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Summary and Conclusions

7.1 SUMMARY

Nanocrystalline titania with different particle sizes and phases were synthesized at sub-zero temperatures. At −20 and −10 °C temperature, there was an increment in lattice strain at grain boundaries with more number of grains. Thus, it creates a feasible ambiance for slower nucleation than growth which increases the chances of formation of the larger size particle, and thus the rod-shaped nanostructures were observed by HRTEM images at −20 and −10°C. Moreover, at these temperatures, higher weight percent in rutile was observed in comparison to anatase with decreased defects in the particles. When nucleation rate is higher than the growth rate, oval-shaped nanostructures were formed at −40 and −30°C with major anatase phase. These observations are supported by surface area analysis. This preparation method provides a viable, easy and cost effective synthetic procedure for large scale production. Remarkably, enhancement in both photocurrent density and photoconversion efficiency, 18.46 mA cm^{-2} and 8.6% respectively were reported for the −40°C DSSC. Enhancement arises from high percentage of anatase phase (0.5%), optimized film thickness (14.5 mm), increased charge transport along with decrease in recombination rate at electrolyte–dye–photoanode (3.124/Ω), higher Rrms (0.130 mm) with different size and shape nanoparticles harvest more light. The present work provides a simple, controlled one step process to synthesize TiO_2 and its application in DSSC with high performance open new window towards more applications like batteries, photocatalysis and biosensors etc.

The anatase TiO_2 solid nanospheres decorated with different percentages of ZnO are synthesized by a hydrated salt-assisted hydrothermal method. The aggregate structure leads to good light-scattering properties along with a surface area appropriate for electron trapping. The heterojunction spheres exhibit higher photocurrent density, up to 18.96 mA cm^{-2}, which is due to spherical architecture increasing the number anchoring sites for dye molecules with enhanced scattering effect. With 1% ZnO, solid nanospheres the maximum photoconversion efficiency was about 8.07%. An enhancement of open-circuit voltage was observed for the ZnO decoration. These improvements are attributed to enhanced electron transport efficiency and lower recombination with a better light-harvesting structure.

The HfO_2 nanodots increase the defect density upon hydrogenation and shift the optical absorption of H-HfO_2/TiO_2 from IR towards the visible region. This is clearly seen from an increase in band gap from 2.03 eV to 2.4 eV. Owing to the increased surface area, there is a clear enhancement in the dye uptake capability of H-HfO_2/TiO_2 (10.1×10^{-9} mol cm^{-2}) compared to H-TiO_2. The DSSC fabricated using H-HfO_2/TiO_2 with an optimal band gap of 2.4 eV exhibits an efficiency of 8.6% with a photocurrent density of 21.7 mA cm^{-2}.

Graphene was synthesized from graphite by reduction of graphene oxide by hydrazine hydrate and used as counter electrode in the DSSC. The graphene counter electrodes were explored by three different methods, drop casting, spin coating and screen printing with different thermal annealing temperatures. Screen printing technique has shown uniform surface, no agglomeration of nanoparticles in the film, high film adhesiveness to substrate and less amount of morphological variation at different baking temperatures. Various carbon material coated stainless steel substrate as counter electrode were examined. The sheet resistance substrate and agglomeration of carbon materials directly influenced photo conversion efficiency performance of the cell of the cell. The DSSCs with a SS-graphene counter electrode has reported highest efficiency compared to others cells.

All photovoltaic parameters decreased when active area reduced from 0.09 to 0.04 cm^2. The photovoltaic cell performance of the -40°C cell was reduced by $\Delta\eta \sim 10\%$ on replacing Pt counter electrode with graphene. The highest photo conversion efficiency (9.6%) has been reported with Pt counter electrode, whereas same composition with graphene counter electrode shows 8.6% efficiency where active area of photoanode was 0.04 cm^2.

In photo-assisted degradation for harmful compounds like Cr(VI) and industrial dye pollutants, prepared sub-zero temperature TiO_2, ZnO-TiO_2 and hydrogenated HfO_2/TiO_2 solid nanosphere were proven to be efficient material with filter membrane for water treatment. The photocatalytic degradation of Cr(VI) with -40°C TiO_2 membrane reported ~75% yield where 1% ZnO doped TiO_2 showed fast removal and 80% degradation of Cr(VI) within 60 minutes. Even after continuous four cycles these results were reported 95% degradation. The H-HfO_2/TiO_2 membrane showed increase in degradation efficiency with high rate constant, 0.0061 min^{-1}.

7.2 CONCLUDING REMARKS

This thesis states the detailed and complete analysis of TiO_2 synthesized by one-step sub-zero temperature method with well crystallized anatase and rutile nanoparticles. The reaction temperature of synthesis process exhibits variation in phase composition which implies morphological changes such as size and shape of nanoparticles. This change is mainly caused by phase combination, lattice strain, defects present on the grain boundaries and nucleation-growth rate of particles. A polydisperse aggregate structure of ZnO–TiO_2 nanospheres is demonstrated to be an excellent photoanode material and shows excellent light trapping architecture with enhanced electron transport. Hydrogenated TiO_2 doped with HfO_2 nanodots opens a new window towards usage of dielectric material in DSSC. It enhances optical light trapping effects and increases the surface area of TiO_2 with the addition of HfO_2 nanodots followed by its hydrogenation. Chemically synthesized graphene contains functional groups even after its reduction, and is the main reason behind the reduced DSSC performance compared to DSSC fabricated with commercial graphene counter electrode. As a substrate at counter electrode instead of FTO stainless steels sheet resistance have direct influence on performance and fill factor of DSSC. Highest efficiency was observed with smaller active area due to reduced electron-hole recombination in the solar cell. The photo assisted catalytic material doped filter membrane reports the successful removal of harmful contaminants from water with cost-effective, reproducible and scalable way.

7.3 FUTURE WORK

Apart from efficient photoanode and photocatalyst, these high surface area subzero temperature TiO_2 can be explored in various application like drug delivery and sensor where controlled morphology and phase plays a crucial role.

Hydrogenated close shell metal oxide in solid nanosphere assembly is a promising candidate for high-performance DSSC and water treatment. Hence, to understand band gap engineering and other phenomena it is essential to explore more close shell metal oxide.

With highly efficient solar cells, it is very important to understand stability and large-scale parameter for exploring these materials commercially. And these materials need to be further studied with emerging technologies like perovskite and hybrid solar cells.

The graphene counter electrode could be very useful for large size cells, reducing the manufacturing cost and developing new type flexible DSSCs.