Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information

Tailoring the Properties of Aqueous/Ionic Liquids Interface for Tunable Synthesis and Self-Assembly of ZnS Nanoparticles

Kaisheng Yao,[a] Weiwei Lu,[ab] Xinying Li[b] and Jianji Wang*[b]

[a]*School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang, Henan 471023, P. R. China*

[b]*Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China*

.

*Author to whom all correspondence should be addressed.

E-mail: jwang@henannu.edu.cn

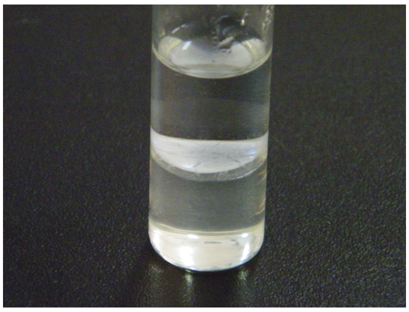

Fig. S1 Photo of ZnS film deposited at the interface of $[C_4mim][PF_6]$-H_2O at 50℃ for 5 h of reaction.

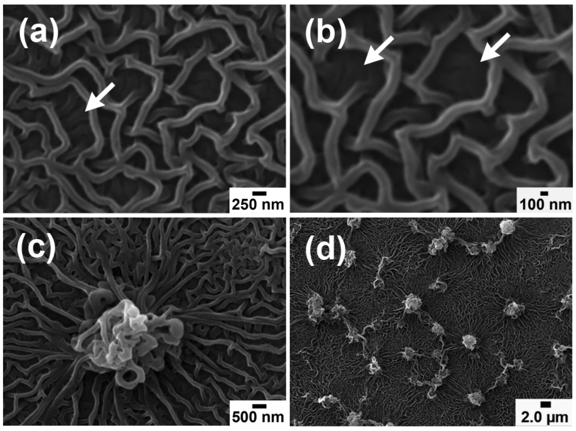

Fig. S2 SEM images of the ZnS films prepared at 50 ℃ for 5 h of reaction at $[C_8mim][Tf_2N]$-H_2O interfaces: (a) and (b), high magnified dragon parts, and (c) and (d), different magnified flower parts.

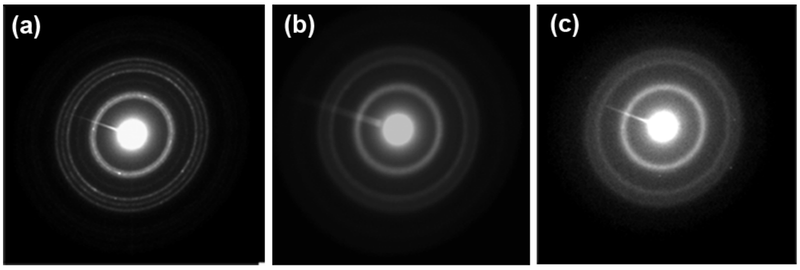

Fig. S3 SAED patterns of the ZnS samples deposited at different IL-H_2O interfaces: (a), $[C_8mim][PF_6]$-H_2O; (b), $[C_8mim][Tf_2N]$-H_2O; and (c), $[C_8mim][BF_4]$-H_2O.

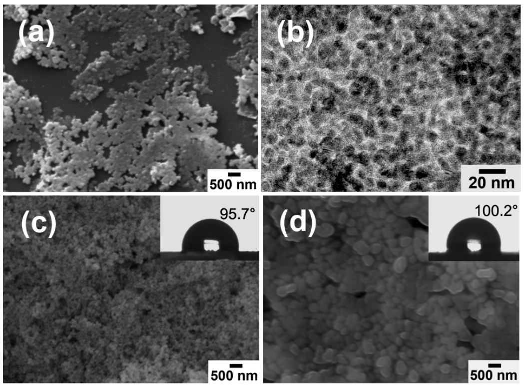

Fig. S4 (a) SEM and (b) TEM images of the ZnS films prepared at 50 ℃ for 5 h of reaction at $[C_4mim][PF_6]$-H_2O interface; (c), SEM image of the ZnS films prepared at 25 ℃ for 10 h of reaction at $[C_4mim][PF_6]$-H_2O interface; and (d), SEM image of the ZnS films prepared at 60 ℃ for 5 h of reaction at $[C_4mim][PF_6]$-H_2O interface.

