Preparation of polymer nano-photocatalysts by using triton X-100 to improve performance of photocatalytic hydrogen generation

Yanyu Zhang, Palas Baran Pati, Haining Tian*

Physical Chemistry, Department of Chemistry-Ångström Lab., Uppsala University, Sweden

*Corresponding author

Abstract

Organic semiconducting polymer nano-particles, as nano-photocatalysts for light driven proton reduction, have been prepared by using Triton X-100 as surfactant. The nano-photocatalysts prepared by Triton X-100 showed well dispersibility in water and no precipitation observed after photocatalysis. The effect of molecular weight and concentration on photocatalysis has been investigated, indicating that the particle size shows significant influence on photocatalytic performance. The sample with 100 µg/ml photocatalysts gave the best hydrogen evolution amount of 0.4 µmol/ml and apparent quantum yield of 1.3% at 450 nm. Copyright © 2018 VBRI Press.

Keywords: Solar Energy, photocatalysis, polymer, nanoparticles, hydrogen.

Introduction

Water splitting is a well-known way to produce hydrogen, which as an energy carrier has high energy density.[1] Using sun light to carry out the reaction can make the whole process more sustainable[2] and also it is a way to store solar energy. Water splitting involves two sub-reactions: water oxidation and proton reduction. Proton reduction is the stage to produce hydrogen. Developing and investigating photocatalysts for this reaction is therefore desirable. The traditional photocatalytic proton reduction are mainly based on metal oxides[3] or combination of photosensitizers and metal-complex catalysts[4-8]. Recently, using pure organic photocatalyts to perform light driven proton reduction has been attracting scientists' interests, since this kind of materials are more environmental-friendly and economic in comparison to other metal-based materials. The most representative one is the graphitic carbon nitride (g-C$_3$N$_4$), which was firstly reported by Antonietti and co-workers.[9-10] The bottleneck of g-C$_3$N$_4$ is that its band gap is too large to absorb long wavelength visible light. Organic semiconducting polymers can solve the issue by finely tuning the block units in their backbone to adjust Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) levels. On the basis of this concept, many organic polymers have been developed for light driven proton reduction[10], such as planarized polymers [11-12], poly(azomethine)s[13], covalent organic framework[14-16], phenyl-triazine oligomers[17], microporous organic nanorods[18], heptazine networks[19], polybenzothiadiazoles[20] and porous conjugated polymers[21-22]. However, these hydrophobic organic polymer photocatalysts suffer from the dispersibility in water, which actually hinder their photocatalytic performance. Most recently, our group adopted well water-dispersible polymer nanoparticles, also called polymer nano-dots (Pdots)[23-24], prepared by nanoscale precipitation method, for light driven proton reduction. This kind of method allows us to use an amphiphilic co-polymer polystyrene grafting with carboxyl groups functionalized ethylene oxide (PS-PEG-COOH) (see Figure 1) to twin/aggregate with hydrophilic organic polymers, resulting in hydrophilic nano-particles. Still, the method is not perfect. One of the main drawbacks of this method is that the formed particles from this method is not uniform. We have to filter the big particles before measurement; otherwise, the big particles will make all polymers precipitated out fast upon light illumination and eventually lead to unsatisfactory photocatalytic performance. The other one is that it is hard to increase the concentration of Pdots by this way; the serious precipitation of polymers along with increasing concentration was observed. Therefore, we need a new way, which can help us to increase the stability of polymer particles in water and also to prepare high concentrated polymer nano-photocatalysts for improvement of apparent quantum yield (AQY). Inspired from the reported work on preparation of polymer nanoparticles[25] and dispersion of photocatalysts[26-27] by using Triton X-100 surfactant, we therefore prepared the polymer nano-photocatalysts by using Triton X-100 and investigated the performance of prepared photocatalysts for light driven proton reduction.

