Photochemistry in $CuInS_2$ Quantum Dots/Polyoxometalate System

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Abstract* – Energy transfer involving semiconductor quantum dots (QDs) has received increased attention in recent years because of high photostability and size-tunable optical properties. Here, we study photochemistry in quantum dot/polyoxometalate (POMs) systems and utilize quantum dots as light antenna that captures visible light to sensitize wide band gap POMs. We also demonstrate the photoenergy storage properties of $CuInS_2$ QD/POM systems. The PL quenching and the decrease in PL lifetime are clear indication that the excited electron of $CuInS_2$ was deactivated by electron transfer to POM such as $PMo_{12}O_{40}$, $W_{10}O_{32}$ and $SiW_{10}O_{36}$ that were hybridized with a cationic surfactant and dispersed together in an organic solvent. The quantum yields of $CuInS_2$ QDs were 2.32% with 3.9 nm in particle size. Irradiating QD/POM systems with visible light generates a one-electron reduced form of POMs, suggesting the reduction of POMs. Photoenergy can be stored as reduced POM under deaerated conditions by visible light. Stored electron in POM can be discharged afterwards via reductive reactions such as oxygen under the dark.

***Index Terms* – Quantum dots, polyoxometalate, photoenergy.**

INTRODUCTION

Quantum dots (QDs) as luminescent semiconductors have been eagerly explored because of their flexible solution processing, band gap tunability, high photoluminescent quantum yields, and narrow emission peaks with a broad band gap excitation and high photosensitivity [1]. Because of their promising optical properties, their utilization in photoenergy conversion has been attracting much attention. Some quantum dots show high photocatalytic activities such as water reduction and organic decomposition [1][2]. As nanoscale clusters, polyoxometalates (abbreviated POMs) have also been an active research target for many years. POM is a unique class of inorganic metal-oxide clusters having distinctive physical and chemical properties such as strong bronsted acidity and strong oxidizing capability [3].

They also have stable redox properties and can trap and accommodate photo-excited electrons without changing their crystal structure, but have limited photocatalytic activities only in UV region (wavelength below 400 nm). We expect that coupling quantum dots with POMs could form a new class of optical material families, which exhibit photoactivity even under visible light irradiation due to tunable bandgaps of quantum dots. Here, we study photochemistry in quantum dot/polyoxometalate systems and utilize quantum dots as light antenna that captures visible light to sensitize wide band gap POMs. We also demonstrate the photoenegy storage properties of QD/POM systems.

EXPERIMENTAL METHOD

Synthesis was done by mixing $Cu(acac)_2$ and $In(acac)_3$ in 1-dodecanethiol inside a three-necked flask and heated at 100ºC for 30 minutes under vacuum conditions. The temperature then raised to and be hold for 1 hour at certain temperatures (200ºC, 215ºC and 230ºC) under argon gas flow. The products were washed three times by precipitation using hexane with excess ethanol.

POM-surfactant hybrids were prepared by mixing DODA (dioctadecylammonium brimide) and POMs such as $SiW_{12}O_{40}^{4-}$, $W_{10}O_{32}^{4-}$ and $PW_{12}O_{40}^{3-}$ in water. Commercial reagents of $SiW_{12}O_{40}^{4-}$ and $PMo_{12}O_{40}^{3-}$ were used without any further purification. $W_{10}O_{32}^{4-}$ was prepared by polycondentation WO^{4-} from 30 mL of Na_2WO_4 solution with HCl at pH 2. The light yellow precipitates were collected by evaporation.

The colloidal size of quantum dots was determined with a DLS spectrophotometer. The crystal structure was observed by using XRD with CuKα radiation and TEM observation. Steady state PL spectra and the light absorption properties were obtained with a spectrometer. Fluorescence lifetimes measured with a commercial instrument. The photocatalytic measurements were done by dissolving quantum dots together with POM/DODA catalyst in hexane. Optical characterization was performed after removing oxygen. Triethylamine was added as an electron donor to avoid the direct photooxidation of quantum dots in the phase aqueous solution. The solution was exposed with UV light by using a 150 W Xe lamp with 500 nm optical cut-off filter for 1-30 minutes.

