Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

In-situ preparation of $CuInS_2$ films on a flexible copper foil and their application in thin film solar cells

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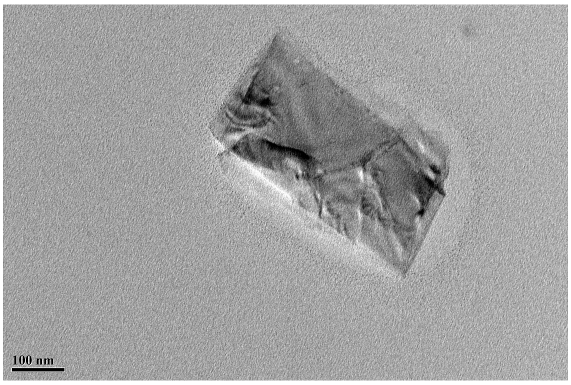

Fig. S1 TEM image of a CIS nanosheet peeled from the as-grown CIS film.

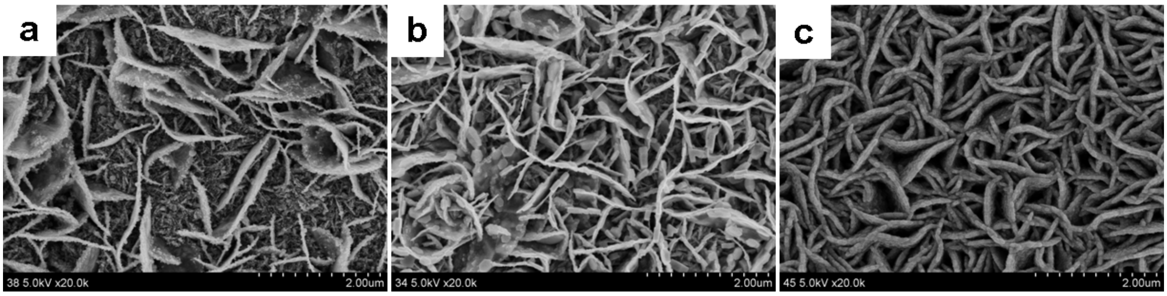

Fig. S2 SEM images show the CIS films obtained for (a) 2 h, (b) 8 h and (c) 16 h by treating Cu foils in ethylene glycol solution containing $InCl_3 \cdot 4H_2O$ (0.025 M) and thioacetamide (0.05 M) at 180 °C in the autoclave. As shown from these images, the reaction time shows a significant effect on the thickness, in particular, the density of the CIS ordered nanosheets on the Cu foil. In a short time (e.g., 2h), only a small amount of the CIS nanosheets grow loosely on the Cu foil, and the thickness of these nanosheets is estimated to be ~ 30 nm (Fig. S2a). As the reaction time increase to 8 h, a great quantity of the CIS nanosheets appears on the Cu foil, and the density of the nanosheets obviously increase (Fig. S2b). With the reaction time further increasing to 16 h, the thickness and the density of the CIS nanosheets both further increase to a higher degree (Fig. S2c, the nanosheets with a thickness of ~ 130 nm).

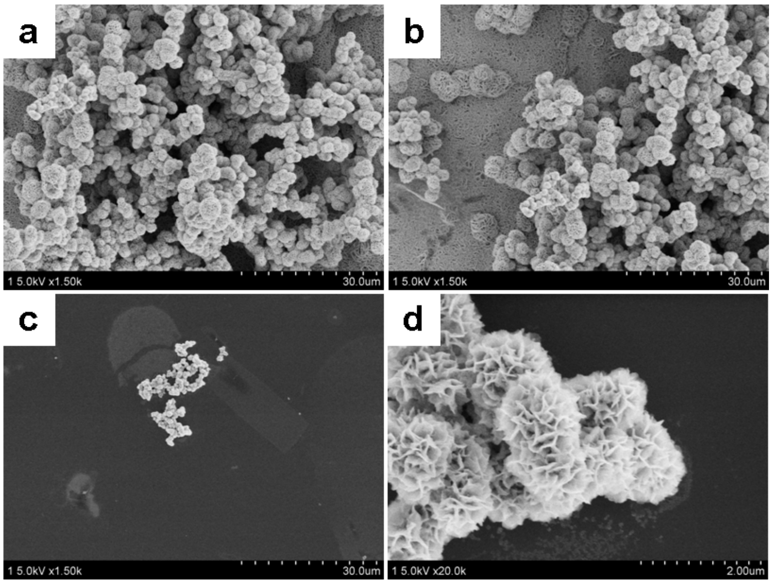

Fig. S3 SEM images show the CIS films by using Cu foil (a, b) and silicon wafer (c, d) as substrates in ethylene glycol solution containing $InCl_3 \cdot 4H_2O$ (0.05 M) and thioacetamide (0.10 M) at 180 °C for 16 h in the autoclave. As shown in Fig. S3a and S3b, a double-layered film consisting of a lower layer of uniform ordered potato chips shaped CIS nanosheets and a upper layer of the flower shaped superstructures form on the Cu foil. As shown in Fig. S3c and S3d, only a few of the CIS flower shaped superstructures instead of the double-layered films scatters and deposits on the Si wafer. So, it suggests that a heterogeneous process happened on the Cu foil and a homogeneous process gone on in the solution are due to the growth of the CIS films including single-layered and double-layered CIS films. Firstly, a heterogeneous nucleation and vertical growth processes occur on the copper surface to form uniform ordered potato chips shaped nanosheets via the chemical solution reaction ($Cu^{+} + In^{3+} + S^{2-} \rightarrow CuInS_2$), in which Cu^{+} is originated from the copper substrate, S^{2-} and In^{3+} come from thioacetamide and $InCl_3 \cdot 4H_2O$, respectively. Meanwhile, with a continuous supply of Cu^{+}, S^{2-}, and In^{3+} in the solution, a homogeneous nucleation and growth result in the formation of the flower shaped superstructures which disperse in the solution, and some of these flower shaped superstructures deposit on the earlier formed layer of ordered potato chips shaped nanosheets, forming a double-layered structure somewhere on the Cu foil.

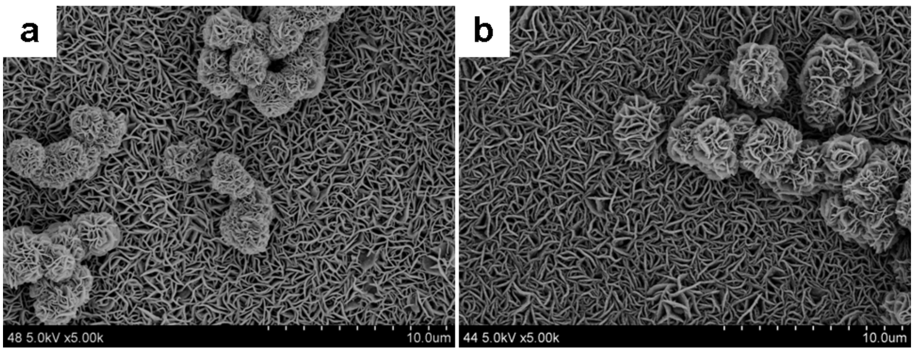

Fig. S4 SEM images show the CIS film before (a) and after (b) the bending process. No CIS material was observed to fall off from the films during the bending process, and no obvious cracks were found to form inside the CIS film after the bending, as shown in Fig. S4b. These results suggest that after the bending the grown CIS films still have a good stability or a considerably strong adhered force on the Cu foil, which should be attributed to the fact that the Cu foil not only acts as one of the source materials but also directly serves as the substrate, resulting in *in-situ* growth of the CIS nanosheet alignments.