Experimental

General

Poly [(9,9-dioctylfluorenyl-2,7-diyl) -co- (1,4-benzo {2,1′,3}-thiadiazole)] (PFBT/F8BT) with MW 250000 was purchased from Ossila, UK and the one with MW avg. 20 000 was purchased from Sigma-Aldrich. The co-polymer, PS-PEG-COOH, (polystyrene grafted with ethylene oxide and carboxyl groups) was purchased from Polymer Source Inc., Canada. Tetrahydrofuran (THF) and Triton X-100 (MW 80000) were obtained from Sigma-Aldrich and used as received.

Preparation of PFBT nano-photocatalysts

PFBT was dissolved into THF to make a concentration of 1.0 mg/mL. Then, a certain volume (**Table 1**) of PFBT THF solution is added into 40 mL 1.5% Triton X-100 aqueous solution, followed with sonication until a homogeneous solution formed. Subsequently, the THF is removed by continuously purging argon, with sonicating 9 minutes in every 30 minutes, and then a stable PFBT nanoparticle solution was prepared.

Table.1 The volume of PFBT/THF used for synthesizing different concentration of polymer nanodots solution.

Volume of 1 mg/mL PFBT THF solution (mL)	1	2	4	8
Concentration of photocatalyst solution (µg/mL)	25	50	100	200

Photocatalytic hydrogen generation test

4 mL of polymer nano-photocatalyst solution with 0.2 M ascorbic acid was adjusted to pH 4.0 (by 1 M NaOH solution). Then the solution is transferred to a cuvette sealed with a septum and irradiated by a LED PAR38 lamp (17 W, 5000K, Zenaro Lighting GmbH, $\lambda > 420$ nm). The light intensity of LED lamp was adjusted to be similar to the light intensity of visible light region in standard 1 sun. It is calibrated by solar cell. The produced hydrogen was detected by a Unisense micro hydrogen sensor, calibrated by known concentration of hydrogen dissolved in water and polarized at 1000 mV potential to keep the sensor stable.

Dynamic Light Scattering (DLS) measurement

DLS is measured by suing A Zetasizer Nano-S from Malvern Instruments Nordic AB to estimate the size of polymer nano particles.

Apparent quantum yield measurements

The condition of measuring and calculating apparent quantum yield is almost the same as hydrogen generation but under a determinate wavelength λ=450 nm. 300 watt Xe lamp (AULTT CEL-HXF300/CEL-HXUV300) was used as light source equipped a fly-eye lens, AM1.5G

filter, UV filter (> 400 nm) and a 450 nm band pass filter. The light intensity was measured by a Coherent LabMax_T0 sensor.

Apparent quantum yield can be calculated by the equation:

$$\emptyset = \frac{2 \times moles\ of\ hydrogen}{moles\ of\ incident\ photons} \qquad (eq.1)$$

The amount of incident photons n_p can be calculated by:

$$n_p = \frac{It\lambda}{hcN_A} \qquad (eq.2)$$

In eq.2, I represents the energy of our sample absorbed in a unit time; λ is the incident light wavelength; t is the irradiation time; h, c, and N_A are the physical constant – Plank constant, light speed and Avogadro constant, respectively.

Results and discussion

In this work, we still use Poly[(9,9′-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1′,3} thiadiazole)] (named as PFBT or F8BT) as the semiconducting polymer to prepare the nano-photocatalysts. Figure 1 shows the molecular structures of PFBT, PS-PEG-COOH and Triton X-100.
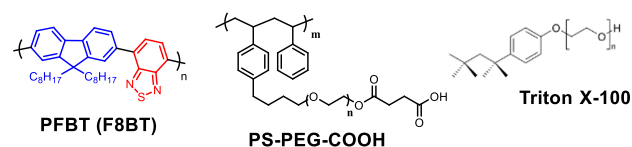

Fig. 1. Molecular Structures of the compounds F8BT, PS-PEG-COOH and Triton X-100 used in this study.

