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Perovskite quantum dot and methods to increase its stability

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Abstract. Perovskite is new major topic in the nanosemiconductor material area, as the excellent property for the perovskite quantum dot which is useful in the optoelectronic devices. These perovskite quantum dots can be widely used in Light-Emitting Diode (LEDs), lasers, and solar cells. However, the perovskite quantum dot is instability which limit the widespread use in daily life and factory, environment factors such as Ultraviolet (UV) light, oxygen, water moisture and hot temperature can all affect the stability of the perovskite quantum dot due to the internal structure and property is unstable. In order to make perovskite quantum dots widely used in daily-life optoelectronic devices, it is important to find the method to increase the stability such as ion doping, surface coating and ligand attach, those method can balance the defect on the structure and surface which is the major goal of this article. To conclude all of this, stability enhancement requires control of lattice defects, surface chemistry and environmental protection.

Keywords: perovskite, quantum dot, stability

1. Introduction

Perovskite quantum dot as one of nanosemicondor material with the chemical form as ABX_3, which A and B refer the monovalent charge and divalent cation, here X is halogen ion, by the chemical form, the perovskite quantum can be separate into two type, all-inorganic type and organic-inorganic type [1]. The classification depends on the containment element or ion is organic or inorganic inside the ABX_3 form.

Perovskite quantum dot is a kind of important material in optoelectronic devices area due to its excellent property is suitable relate to optoelectronic devices. There are several major properties that make perovskite quantum dot excellent for use, which include high luminescence quantum yields, controllable emission photon wavelength, narrow line-width luminescence emission and so on [1, 2]. Those property is suitable for the optoelectronic devices and can use for LED, laser and solar cell.

However, its low stability limits its use. The low stability can be separated into two parts: internal factors, which include ligand detachment, lattace and surface defects, ion migration and so on and external factors, which include moisture, oxygen, UV light and high temperature. Actually, the external factor happen because it affect or strength some of the internal factors.

This article will introduce two major method for producing perovskite quantum dot which are hot-injection method and room temperature reprecipitation method [3], both method have its own advantage and disadvantage for using. Also, for the different external and internal factor for affect the stability of perovskite quantum dot, there are some different methods for decrease the effect from those factors. As the methods of

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increasing the stability of perovskite quantum dot being used, the perovskite quantum can be used in real life as the optoelectronic devices more frequently.

2. Introduction of the perovskite quantum dot

A perovskite quantum dot or also called a metal halid perovskite quantum dot, is a kind of nanomaterial that has the chemical form ABX_3; here, A represents the monovalent charge cation and B refers to the divalent charge cation, for X here in the perovskite quantum chemical form, it is refer to halogen anion [1]. Like $CsPbCl_3$ is a kind of perovskite that Cs refer to A and Pb refer to B and Cl refer to X to form the ABX_3 chemical form. Perovskite quantum dot also have a special kind of crystal structure, that B type cation coordinate with the six X type anion to form the octehedral structure [1]. This octahedral structure can be seen as the skeleton of the perovskite. Between the octehedral skeleton structure, there is a space for placing the A-type cation, which stays in the middle of the space [1].

Perovskite nanomaterials can be separated into two types: one is organic-inorganic perovskite and one is all-inorganic perovskite, the difference between two type of perovskite is depend of A type cation [1]. For perovskite's A that belongs to the organic mono valent charge action like MA^+ which refer to $CH_3NH_3^+$, the perovskite is belong to organic-inorganic type, for the A belongs to inorganic cation like Cs^+, the perovskite is all-inorganic type as both A and B are inorganic. Actually, there are other types of classification, which are lead-free or lead-containing perovskites. The reason for having such a classification is that lead-containing perovskites are toxic to use [1, 4]; scientists are trying to replace the Pb with other kinds of less toxic metal ions in order to decrease the toxicity of the perovskite nanomaterial.

For Colloidal semiconductor nanocrystals which include the perovskite quantum dot, one of the most important characteristic is the absorption and emission of excition is depend on the quantum confinement and size of the crystal [1]. By controlling the size or structure of the semiconductor nanocrystals, it is possible to control the characteristics of the exciton emission and absorption. Also, adding different impurities could lead to different photon emission pathways with different wavelengths [1].

