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Characterization of Colloidal Quantum Dot Ligand Exchange by X-ray Photoelectron Spectroscopy

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Colloidal quantum dots (CQDs) are chemically synthesized semiconductor nanoparticles with size-dependent wavelength tunability. Chemical synthesis of CQDs involves the attachment of long organic surface ligands to prevent aggregation; however, these ligands also impede charge transport. Therefore, it is beneficial to exchange longer surface ligands for shorter ones for optoelectronic devices. Typical characterization techniques used to analyze surface ligand exchange include Fourier-transform infrared spectroscopy, x-ray diffraction, transmission electron microscopy, and nuclear magnetic resonance spectroscopy, yet these techniques do not provide a simultaneously direct, quantitative, and sensitive method for evaluating surface ligands on CQDs. In contrast, x-ray photoelectron spectroscopy (XPS) can provide nanoscale sensitivity for quantitative analysis of CQD surface ligand exchange. A unique aspect of this work is that a fingerprint is identified for shorter surface ligands by resolving the regional XPS spectrum corresponding to different types of carbon bonds. In addition, a deposition technique known as resonant infrared matrix-assisted pulsed laser evaporation is used to improve the CQD film uniformity such that stronger XPS signals are obtained, enabling more accurate analysis of the ligand exchange process.

Key words: Colloidal quantum dots, surface ligands, ligand exchange, RIR-MAPLE, XPS

INTRODUCTION

Colloidal quantum dots (CQDs) are chemically synthesized semiconductor nanoparticles with special optical properties favorable for use in various devices including organic photovoltaics (OPVs) and photodetectors.[1–3] A useful optical property is the size-dependent wavelength tunability from the visible to the near-infrared regions. Chemical synthesis of CQDs involves attachment of organic surface ligands to stabilize the CQDs and prevent aggregation and precipitation[4]; however, these ligands also impede charge transport in optoelectronic devices. Therefore, it is beneficial to remove the ligands after CQD deposition or to exchange longer surface ligands required for synthesis for shorter ones. There have been many strategies developed to remove insulating ligands, such as chemical washing, gentle annealing, and even vacuum stripping.[5–8] Most commonly, butylamine and pyridine have been used as weak (shorter) ligands to replace strong (longer) ligands such as oleic acid (OA), trioctylphosphine oxide (TOPO) or octyldecylamine (ODA). By following a series of successive precipitation steps, ligand exchange can be performed on CQD surfaces in a relatively easy and direct manner.[9]

Typical characterization techniques used to analyze surface ligand exchange include Fourier-transform infrared (FTIR) spectroscopy to provide qualitative information on the organic ligands present,[10] x-ray diffraction (XRD) to monitor the crystalline properties of CQDs before and after ligand exchange,[11] and transmission electron microscopy (TEM) to provide

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