Fig. 2 shows the nano-scale precipitation methods based on PS-PEG-COOH and Triton X-100. The previous method (Figure 2a) is to dissolve PFBT and amphiphilic co-polymer PS-PEG-COOH in THF and then pour the solution into pure water. After removing the THF with Ar degassing, the Pdot is subsequently formed. For the present method **(Fig. 2a)** used in this work is to add the PFBT THF solution into 1.5% (w/w) Triton X-100 aqueous solution and then followed by removing THF with Ar degassing. Triton X-100 plays the similar role as of co-polymer PS-PEG-COOH does in the old method, twinning with PFBT to form nano-particles with hydrophilic surface. Moreover, Triton X-100 is a surfactant, which can further stabilize the dispersion of polymer nano-particles in the water.

With the help from Triton X-100, we were able to prepare well dispersed PFBT nano-particles in aqueous phase (see solution picture in **Fig. 2b**). The particle size is more than 100 nm. We therefore name the prepared nano-particles from Triton X-100 as nano-photocatalytst instead of Pdots photocatalysts that we prepared from the co-polymer method **(Fig. 2a)**. Also during the

preparation, we did not see the precipitation of PFBT polymer; it suggests that all PFBT polymers are converted into PFBT nano-particles. This result encourages us to carry out two following studies: the effect of molecular weight of PFBT on photocatalysis and increasing concentration of nano-photocatalysts to improve the AQY.
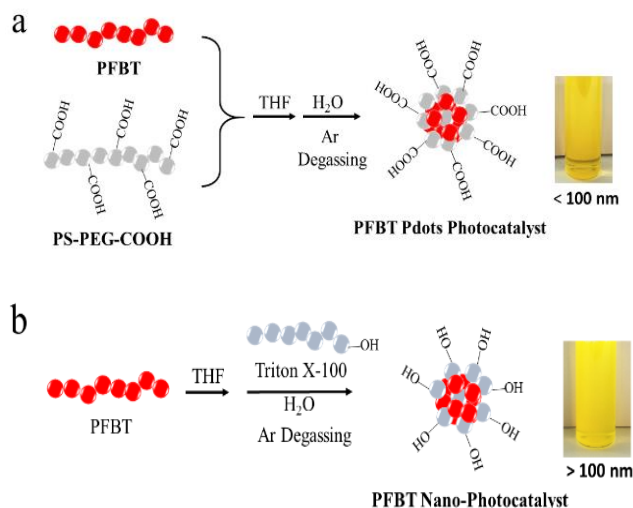

Fig. 2. The schematic drawings of preparation of PFBT Pdots photocatalysts (a) and nano-photocatalyst (b).

We chose two PFBT polymers with different molecular weight (MW), avg. 250 000 g/mol (l-PFBT) and avg. 20 000 g/mol (s-PFBT). l-PFBT is the one that used in our previous studies on Pdots photocatalysts[23-24]. Interestingly, we were not able to prepare Pdots photocatalysts from s-PFBT by using the co-polymer method, we only got big particles of polymer precipitated. However, when we used the Triton X-100 method, it is possible to prepare the nano-photocatalysts from both l-PFBT and s-PFBT. The particle size is around 300-400nm. Although particle size of nano-photocatalysts based on l-PFBT (l-NPcat) is much bigger than that of Pdots photocatalysts prepared from l-PFBT, implying that the nano-photocatalysts have smaller surface area than Pdots photocatalysts; they both showed similar performance. It is probably because there are many Triton X-100 molecules in nano-photocatalysts, which may create more proton tunnels inside of the big particles and help with the photocatalysis.

