration of CTAB is low (2 mM) and moderate (3 mM), the shape of nanoparticles is spherical with the average size around 14 nm and 17 nm respectively. At high concentration (4 mM), anisotropy appears along with the different shapes of nanoparticles (oval, rod, cubical, pentagonal and prismatic). Their size were found to be 18 nm, 123 nm, 35 nm, 25 nm and 38 nm respectively. NBD patterns confirm the single crystalline nature of Ag nanoparticles. The mechanism behind the appearance of different shapes was explained on the basis of activation energy of different planes. UV-Vis spectra of Ag nanoparticles represent single SPR peak around 400 nm in case of 2 mM and 3 mM, which corresponds to spherical shape of Ag nanoparticles. While at 4 mM, spectrum became broadened, which after deconvolution was fitted with five lorentzian peaks: 385 nm, 437 nm, 510 nm, 644 nm and 739 nm. These peaks represent the presence of rod, oval, cubical, prismatic and pentagonal shaped Ag nanoparticles. Dephasing time for Ag nanoparticles come out to be 5.54 fs and 9 fs at low and moderate concentrations of CTAB while for high concentration of CTAB, dephasing times were estimated to be 4.75 fs, 4.4 fs, 6.16 fs, 2.4 fs and 4.79 fs for oval, rod, cubical, pentagonal and prismatic shaped Ag nanoparticles respectively. UV-Vis spectroscopy of N719 dye incorporated with Ag nanoparticles prepared at different CTAB concentrations was recorded and enhancement of 10.5%, 21.28% and 64.59% was observed in case of 2 mM, 3 mM and 4 mM CTAB concentrations. In addition to this, enhancement in 4 mM is spreaded over entire visible regime instead of enhancement around a particular wavelength as in the cases of 2 mM and 3 mM respectively. This broadened enhancement is due to the presence of multiple SPR's in case of 4 mM CTAB in comparison to single SPR in 2 mM and 3 mM CTAB concentrations. Thus different anisotropic shaped single crystalline Ag nanoparticles can enhance the absorption cross-section of N719 dye over entire visible range as compared to spherical shaped single crystalline Ag nanoparticles.

Although enormous work has been done regarding efficient light harvesters and back recombination inhibitors for the fabrication of improved DSSCs, yet it is expected that the investigations present in this thesis would be worth for the utilization in DSSC application. Further, the effect of size, shape, pore size of mesoporous silica on the DSSC efficiency and fabrication of DSSCs incorporated with different anisotropic shaped single crystalline Ag nanoparticles would be an interesting field of investigation.

5. SUMMARY