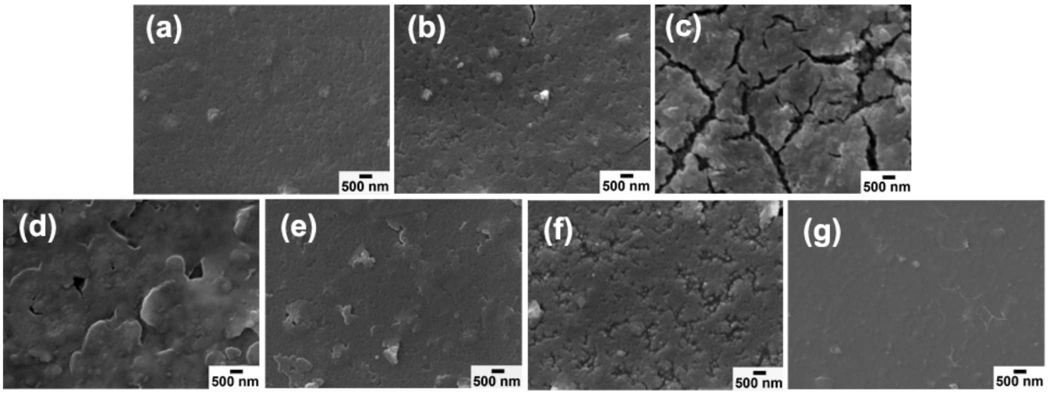

Fig. S5 SEM images of the back sides of the ZnS films prepared at 50 ℃ for 5 h of reaction at different IL-H_2O interfaces: (a), $[C_8mim][PF_6]$-H_2O; (b), $[C_8mim][Tf_2N]$-H_2O; (c), $[C_8mim][BF_4]$-H_2O; (d), $[C_2mim][Tf_2N]$-H_2O; (e), $[C_4mim][Tf_2N]$-H_2O; (f), $[C_{12}mim][Tf_2N]$-H_2O; and (g), $[C_4mim][PF_6]$-H_2O.

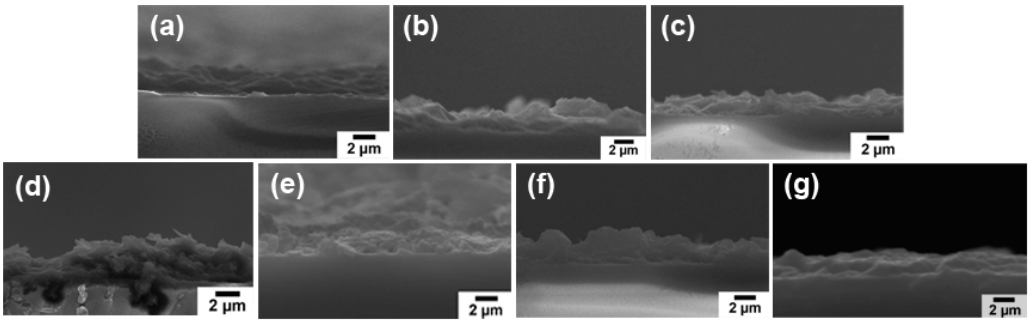

Fig. S6 The thickness estimation from SEM images of the ZnS films prepared at 50 ℃ for 5 h of reaction at different IL-H_2O interfaces: (a), $[C_8mim][PF_6]$-H_2O; (b), $[C_8mim][Tf_2N]$-H_2O; (c), $[C_8mim][BF_4]$-H_2O; (d), $[C_2mim][Tf_2N]$-H_2O; (e), $[C_4mim][Tf_2N]$-H_2O; (f), $[C_{12}mim][Tf_2N]$-H_2O; and (g), $[C_4mim][PF_6]$-H_2O.

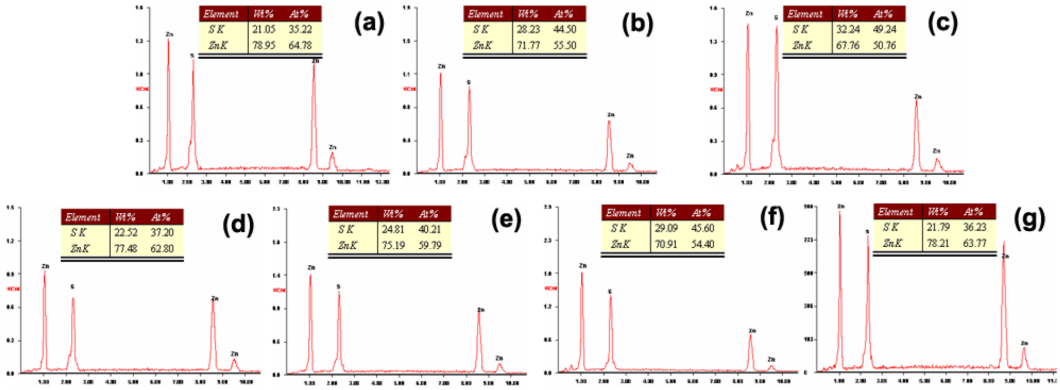

Fig. S7 EDX spectra of the ZnS films prepared at 50 ℃ for 5 h of reaction at different IL-H_2O interfaces: (a), [C_8mim][PF_6]-H_2O; (b), [C_8mim][Tf_2N]-H_2O; (c), [C_8mim][BF_4]-H_2O; (d), [C_2mim][Tf_2N]-H_2O; (e), [C_4mim][Tf_2N]-H_2O; (f), [C_{12}mim][Tf_2N]-H_2O; and (g), [C_4mim][PF_6]-H_2O.

