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Sensing application of an optical fiber dip coated with L-Cystein ethyl ester hydrochloride capped ZnTe quantum dots

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Optical fiber in conjunction with ZnTe quantum dots (QDs) is investigated for sensing application. ZnTe QDs, are synthesized by a simple chemical bottom up approach. Quantum dots are capped with L-Cystein ethyl ester hydrochloride (LEEH), to increase their stability. Then LEEH capped ZnTe QDs, whose size is estimated as 2.29 nm by effective mass approximation (EMA), are dip-coated on a cladding removed optical fiber. Different concentrations of alcohol and ammonia are used to investigate the sensing behavior. It is found that sensitivity of the sensor increases with the use of QDs for both alcohol and ammonia.

Keywords: *cladding removed optical fiber; optical fiber sensor; ZnTe quantum dots*

1. Introduction

Quantum dots (QDs) are tiny particles or nanocrystals of semiconducting material with diameters in the range of 2 nm to 10 nm (10 to 50 atoms). In recent years, QDs have been widely investigated due to their unique photophysical and photochemical properties (such as quantum-size effect, dielectric confinement effect and surface effect), becoming desirable in the fields of physics, chemistry, material science and biology.

Recently, quantum dots embedded coating on optical fibers have been developed to detect gases [1, 2], pH [3], temperature [4], humidity [5, 6] and bimolecules [7, 8]. There are various schemes described in literature, for optical fiber sensors such as Bent optical fiber sensor [9], tapered optical fiber sensors and cladding removed optical fiber sensor [10]. All these sensors are based on the principle of significant interaction between an external medium and the evanescent field outside the core of the fiber.

Cladding removed optical fiber (CROF) sensors with nanoparticles (NPs)-based coating have been developed recently to detect humidity [10, 11], ethanol [12], ammonia [13], methanol [14]. Kodaira et al. [15] proposed a sensor for gas detection using SiO_2 nanoparticles while Mariammal et al. [12] developed sensors for ethanol detection using CuO: SnO_2 NPs coating. But all these investigations used two different NPs, as a coating material for the realization of the sensor. Here, we propose a single QD (ZnTe) coated CROF for sensing alcohol as well as ammonia. To the best of our knowledge this is the first ZnTe coated CROF investigated for possible application in sensing, which is not toxic unlike cadmium based QD sensor.

In the present work, 5 cm cladding has been removed in the middle of 1 m glass fiber along its length to form a CROF. CROF was then coated with ZnTe quantum dots capped with LEEH and it worked as a sensing arm. The arm was exposed to various concentrations of alcohol and ammonia solutions to investigate variation of intensity at the output of the fiber when the input of the fiber was illuminated by a laser diode (L.D).

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2. Experimental

2.1. Synthesis of LEEH capped ZnTe QDs

Aqueous solutions of 0.5 mM $NaBH_4$, 0.5 mM Te, 2.77 mM $ZnCl_2$ and 0.1 mM LEEH (all chemicals from sigma Aldrich) were prepared separately. The first solution was prepared by taking 0.5 mM of $NaBH_4$ in 10 mL millipore water and 0.5 mM of Te in 10 mL of millipore water. This solution was allowed to stir at 60 °C for 1 hour. The following reaction took place:

$$4NaBH_4 + 2Te + 7H_2O \rightarrow 2NaHTe + Na_2B_4O_7 + 14H_2 \qquad (1)$$

Then the second solution was prepared by taking 2.77 mM of $ZnCl_2$ in 10 mL of millipore water and 0.1 mM of LEEH in 10 mL of millipore water. This solution was allowed to stir for 30 minutes at 45 °C. The above two solutions were mixed and stirred for 2 hour at 80 °C. The solution was poured in air tight bottle and the UV absorption spectra were recorded. The spectrum is shown in Fig. 1.

