Synthesis of InP/ZnS Nanocrystals Under Mild Conditions

Edwin A. Baquero, Wilfried-Solo Ojo, Angelique Gillet, Bruno Chaudret, Fabien Delpech,* and Céline Nayral*

Université de Toulouse; INSA, UPS, CNRS; LPCNO (Laboratoire de Physique et Chimie des Nano-Objets), 135 avenue de Rangueil, F-31077 Toulouse, France ebaquero@insa-toulouse.fr

Abstract

The synthesis of InP Quantum Dots (QDs) under mild conditions remains a challenge in nanochemistry. Recently, we have demonstrated that the use of classical high-temperature procedure, following the protocol reported by Peng and co-workers (Scheme 1a),^[1] promotes decarboxylation processes of the stabilizers (fatty carboxylic acids) as side reactions. Concomitant formation of water oxidized the surface of the particles and therefore, inhibited their growth.^[2,3]

The original strategy presented here consists in the use of a highly reactive indium precursor such as $In(amidinate)_3$ complex, which in the presence of $P(SiMe_3)_3$ as phosphorous source and both hexadecylamine (HDA) and palmitic acid (PA) as stabilizers, leads to the formation of InP nanocrystals at lower temperatures (Scheme 1b), followed by a shelling process with ZnS insuring the air stability of the QDs(Scheme 1c). This unprecedented methodology at low temperature avoided the undesired reactions above mentioned, leading to the formation of non oxidized InP QDs. We observed the presence of oxides at the surface after the ZnS coating process, and our findings showed that it is mainly due to an amidation process, which is taking place with formation of water. Thus, different oxidative conditions due to side-reactions have been identified and the possibilities to avoid the QDs surface oxidation by using low temperatures or a reductive atmosphere will be exposed. The QDs were fully characterized by TEM, and spectroscopic techniques such as UV-Vis, Photoluminescence Spectroscopy, and solution and solid state ¹H, ¹³C, ³¹P NMR techniques.



Scheme 1. Synthesis of 1a) InP QDs developed by Peng and co-workers.^[1] 1b) InP QDs described in this work and 1c) Coating process of InP QDs with ZnS.

References

[1] D. Battaglia, X. Peng, Nano Letters, 2 (2002) 1027.

[2] A. Cros-Gagneux, F. Delpech, C. Nayral, A. Cornejo, Y. Coppel, B. Chaudret, J. Am. Chem. Soc., **132** (2010) 18147.

[3] H. Virieux, M. L. Troedec, A. Cros-Gagneux, W. Solo-Ojo, F. Delpech, C. Nayral, H. Martinez, B. Chaudret, J. Am. Chem. Soc., **134** (2012) 19701.