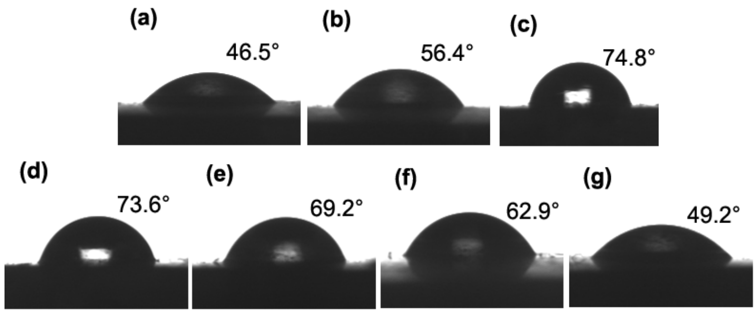

Fig. S8 The CA measurements of a water droplet on the back sides of the ZnS films prepared at 50 ℃ for 5 h of reaction at different IL-H_2O interfaces: (a), [C_8mim][PF_6]-H_2O; (b), [C_8mim][Tf_2N]-H_2O; (c), [C_8mim][BF_4]-H_2O; (d), [C_2mim][Tf_2N]-H_2O; (e), [C_4mim][Tf_2N]-H_2O; (f), [C_{12}mim][Tf_2N]-H_2O; and (g), [C_4mim][PF_6]-H_2O.

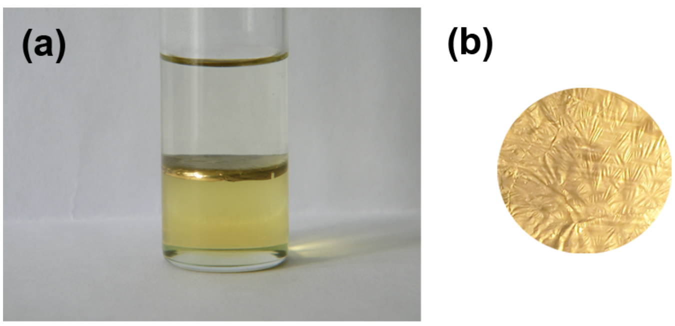

Fig. S9 Photos of gold films deposited at the interface of [C_8mim][Tf_2N]-H_2O (the pale yellow of subphase is the color of IL): (a), side view; and (b), top view.

Formation mechanism of the ZnS films prepared at [C_8mim][Tf_2N]-H_2O interface

It is known that in [C_8mim][Tf_2N]-H_2O interface regions, the non-polar and polar domains coexist. The non-polar domains are formed from the aggregation of the alkyl chains via the short-range van der Waals interaction, while the polar domains are formed from electrostatic interaction of anions, the charged imidazolium rings and small water clusters.[1,2] The polar domains have the form of continuous 3D networks of ionic channels, and the non-polar domains are restricted in these polar networks and are also continuous ones.[1] They take the shapes as wormlike or wirelike structures. In the course of interfacial reaction, the dragons were gradually formed in the template of 3D wirelike structures of the non-polar domains. Due to the close stacking of the non-polar domains of lower layers, the tightly packed wires were formed in these layers. In order to further reduce the interfacial energy, some wires welded together as arrowed in Fig. S2b. The formation of the looser dragons of the top layer originated from the more water clusters involved in the upper layer of the interface regions, which loosen the stacking of the non-polar domains and then caused the formation of dragons with loose arranges in the surface layer of ZnS films.[3]

The structures of ILs-H_2O interfaces are quite different from oil-water interface, they are relatively rougher and display fluctuated troughs and mounds in the interface regions.[4] Some nonpolar domains inserted into the polar mounds and formed more compact assembly.[5] Thus, in the template of the assembly of nonpolar domains in mounds, the flowerlike structures were gradually formed.

In addition, the liquid-liquid interfaces are under far-from-equilibrium conditions, which contribute to the formation of the dissipative structures. Kimizuka et al prepared gold nanowires with aperiodically arrayed holes by photoconversion of dissipative nanostructures emerged at the chloroform-aqueous interface, and they believed that the gold nanowires were formed only via non-equilibrium pre-organization of precursor ions at the interface.[6] In our case, a large amount of fluctuations in the interface regions resulted in the formation of dissipative structures, which then directed the formation of dragons as well as flowers. Yet, the periodical or oscillatory patterns of flowers and dragons are the salient features of dissipative structures.[6,7]

From the above analysis, it seems likely that the special ILs-H_2O interfaces lead to the formations of continuous non-polar domains, mounds and dissipative structures which together prompted the formation of ZnS films with beautiful dragons and flowers.

References

[1] J. N. A. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B*, 2006, **110**, 3330-3335.

[2] W. Jiang, Y. Wang, G. A. Voth, *J. Phys. Chem. B*, 2007, **111**, 4812-4818.

[3] S. Saha and H. Hamaguchi, *J. Phys. Chem. B*, 2006, **110**, 2777-2781.

[4] A. Chaumont, R. Schurhammer and G. Wipff, *J. Phys. Chem. B*, 2006, **109**, 18964-18973.

[5] N. Sieffert and G. Wipff, *J. Phys. Chem. B*, 2006, **110**, 13076-13085.

[6] T. Soejima, M. Morikawa and N. Kimizuka, *Small*, 2009, **18**, 2043-2047.

[7] G. M. Whitesides, *Science*, 2002, **295**, 2418-2421.