Surprisingly, the nano-photocatalysts prepared from s-PBFT (s-NPcat) showed enhanced photocatalytic performance for light driven proton reduction than l-NPcat **(Fig. 3a)** s-NPcat rendered a hydrogen amount of 13 mmol/g (mmol hydrogen per gram catalyst). However, l-NPcat gave a much lower value of 4 mmol/g. From DLS test **(Fig. 3b),** one can see s-NPcat has smaller particle size than l-NPcat, which should have the larger surface area under the same preparation condition. Also, another reason is that the s-NPcat particle could contain more individual PFBT polymers than the l-NPcat, which increase the probability of interaction between two

individual polymers during the photocatalytic performance. As we studied in the previous work[24], the photocatalytic reaction between two individual polymers can lower the energy barrier of proton reduction reaction, which is one of the main reasons why the Pdots system works efficiently as photocatalysts. Apparently, more polymers in an s-NPcat particle with smaller size and enough proton tunnels should be responsible for the enhancement.
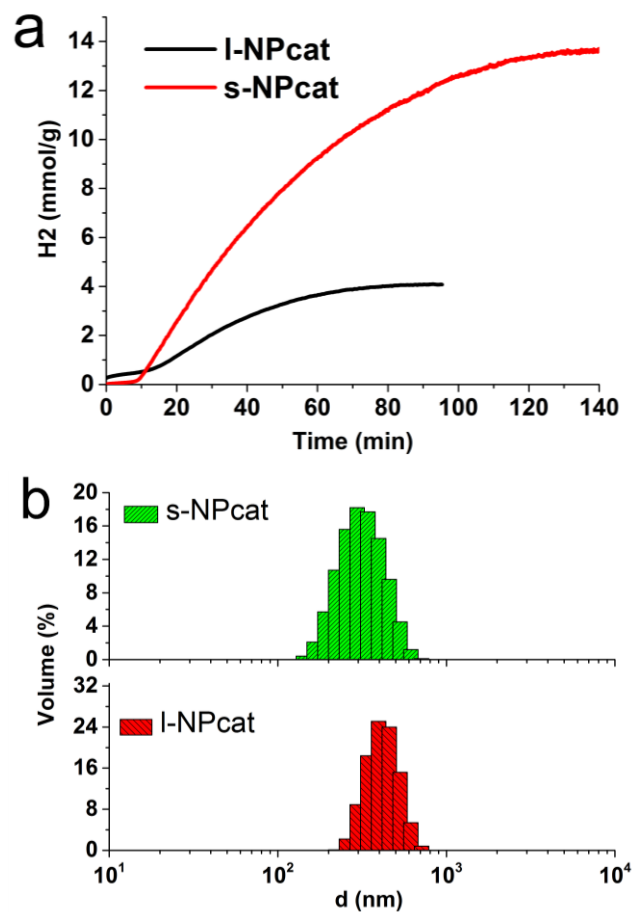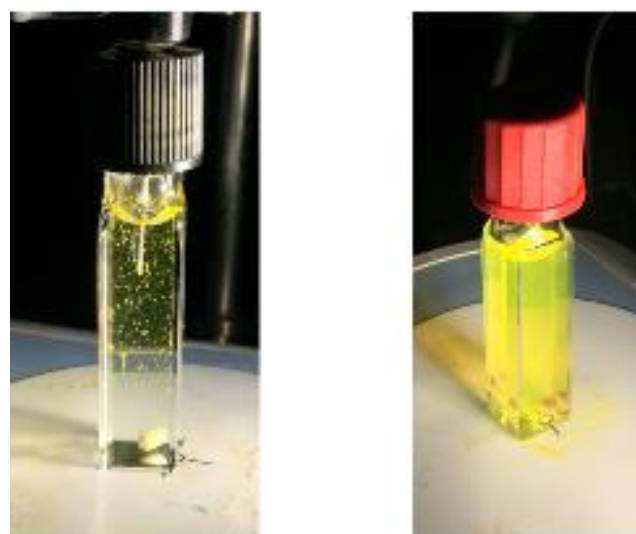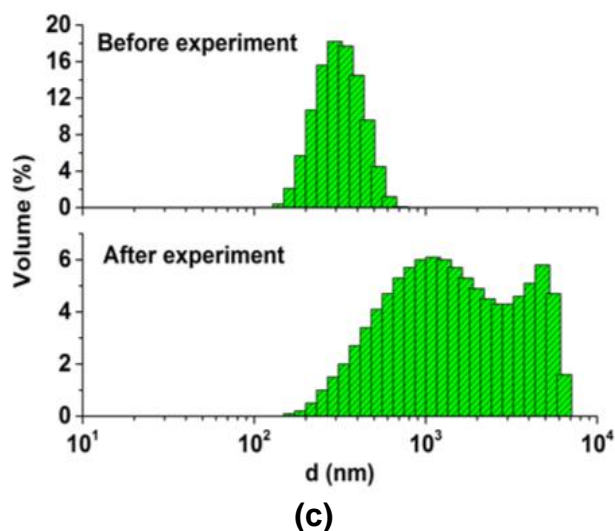