High Luminescence Quantum Yield (PLQY) is another important characteristic for perovskite quantum dot or metal halid perovskite quantum dot, this refers to the perovskite emitting a high percentage of the photons it absorbs. For perovskite quantum dot, it can reach 90% luminescence quantum yield without surface treatment [1]. Also, after having suitable ligand treatment or doping treatment, the luminescence quantum yield can reach to around 100% [1]. Furthermore, by controlling the ratio of the mixed halid, the bandgap can be tuned to cover the whole range of the visible spectrum [1].

For perovskite quantum dot, it also have many other characteristic such as the line-width of photo luminescence emission is narrow and low stability [1, 2].

As those characteristic such as high luminescence quantum yields or controllable of photon emission wavelength, perovskite quantum dot is important in optoelectronic devices. Perovskite quantum dot material is suitable for making solar cells due to strong light absorption, lasers due to narrow emission and LEDs due to controllable emission wavelength [1]. For example, $CsPbCl_3$ can be used as a laser or solar cell [4]. However, due to the low stability of the perovskite quantum dot, most devices made by perovskite quantum dot can only work well in certain environments. Despite those excellent characteristic, the poor environment stability of perovskite quantum dot is major issue for letting perovskite quantum dot being widespread used.

3. The factors causing low stability

One of property of perovskite quantum dot is the low stability, those low stability issue can cause by two type of the reasons which are internal factors and external factors. The internal factors are mostly about the structure and its chemical property, the external factors are mostly about the environment causing low stability issues happen.

For the internal factors, ion migration is one of the most important internal factors that cause perovskite quantum dot low stability happen as for perovskite quantum dot, its ion migration energy is low and ion are easy to migrate [1]. Also, another idea is that perovskite quantum dot has low halid vacancy formation energy; this leads to the result that their lattice easily forms defects [4]. By combining these two ideas, perovskite quantum dots have low halid vacancy formation energy and low ion migration energy; these two kinds of energy can easily cause vacancy and interstitial defects. This means the halid vacancy and ion migration are easily happen which lead to change of the forming and structure. Finally, the stability are decrease due to the changing.

Another internal factor is ligand detachment and its side effect of surface defects. For some of the ligand like long chain ligand such as Oleic Acid (OA) and Oleylamine (OLA) are weak bond ligand, as the weak relation between the crystal and ligand, the ligands are easily being detach from the perovskite crystal [4]. The ligand detachment issue will increase the effect of surface defect and also cause the quantum dot connect together increasing size [5]. After surface defects appear, nonradiative recombination and structural degradation issues will also happen, and then PLQY will also decrease [5]. So, for some kinds of weak-bond ligands, the ligands will easily detach and cause the issue in structure and size of the crystal, then finally lead to the decreasing of the stability and PLQY.

Actually, most of the environment issue are cause by the structure or the chemical property of the perovskite quantum dot. Take an example: for lead-containing perovskite quantum dot, it can dissolve highly in large amounts of polar solvent. After that, in the solution, both ligand and perovskite quantum dot are highly ionic. Also, the low melting point leads to perovskite quantum dot are easily reorganize to high density form under high temperature situation [1]. So, the low stability of perovskite quantum dot under certain situation are not directly cause by the situation, its chemical property, surface defect, highly ionic and other reason are the one that let perovskite quantum dot easy being affected by the environment situation.

For the external property, it can separate in two four category which include moisture, oxygen, temperature and UV light. For water moisture, as perovskite quantum dots are soluble in most polar solvents, the perovskite are easily solute in water [1]. This limits the use of the device that contain the perovskite that lead it is hardly to use those device in the place with high humidity such as high precipitation area.

For UV light issue, UV light can cause the ion in the perovskite quantum dot migrating, further more, for some kind of perovskite quantum dot, facing the electronillumination may let the perovskite quantum dot degrade into other compound [1]. This shows the limitation of using perovskite devices directly under sunlight.

Oxygen may also affect the stability of perovskite quantum dots. Oxygen can also cause degradation of perovskite quantum dots [1]. Also, oxygen may oxidize the perovskite and increase the instability of perovskite quantum dots [1].

Same as oxygen and UV light, the high temperature situation can also lead the degrade of perovskite quantum dot [1]. For the testing between the PL value for perovskite quantum dot and the temperature, it shows that when increasing the temperature, the PL value of the perovskite quantum dot are decrease [6]. This testing also indicates that high temperature may also lead to instability in perovskite quantum dot. By testing quantum dot PL under 80 degree Celsius and 100 degree Celsius, the PL drop from 95% of original to 72.92%

of original which also prove the temperature affect the PL for perovskite [7]. All of this is because, as the temperature increases, the ions in perovskite start to migrate more and increasing the amount of defects at the surface. Then finally result as increase instability or decrease the performance of the perovskite quantum dot [8].