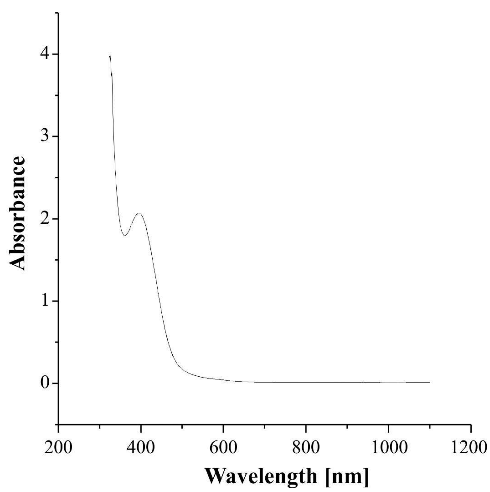

Fig. 1. Variation of absorbance with wavelength.

The size of the ZnTe QDs was estimated from the absorption spectra using EMA:

$$\left[E_g^* - E_g^{bulk} + \frac{0.124e^4}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)\right] r^2 + \left[\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right] r - \frac{\hbar^2\pi^2}{2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) = 0 \qquad (2)$$

where E_g^* is band gap energy of the nanoparticle = 2.87 nm, E_g^{bulk} is band gap energy of the bulk ZnTe at room temperature = 2.25 eV, h is Planck's constant, r is particle radius, m_e is the mass of a free electron, m_e^* is 0.11 m_e (effective mass of a conduction band electron of ZnTe), m_h^* is 0.6 m_e (effective mass of a valence band hole of ZnTe), e is elementary charge, ε_0 is permittivity of free space, ε is relative permittivity or dielectric constant of ZnTe. We have calculated the diameter of the QD [16] and the particle size was estimated as 2.29±0.16 nm.

2.2. Fabrication of the optical fiber quantum dots sensor

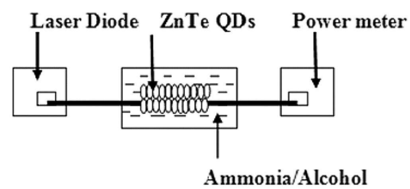

Fig. 2. Experimental setup.

The glass fiber used in the present work was of 1 m length. At the center, along its length a 5 cm cladding was first removed. After removing the cladding, the fiber was cleaned with acetone, dried and then washed in distilled water, allowed to dry for some time and then dipped in synthesized ZnTe QD solution for approximately half an hour, and then the fiber was taken out from the quantum dot solution and allowed to dry for 1 hour under a 100 W lamp.

To test the sensing action, the sensing arm was immersed in alcohol of 0.08 g/cm^3. One end of the fiber was illuminated by L.D (650 nm) and the output power from the other end of the fiber was measured by a power meter. The schematic experimental arrangement is shown in Fig. 2. The experiment was repeated with concentrations of 0.08 g/cm^3, 0.12 g/cm^3, 0.16 g/cm^3, 0.20 g/cm^3, 0.24 g/cm^3. A similar procedure was also followed for ammonia.

3. Results and discussion

In Fig. 3 the variation of transmission power with concentration of alcohol is shown. We have investigated two configurations A – without ZnTe QDs coating on the CROF and B – with ZnTe QDs coating on the CROF. A peculiar behavior is observed in the variation of transmission power, as shown in Fig. 3. In configuration B, the transmission power decreases linearly with the increase of alcohol concentration. To confirm this, QDs were prepared three times following the same procedure. For all these samples (B_1, B_2, B_3) a similar trend (linear variation) in the variation of power with alcohol concentration is observed; transmission power is found to decrease in this case.

As there is a linear variation of transmission power with alcohol concentration, both the configurations A and B are suitable for sensing application, but it was found that ZnTe QDs coated CROF is 10 times more sensitive than the corresponding uncoated CROF. Stability of QDs is another important parameter in the sensing application. It was found that the synthesized QDs were stable which was verified by analysing UV-Vis spectrum over a period of one month. When the experiment for the same configuration was performed after one month, a similar trend as that of configuration 'A' was observed, but with comparatively lower transmission power.