Fig. 3. The photocatalytic performance (a) and DLS data (b) of l-NPcat and s-NPcat. Concentration: 25 µg/mL.

From our previous study[23], the photocatalytic process of PFBT Pdots photocatalysts became slowly after 1.5 h light illumination until deactivated because serious precipitation was caused by aggregation of nano-particles **(see Fig. 4a)**. As expected, we did not see any precipitation formed from s-NPcat owing to the contribution of Triton X-100 surfactant **(Fig. 4b)**. However, the photocatalytic performance still became slack in 2 h **(Fig. 3a)**. To figure out the reason, we measured DLS before and after the photocatalysis and found that the particle size became much bigger after photocatalytic reaction, from initial 300-400 nm to eventual 1-5 µm. The aggregation shrinks the surface area of nano-particles and may also change the proton tunnels inside of the particles, which could be responsible for the deactivation of photocatalytic reaction.

Fig. 5. The pictures of difference concentrated s-NPcat samples (a, from left to right: 25, 50, 100 and 200 µg/mL), DLS data of different samples (b) and photocatalytic performance of different samples with Y axis of hydrogen amount per volume (c) and per gram catalysts (d).

Fig. 4. The pictures of Pdots (a) and s-NPcat (b) after 1.5 h light illumination and the DLS data of s-NPcat before and after photocatalysis (c).

With these results on hands, we moved one step forward to study the effect of the concentration of s-NPcat on photocatalytic performance and AQY. By simply increasing the amount of s-PDBT, it is straightforward to get different concentrations of s-NPcat samples, 25, 50, 100 and 200 µg/mL **(Fig. 5a).** But the particle sizes become also bigger along with increasing the concentration. From the photocatalytic performance, we can see the 100 and 200 µg/mL s-NPcat samples gave high hydrogen generation value, ca. 0.4 µmol/mL (µmol hydrogen per mL solution), which is attributed to the high concentration. However, if the hydrogen generation unit is normalized by photocatalyst weight to µmol/g, one can see the 25 µg/mL s-NPcat sample gave the best value among all samples, 13 mmol/g. Therefore, the particle size is really an important parameter of polymer nano-photocatalysts to obtain good performance.
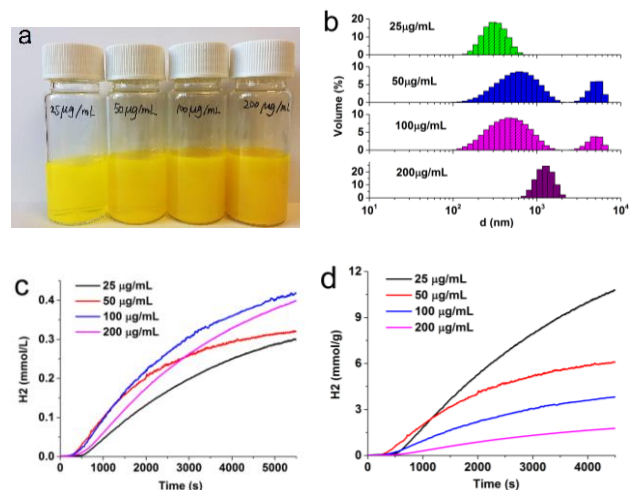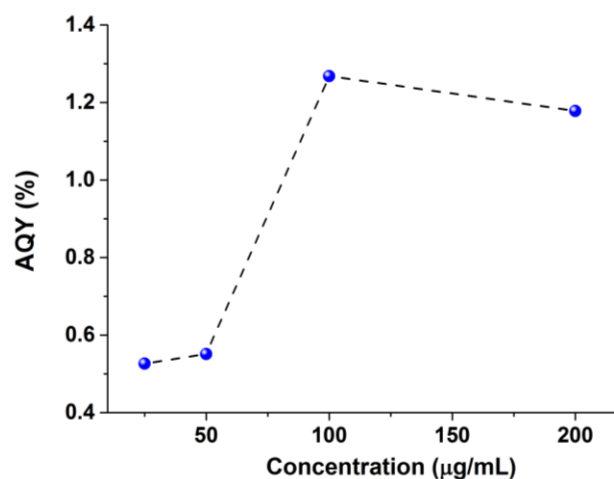