RESULT AND DISCUSSION

The XRD patterns of synthesized $CuInS_2$ are similar with the reference of the tetragonal $CuInS_2$ phase. TEM imaging and DLS measurements for $CuInS_2$ show that the nanocrystal size is about 2-3 nm. Band gap of the $CuInS_2$ sample was estimated by plotting $(\alpha h\nu^2)$ and eV from Uv/Vis absorption data[4]. Band gap value is significantly larger than that of bulk $CuInS_2$ (1.5 eV), indicating the quantum size effect of the very small crystals. The PL emission spectra have a maximum peak at 650 nm wavelength when excited with 470 nm. Optimum quantum yield (QY) is 3.32% with 1.98 nm particle size.

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Table 1. $CuInS_2$ QDs properties at different temperature synthesis

T (°C)	d (nm)	Band Gap (eV)	τ (ns)	QY (%)
200	2.23	1.98	123.27	1.140
215	3.71	1.98	144.34	2.320
230	9.38	1.92	62.94	0.714

The PL emission intensity of QDs decreases by adding POM in the system. PL lifetime measurement was also performed to confirm whether photo-excited charges in the semiconductor particles are efficiently transferred to POMs. The decay time traces have two components: a fast (τ_1) and a slow decay (τ_2) [1] [4]. By adding POM, both components show decreasing behaviors. Moreover, the average PL life time of semiconductor quantum dots apparently decreases by mixing with POMs. The PL quenching and the decrease in PL lifetime are clear indication that the excited electron of $CuInS_2$ was deactivated by electron transfer to POM. Indeed, irradiating QD/POM systems with visible light generates an one-electron reduced form of POMs, suggesting the reduction of POMs. We observed the formation of one-electron reduced POMs as the reaction intermediate by monitoring a change in absorbance after visible light irradiation. This reduced state is stable in the absence of electron acceptors such as oxygen [3]. The energy from the light creates hole-electron pairs. They can be stored in POMs due to its excellent redox properties [3] [4]. When oxygen is introduced into the system, the trapped electron will discharge subsequently by oxygen reduction and the system can return back to the original state. The observed phenomena also indicate that $CuInS_2$ QDs act as antenna to capture visible light and inject electrons to POMs. The results suggest the feasibility of photoenergy charge-discharge cycles based on QD/POM systems.

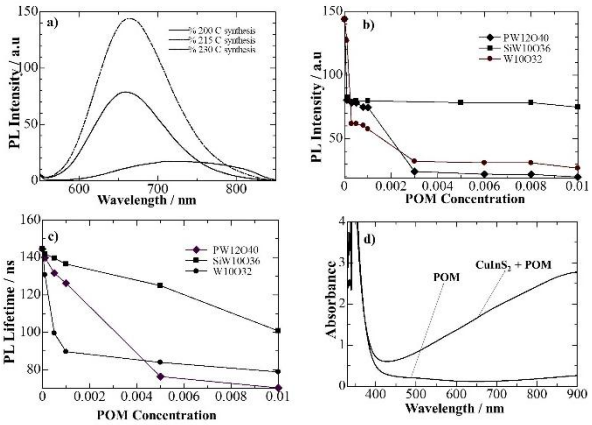

Figure 1. a) PL intensity of $CuInS_2$ QDs, b) PL Intensity quenching by pom, c) pl lifetime quenching by POM and d) absorbance after 30 minutes visible light irradiation.

CONCLUSION

In summary, we have demonstrated visible-light induced electron transfer from CuInS2 quantum dots (QDs) to polyoxometalates (POMs) that are hybridized with the cationic surfactant in an organic solvent under visible light irradiation. Using $CuInS_2$ QDs as antenna that captures visible light, photocatalytic reactions can take place even under visible light irradiation. The result indicates the feasibility of using reduced POMs as a reservoir for electrons that are photogenerated in QDs by visible light excitation. This system potentially stores solar energy and drives reduction reactions under dark.

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