However, for ammonia as a measurand, the variation is somewhat different as shown in Fig. 4. In this case, the transmission power increases with ammonia concentration for ZnTe coated CROF (C_1, C_2, C_3) and uncoated CROF (D). C_1, C_2, C_3 are the configurations of coated CROF for three different samples of ZnTe QDs synthesized following the same procedure. The sensitivity of the coated CROF was found to be 6 times higher than for similar configuration uncoated fiber.

The reason for the change of transmission power in a coated CROF with the measurand concentration can be explained as follows:

When the cladding is intentionally replaced by sensitive coatings, there could be a significant interaction between the external medium and the evanescent field [17] to the guided light. The optical properties of alcohol and ammonia determine the change in this evanescent field interaction.

However, the reason for the decrease in the transmission power in the uncoated CROF is still not clear. It may be due to its non-polar nature compared to polar nature of ammonia where the transmission power increases with concentration.

The experimental results explained above, lead us to believe that coating ZnTe QDs on a CROF can improve the sensitivity of the sensor used to measure concentration of alcohol and ammonia.

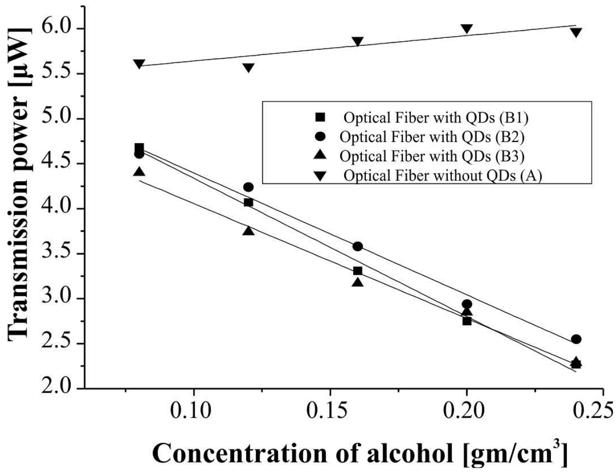

Fig. 3. Transmission power vs. alcohol concentration measured using 650 nm light source for 5 cm cladding removed optical fiber exposed to alcohol solution.

4. Conclusions

In this paper, small size LEEH capped ZnTe QDs have been synthesized using a simple chemical approach. The synthesized QDs were then coated on a cladding removed optical fiber (CROF) to realize sensing application. Transmission power measurements for two different materials, alcohol and ammonia were carried out, using ZnTe QDs coated and uncoated CROF configurations. It was found that ZnTe coated CROF was more sensitive to alcohol and ammonia (10 times for alcohol, 6 times for ammonia) compared to a similar uncoated CROF. As the ZnTe QDs are nontoxic, they are a better candidates for alcohol or ammonia concentration measurement in comparison to cadmium QD based sensors.

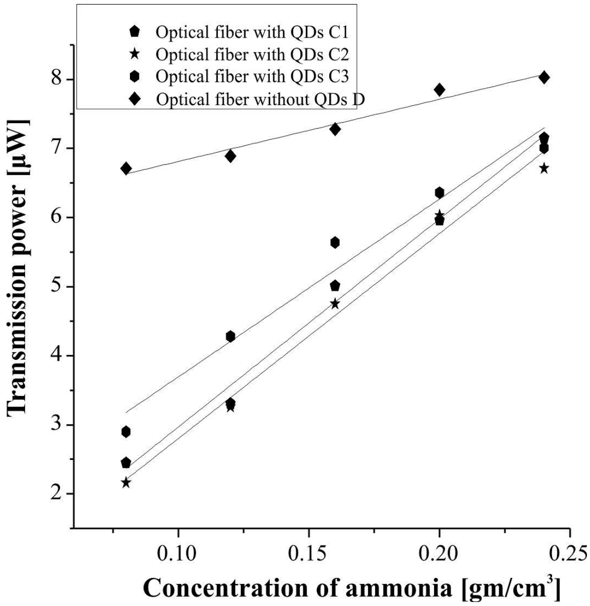

Fig. 4. Transmission power vs. ammonia concentration measured using 650 nm light source for 5 cm cladding removed optical fiber exposed to ammonia solution.

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