Fig. 6. AQY data of different samples tested at 450 nm.

From AQY test, we can see the concentrated samples give high AQY value, but the increment of AQY is not linear with the increment of concentration of photocatalysts. The best AQY value was obtained by the sample with 100 µg/mL is 1.3% at 450 nm.

Conclusion

In summary, we use Triton X-100 instead of co-polymer PS-PEG-COOH to prepare PFBT nano-photocatalysts. The Triton X-100 method can also prepare nano-photocatalysts from the PFBT samples with small molecular weight, which cannot be prepared by co-polymer method. The prepared PFBT nano-photocatalysts are more stable than the Pdots photocatalysts owing to the surfactant property of Triton X-100. However, the aggregation is still existed during the photocatalysis, which is the main reason of deactivation of photocatalyst. With Triton X-100 method, it is also facile to prepare high concentrated photocatalysts solution, which is

effective way to increase the apparent quantum yield of photocatalysis. How to maintain small particle size during photocatalysis as well as along with increasing concentration are the questions left behind this work and also the on-going projects in our group.

Author's contributions

Conceived the plan: H.T.; Performed the expeirments: Y. Z., P. B. P; Data analysis: H.T., Y. Z., P. B. P; Wrote the paper: H.T., Y. Z.. Authors have no competing financial interests.

