ZnO-based hybrid solar cells

ZnO has received much attention over the past few years because it has a wide range of properties, including conductivity from metallic to insulating (including *n*-type and *p*-type conductivity), high transparency, piezoelectricity, wide-bandgap semi-conductivity, room-temperature ferromagnetism, and chemical-sensing effects. As an *n*-type semiconductor, ZnO, has several potential advantages over TiO_2 such as better electron mobility and low crystallization temperature. To improve the photovoltaic performance of ZnO-based devices, an interconnected mesoporous inorganic nanostructure is favorable which can provide a high surface-to-volume ratio for exciton separation within their lifetime and a good pathway for charge carrier transport.

To fabricate mesoporous inorganic ZnO semiconductors, various methods can be employed, such as chemical vapor deposition, wet chemical methods and hydrothermal synthesis. Among these methods, the diblock copolymer assisted sol-gel approach has been corroborated by countless reports to be powerful in morphology tunability. Based on this strategy, our group successfully achieved various ZnO morphologies by modifying the conditions during the preparation process. For example, Sarkar *et al.* firstly synthesized ZnO films with multiple morphologies including foamlike structures, wormlike aggregates, circular vesicles, and spherical granules by adjusting weight fractions of the ingredients and constructed a ternary phase diagram to show the compositional boundaries of the investigated morphologies.[1] Although spin-coating, as a laboratory-based routine, has been extensively used for the thin film deposition. Sarkar *et al.* showed that large-scale industrial techniques, such as spray-coating and screen-printing, significantly influence the final ZnO morphologies and film thickness due to the completely different film formation mechanisms.[2,3] Directly after obtaining the hybrid film deposited from the solution of micelles, another annealing process is still needed for further phase-separation and to enhance the self-assembly of the nanostructure. Concerning the two kind of annealing methods, Wang *et al*. demonstrated a low-temperature route to fabricate ZnO films with different nanostructure by controlling the thermal annealing temperature.[4] Sarkar *et al.* investigated the effect of time-dependent solvent annealing on the pore size of the final ZnO nanoporous film.[5] For obtaining pure inorganic ZnO films, Wang *et al.* utilized two different template removal approaches, ultraviolet irradiation and high-temperature sintering, to compare their respective impact on the pore size and the film collapse.[6]

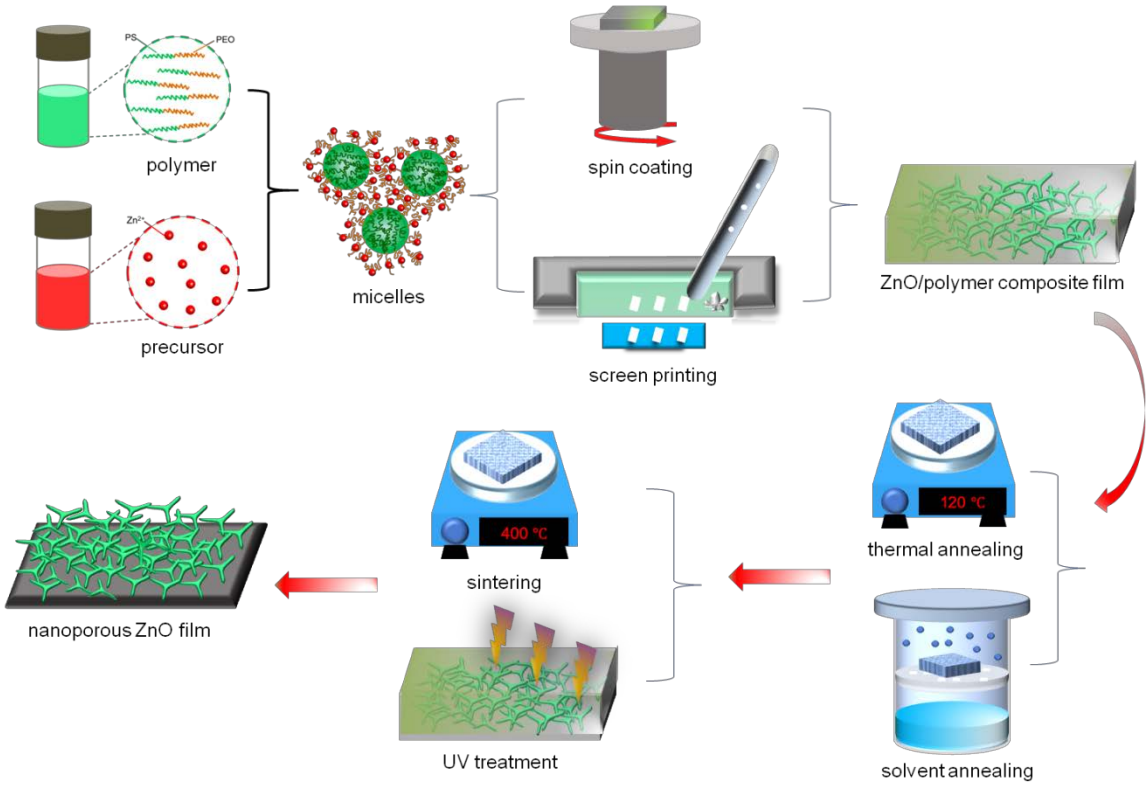

Figure 1. Schematic representation of the steps involved in the fabrication of mesoporous ZnO films.

To date, besides exploring the way to tune the nanostructured morphology of the ZnO films, our group also focused on improving the photovoltaic performance of ZnO-based solid-state dye-sensitized solar cells (ssDSSCs) and investigating the corresponding correlation between the film morphology and the device performance. Both Sarkar *et al.* and Wang *et al.* revealed that mesoporous ZnO films with appropriate pore size and better interconnected network structures are important for the performance optimization. As a challenging issue in backfilling the mesopores, larger pores favor the backfilling of the dye molecules and *p*-type organic semiconductors, but on the other hand also decreases the surface-to-volume ratio. Therefore, it needs to be balanced. As another factor limiting the device performance, an interconnected network is also necessary for providing a good pathway for electron transport to the corresponding electrode, thus promoting the exciton separation and hindering the charge recombination.[4-6] For ZnO-based hybrid bulk-heterojunction solar cells, it is challenging to fabricate ZnO/P3HT active layers because of the unfavorable interaction of the polymer solution with the ZnO nanostructure. To overcome this incompatible problem, Wang *et al.* presented a promising approach for a large-scale preparation of bulk heterojunction P3HT/ZnO films by employing conducting diblock copolymer poly(3-hexylthiophene)-block-poly (ethylene oxide) (P3HT-*b*-PEO).[7,8]

With respect to future investigations, there are still some challenges need to be addressed. The current research methods are mainly focusing on a sol-gel technique combined with the block copolymer as the structure-directing agent, although it has been proved to be powerful and efficient in producing a vast range of morphologies, the fabrication usually suffers from multiple, tedious steps and the obtained nanostructure strongly depends on the precise control of the experimental parameters. To this end, a direct access can be explored to acquire some certain desired features, such as highly crystalline mesoporous ZnO films, or a one-pot synthesis route can be developed to meet the requirements of lower energy consumption in production and less environmental impact. For application in solar cells, an optimal film thickness is indispensable for improving the photovoltaic performance, consequently, more deposition method, such as slot-die printing, and blade-coating will be exploited for the production of large scale ZnO films. Meanwhile, corresponding morphology evolution can be probed in situ to gain more detailed understanding of the mechanisms governing the film morphology.

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