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Full Length Article

Surface defect modification of ZnO quantum dots based on rare earth acetylacetonate and their impacts on optical performance

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ABSTRACT

The surface defect modification has an important effect on the application of ZnO quantum dots, and it has gained much progress in recently years, propelled by the development of additives. Our research efforts are directed toward developing a new surface modification additive $RE(AcAc)_3$ (RE = Ce, Dy, Tb) to achieve fine ZnO QDs and adjust their surface properties. $RE(AcAc)_3$/ZnO QDs nanostructured materials have been designed and prepared, and particular emphasis has been given to the relation between the surface modification and optical properties. The effects of RE(III) acetylacetonate modification on the FT-IR, TEM images and photoluminescence (PL) spectra were investigated, and the surface defect modification principle and effect were discussed in details. The band gap (E_g) was also calculated to prove the surface modification effect. For the $RE(AcAc)_3$/ZnO QDs complex materials, stable linkage occurs because of the affinity of —COOH from acetylacetonate anionic ligand to zinc oxide surfaces, with attachment to the zinc oxide by hydrogen bonding between the protons of the hydroxyl groups on the surface of ZnO QDs and the π–system of acetylacetone.

1. Introduction

Inorganic nano crystal quantum dot materials have attracted great attention for their heat, light, electricity and magnetism properties caused by quantum confinement effect and have been widely used in the fields of energy, optoelectronic devices, optoelectronics, chemical and other fields [1–4]. The zinc oxide is a typical II–VI semiconductor material, which has the characteristics of high electron affinity, high mobility and large exciton binding energy, and its low cost and simple process [5,6]. As such, it is a widely utilized, versatile material implemented in a diverse range of technological applications, particularly in electronics, optoelectronics [7,8], sensors [9], photocatalysts [10,11], electrodes for solar cells [12] and so on.

Rare earth complexes have been widely used for novel lighting device [13,14]. It is well known that optimizing energy transfer processes from ligands to emitting ions was the most important to obtain the maximum emission from 4*f*-4*f* transitions, for which the choice of ligand is essential [15]. Therefore, an effective kind of β-diketonate [16], such as acetylacetone, was selected as a ligand. In this case, rare earth acetylacetonate could be used as an optical material. However, the point attracting our attention is that the rare earth acetylacetonate can combine with the groups on the surface of ZnO QDs, and it has more complex structure than many linear organic compounds.

The high specific surface area and surface aggregation energy of the ZnO quantum dots greatly limited the excellent properties of quantum dots. It has been shown that in the absence of surface modifiers there is a certain tendency of nano particles to agglomerate due to the well known Ostwald ripening [17]. The necessity of utilizing organic surfactants has become crucial in order to reduce the phenomenon. One strategy to solve this problem is surface modification through organic functionalization to achieve fine particles and adjust their surface properties. Current research efforts are directed toward realizing surface modification of ZnO QDs with organic compounds such as polysiloxane [18], mercaptoacetic acid [19], silane [20], cetyltrimethyl ammonium bromide (CTAB) [21], vinyltrimethoxysilane [22], oleic acid [23,24], polyethylene glycol [25,26] and so on.

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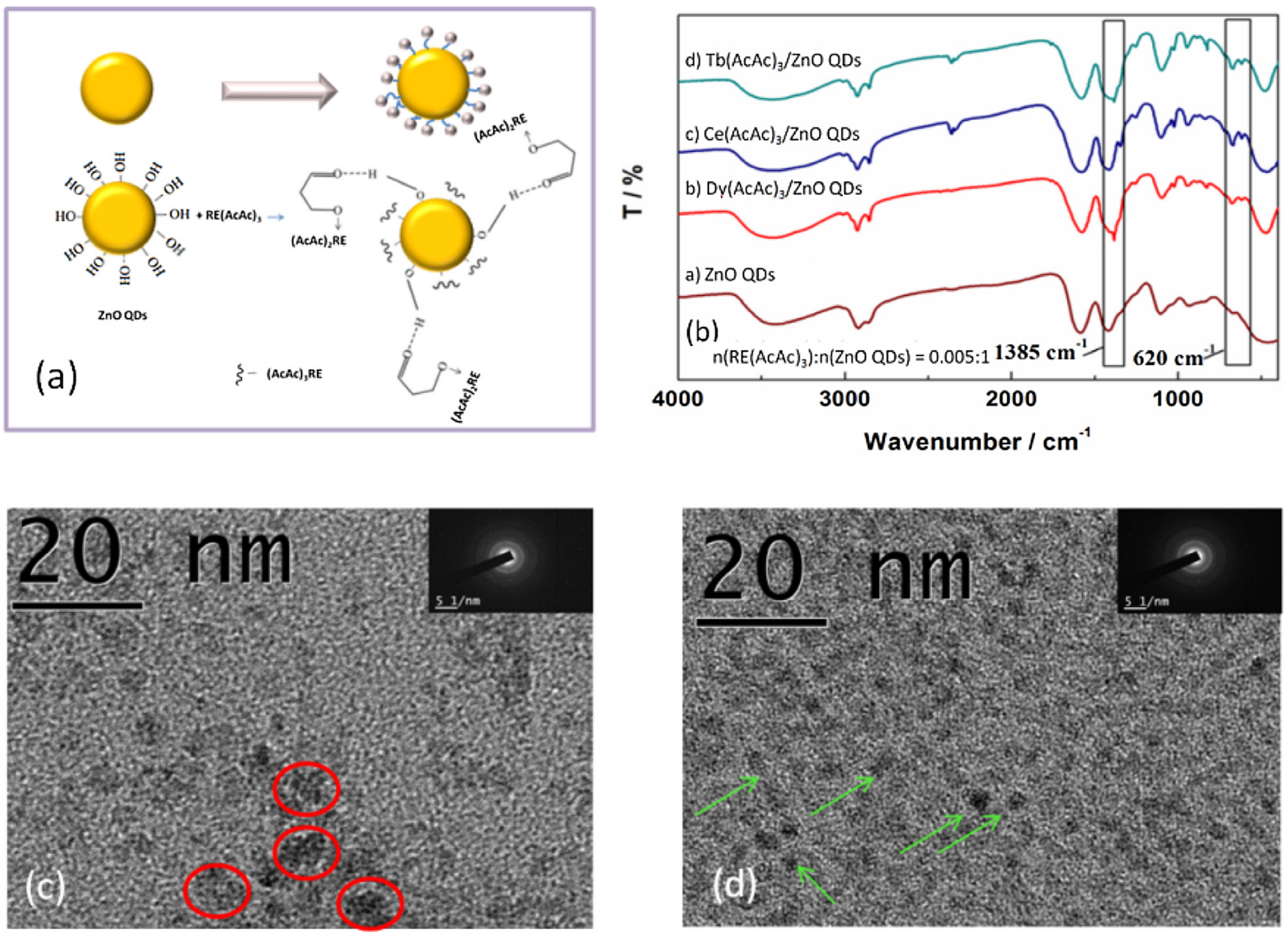