4. Preparation for perovskite quantum dot and methods to increase its stability

For the preparation of perovskite quantum dot, there are two major methods, which are the hot-injection method and the room-temperature reprecipitation method [3]. For the hot-injection method, this method involves having the reaction in solution by adding the reactant quickly into the solution with the other reactant already dissolved in it; after a few seconds, using a cold water bath to cool the solution to room temperature [1]. By the hot-injection method, the output quantum dot size in depend on the reaction temperature, this is because the principle of the method is when the reaction happen, the amount of perovskite quantum dot increase and supersaturated for a certain amount that appear as crystal. The supersaturated amount depends on the reaction temperature. The hot-injection method can be used for producing different sizes or structures of perovskite quantum dot [1]. However, there are still some disadvantages that limit its widespread use, such as requiring high reaction temperature and noble gas to protect the product [1, 3].

The room-temperature reprecipitation method is another major method used to produce perovskite quantum dot. The method is about, doing the reaction in the high soluble solvent such as polar solvent, then pour into a less soluble solvent for precipitation [1]. The reason of this method works is when changing the solvent, the solubility of the perovskite changing and precipitation by crystal appear. For the room-temperature reprecipitation method, it is easy to use and controllable and can widely use in factory, but compare to the hot-injection method, the quality for the perovskite quantum dot is decrease [1].

As the performance of perovskite quantum dots is excellent but stability is low, many methods have been found to increase the stability of perovskite quantum dot. For some long chain ligand such as OA and OAm, the proton exchange are easily happen that lead to the ligand detachment [1]. Also for the widely use ligands OA and OAm, the connect between the perovskite quantum dot and ligand are strong that easily cause the aggregation or the structure changing [1]. In order to solve the issue, ligand modified is one of the possible method for using, by using other ligand set. For example, replace the OA and OAm with octylphosphonic acid as the interaction is strong compare to OA and OAm, then the possible for ligand detachment decrease [1]. Also, for long chain ligand such as OA and OAm, the steric effect may happen and let the coverage quality decrease, if change the ligand to didodecyldimethylammonium bromide which is a shorter kind of ligand, the converge quality of ligand increase [5, 9].

The next method is ion doping; ion doping is one of the major methods for increasing the stability of perovskite quantum dot [3]. By doping many kinds of different ion such as metal ion, the stability increase, take an example, doping suitable amount of potassium ion or other kind of alkali metals can help to avoid the changed in lattice to increase the stability [7]. Also doping the enough amount of the tin ion can increase the PL for perovskite quantum dot and increase the environment stability [5], but for doping over amount of the tin ion may lead to increase the amount of surface defect and cause structure unbalance [6]. Both example indicate that for the ion doping method, the amount of doping is the point to control the stability that over adding will cause the surface defect and decrease stability.

Surface coating and encapsulation are another kind of method for increasing perovskite quantum dot stability. Surface coating can help isolate the perovskite quantum dot from the environment to avoid the

environment affecting the perovskite quantum dot [3]. For example, using silicon dioxide can increase the stability of perovskite quantum dot under high-temperature conditions [5]. Also glass matrix encapsulation can also be used for coating and give the efficiency protect for perovskite quantum dot [6].

5. Conclusion

This article introduces about perovskite quantum dot have excellent property that can be use for optoelectronic device, however its long tern stability is poor. With both external and internal factors, the stability of perovskite quantum dots is affected negatively; internal factors include ligand detachment, lattace and surface defects, ion migration, and external factors, which include oxygen, UV light, moisture and high temperature. The external and internal factor are related together as external factor and strength or cause internal factor happen. Two major producing method are using which include hot-injection method and room temperature reprecipitation method, also several method for increasing the perovskite quantum dot's stability are popular which include ion doping, coating and ligand modified. Both three method can due with the instability in different way which can be used depend on different situation and which internal or external method are happening. Actually, this article still lack on provided the data, as it is clearly to relate the theory or method by providing the product data or information. For the future study, in order to make the perovskite quantum dot widespread using, it is important to find a method that can due with more internal and external factors once which increase the lifetime for optoelectronic device.

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