References

1. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; *Chem. Rev.* **2010,** *110* (11), 6446-6473.
2. Fujishima, A.; Honda, K., *Nature* **1972,** *238* (5358), 37-38.
3. Abe , R.; Higashi, M.; Domen, K., *ChemSusChem* **2011,** *4* (2), 228-237.
4. Li, X.; Wang, M.; Zhang, S.; Pan, J.; Na, Y.; Liu, J.; Åkermark, B.; Sun, L., *J. Phys. Chem. B* **2008,** *112* (27), 8198-8202.
5. Andreiadis, E. S.; Chavarot-Kerlidou, M.; Fontecave, M.; Artero, V., *Photochem. Photobiol.* **2011,** *87* (5), 946-964.
6. Wang, J.-J.; Li, Z.-J.; Li, X.-B.; Fan, X.-B.; Meng, Q.-Y.; Yu, S.; Li, C.-B.; Li, J.-X.; Tung, C.-H.; Wu, L.-Z., *ChemSusChem* **2014**, n/a-n/a.
7. Ozawa, H.; Haga, M.-a.; Sakai, K., *J. Am. Chem. Soc.* **2006,** *128* (15), 4926-4927.
8. White, T. A.; Higgins, S. L. H.; Arachchige, S. M.; Brewer, K. J., *Angew. Chem. Int. Ed.* **2011,** *50* (51), 12209-12213.
9. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M., *Nat Mater* **2009,** *8* (1), 76-80.
10. Zhang, G.; Lan, Z.-A.; Wang, X., *Angew. Chem. Int. Ed.* **2016,** *55* (51), 15712-15727.
11. Yanagida, S.; Kabumoto, A.; Mizumoto, K.; Pac, C.; Yoshino, K., *J. Chem. Soc., Chem. Commun.* **1985,** (8), 474-475.
12. Sprick, R. S.; Bonillo, B.; Clowes, R.; Guiglion, P.; Brownbill, N. J.; Slater, B. J.; Blanc, F.; Zwijnenburg, M. A.; Adams, D. J.; Cooper, A. I., *Angew. Chem. Int. Ed.* **2016,** *55* (5), 1792-1796.
13. Schwab, M. G.; Hamburger, M.; Feng, X.; Shu, J.; Spiess, H. W.; Wang, X.; Antonietti, M.; Mullen, K., *Chem. Commun.* **2010,** *46* (47), 8932-8934.
14. Bi, J.; Fang, W.; Li, L.; Wang, J.; Liang, S.; He, Y.; Liu, M.; Wu, L., *Macromol. Rapid Commun.* **2015,** *36* (20), 1799-1805.
15. Stegbauer, L.; Schwinghammer, K.; Lotsch, B. V., *Chemical Science* **2014,** *5* (7), 2789-2793.
16. Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V., *Nat. Commun.* **2015,** *6*.
17. Schwinghammer, K.; Hug, S.; Mesch, M. B.; Senker, J.; Lotsch, B. V., *Energy Environ. Sci.* **2015,** *8* (11), 3345-3353.
18. Park, J. H.; Ko, K. C.; Park, N.; Shin, H.-W.; Kim, E.; Kang, N.; Hong Ko, J.; Lee, S. M.; Kim, H. J.; Ahn, T. K.; Lee, J. Y.; Son, S. U., *J. Mater. Chem. A* **2014,** *2* (21), 7656-7661.
19. Kailasam, K.; Schmidt, J.; Bildirir, H.; Zhang, G.; Blechert, S.; Wang, X.; Thomas, A., *Macromol. Rapid Commun.* **2013,** *34* (12), 1008-1013.
20. Yang, C.; Ma, B. C.; Zhang, L.; Lin, S.; Ghasimi, S.; Landfester, K.; Zhang, K. A. I.; Wang, X., *Angew. Chem., Int. Ed.* **2016,** *55(32)*, 9202-9209.
21. Li, L.; Cai, Z.; Wu, Q.; Lo, W.-Y.; Zhang, N.; Chen, L. X.; Yu, L., *J. Am. Chem. Soc.* **2016,** *138* (24), 7681-7686.
22. Sprick, R. S.; Jiang, J.-X.; Bonillo, B.; Ren, S.; Ratvijitvech, T.; Guiglion, P.; Zwijnenburg, M. A.; Adams, D. J.; Cooper, A. I., *J. Am. Chem. Soc.* **2015,** *137* (9), 3265-3270.
23. Wang, L.; Fernández-Terán, R.; Zhang, L.; Fernandes, D. L. A.; Tian, L.; Chen, H.; Tian, H., *Angew. Chem. Int. Ed.* **2016,** *55* (40), 12306-12310.
24. Pati, P. B.; Damas, G.; Tian, L.; Fernandes, D. L. A.; Zhang, L.; Pehlivan, I. B.; Edvinsson, T.; Araujo, C. M.; Tian, H., *Energy Environ. Sci.* **2017,** *10* (6), 1372-1376.
25. Dai, R.; Wu, F.; Xu, H.; Chi, Y., *ACS Applied Materials & Interfaces* **2015,** *7* (28), 15160-15167.
26. Wang, X.; Liu, G.; Chen, Z.-G.; Li, F.; Lu, G. Q.; Cheng, H. M., *Electrochem. Commun.* **2009,** *11* (6), 1174-1178.
27. Wang, W.; Chen, J.; Li, C.; Tian, W., *Nat. Commun.* **2014,** *5*, 4647.