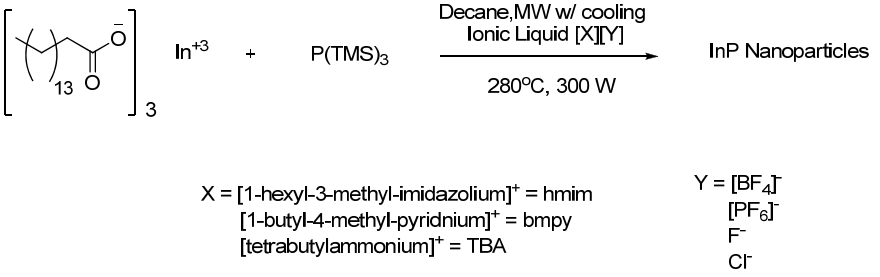
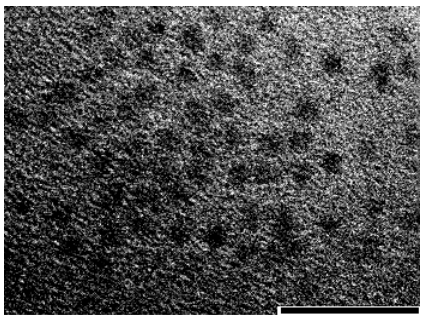
Microwave Induced In-Situ Active Ion Etching of Growing InP Nanocrystals

Quantum dots are interesting nanomaterials that are ideal for optical applications such as high resolution cellular imaging and photovoltaic devices – mainly because of their high quantum yields.[1] CdSe and ZnS are typical semiconductors that have found a wide range of uses, but recent interest has focused on developing InP quantum dots due to their reduced toxicity. This lower toxicity is advantageous in the large scale synthesis of nanocrystals. A major drawback to using InP is the poor photoluminescence quantum yield (PL QY). The poor PL QY has been assigned to the phosphorus vacancies. These vacancies, however, can be removed by active ion etching with HF. This etching increases the PL QY from 4 to > 40%. Although HF etching works to increase PL QY, it is toxic, inconvenient, and leads to decreased yields. Professor Strouse and Derek Lovingood from Florida State University developed an in situ etchant using microwave irradiation that eliminated the hassle of using HF.[2] Their protocol, shown in Scheme 1, used ionic liquids (IL) to generate F^- in situ with microwave heating. Indium hexadecanoate, tris-trimethylsilylphosphine, $P(TMS)_3$, and the desired IL were heated using microwave irradiation at 300W with PowerMAX™ (simultaneous cooling) at 280°C for 15 min.[3] The IL served as an F^- source and as an extremely strong microwave absorber which lead to shorter ramp times.[4]

Scheme 1. Synthesis of InP Nanocrystals





TEM of InP with [hmim][BF_4][5]

Figure 1. Discover® S-Class dedicated microwave instrument

The synthesis of InP with additives [X][Y] are summarized in Table 1. As expected, the larger ratio of IL:In lead to a faster ramp time due to the highly microwave absorbing IL. The ratio that favored the highest PL QY was a 1:10 ratio of In:IL. The best F^- source was $[BF_4]^-$ which lead to the highest PL QY with hmim and bmpy. $[PF_6]^-$ with hmim lead to the next highest PL QY with 24.5. The remaining [X][Y] combinations yielded poorer results. The InP nanocrystal size was 2.7 ± 0.3 nm, as determined by TEM.

The use of microwave irradiation to etch InP nanocrystals resulted in a more efficient, less toxic means to increase the PL QY by using ionic liquids as a F^- source. $[BF_4]^-$[hmim] was the ideal IL which yielded InP etched nanoparticles with a PL QY of 47.1 with a total reaction time of 16 minutes. The authors accomplished this without the use of HF, rendering the procedure safer and more efficient.

Table 1. Ionic Liquids used in InP Synthesis

Anion [Y]	Additive [X]	In:IL ratio	PL QY	Ramp Time (s)
$[BF_4]^-$	hmim	1:10	47.1	70
$[BF_4]^-$	bmpy	1:10	43.2	220
$[BF_4]^-$	TBA	1:10	11.2	170
$[PF_6]^-$	hmim	1:10	24.5	150
$[PF_6]^-$	bmpy	1:01	1.8	302
$[PF_6]^-$	TBA	1:01	1	432
F^-	TBA	1:0.1	1	720
Cl^-	hmim	1:0.1	2.3	670
Cl^-	bmpy	1:0.1	1.5	1332

References

1) Alivisatos, A. P.; Gu, W.; Larabell, C. *Ann. Rev. Biomed. Eng*. **2005**, *7*, 55 – 76.; Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater*. **2005**, *4*, 435 – 46.
2) Lovingood, D. D.; Strouse. F. G. *Nano Lett*. **2008**, *8*, 3394 – 3397. **DOI**: 10.1021/nl802075j
3) The total time at 280 °C is 15 minutes, this does not include ramp time.
4) Leadbeater, N. E.; Torenius, H. M. J*. Org. Chem*. **2002**, *67*, 3145 – 3148
5) Reprinted with permission from Lovingood, D. D.; Strouse. F. G. *Nano Lett*. **2008**, *8*, 3394 – 3397