Fig. 1. (a) Schematic illustration for fabrication of RE(AcAc)$_3$/ZnO QDs; (b)FT-IR spectra of ZnO QDs and RE(AcAc)$_3$ (RE = Ce, Dy and Tb) modified ZnO QDs; (c) (d) The HRTEM images of ZnO QDs and Ce(AcAc)$_3$/ZnO QDs (Ce(AcAc)$_3$:ZnO QDs = 0.005).

In this work, we developed a simple synthetic procedure to attach RE(III) acetylacetonate to zinc oxide QDs for obtaining fine QDs and adjusting their surface properties. Linkage occurs because of the affinity of —COOH from acetylacetonate anionic ligand to zinc oxide surfaces, with attachment to the zinc oxide by hydrogen bonding between the protons of the hydroxyl groups on the surface of ZnO QDs and the π–system of acetyl acetone. Using this method, the surface density of RE(III) acetylacetonate might be controlled by varying the molar ratios of the reactants. The effects of RE(III) acetylacetonate modification on the FT-IR, TEM images and photoluminescence (PL) spectra were investigated, and the optical band energy was calculated. The surface defect modification principle and effect were also discussed.

2. Material and methods

2.1. Materials preparation

2.1.1. ZnO QDs

The ZnO QDs were synthesized by the ultrasonic sol-gel method [27]. 2.2 g (0.01 mol) $Zn(CH_3COO)_2\,2H_2O$ ($Zn(Ac)_2$) was dissolved in 100 mL ethanol with stirring for 30 min, and 0.84 g (0.02 mol) LiOH was dissolved in 50 mL ethanol with stirring for 30 min. Then an appropriate amount of PEG-400 with n(PEG):n(Zn) = 1:1 was added into the $Zn(Ac)_2$ solution with additional stirring for 40 min. The LiOH solution was added into the mixed solution at last, and the ZnO QDs were obtained after continuously stirring at 60 °C for 2 h.

The ZnO QDs were precipitated with oleic acid, and the sediment was centrifuged (4000 rpm, 5 min) and washed with ethanol for two or three times.

2.1.2. Re(AcAc)$_3$/ZnO QDs composite material

The preparation of organically soluble RE(AcAc)$_3$/ZnO QDs were based on the modification of our previously reported method for the synthesis of Ho(AcAc)$_3$/ZnO quantum dots with slight modifications [28]. The rare earth acetylacetonate (RE(AcAc)$_3$, RE = Ce, Dy, and Tb) was dissolved in ethanol. Appropriate amount of RE(AcAc)$_3$ solution was mixed with ZnO QDs with the ratio of n(RE(AcAc)$_3$):n(ZnO QDs) = 0.0025:1, 0.005:1, 0.01:1, 0.02:1, 0.03:1 and 0.04:1. The solution was reacted under ultrasonic radiation at 10 °C for 5 min. At last, the RE(AcAc)$_3$/ZnO QDs composite solution was obtained. The RE(AcAc)$_3$/ZnO QDs thin films were prepared by dispersing the obtained modified nanoparticles by sonication in isopropanol and depositing on glass substrate by spin coating (2000 rpm, 20 s).

2.2. Measurement

The FT-IR spectra were characterized in the 4000–400 cm^{-1} range using an FT-IR spectrometer (NEXUS 670, Thermo, America). The TEM images were observed by transmission electron microscopy (JEM-2100, JOEL, Japan). The photoluminescence spectra were measured by a fluorescent spectrophotometer (Lumina, Thermo, America). The optical band gap energy (Eg) was estimated from the fundamental absorption edge of the RE(AcAc)$_3$/ZnO QDs