CHIN. PHYS. LETT. Vol. 30, No. 11 (2013) 118101

Fabrication and Photostability of Rhodamine-6G Gold Nanoparticle Doped Polymer Optical Fiber *

Suneetha Sebastian**, Ajina C, C. P. G Vallabhan, V. P. N. Nampoori, P. Radhakrishnan, M. Kailasnath

International School of Photonics, Cochin University of Science and Technology, Cochin 22, India

(Received 14 June 2013)

We report on fabrication of a rhodamine-6G-gold-nanoparticle doped polymer optical fiber. The gold nanoparticle is synthesized directly into the monomer solution of the polymer using laser ablation synthesis in liquid. The size of the particle is found from the transmission electron microscopy. Rhodamine-6G is then mixed with the nanoparticle-monomer solution and optical characterization of the solution is investigated. It is found that there is a pronounced quenching of fluorescence of rhodamine 6G due to fluorescence resonance energy transfer. The monomer solution containing rhodamine 6G and gold nanoparticles is now made into a cylindrical rod and drawn into a polymer optical fiber. Further, the photostability is calculated with respect to the pure dye doped polymer optical fiber.

PACS: 81.05.Lg, 81.07.−b DOI: 10.1088/0256-307X/30/11/118101

Poly methyl methacrylate (PMMA) finds applications in photonics especially for developing optical fibers due to its good optical properties such as high transparency, excellent light transmission and ease of fabrication. One of the important advantages of transparent polymers compared to the traditional optical materials such as glass is that it is possible to introduce organic dyes or other compounds into the polymers that can play the role of active components.[1] Recently, dye doped polymer optical fibers (POFs) have found applications in a variety of devices such as fiber amplifiers, fiber lasers and sensors.[2] Gold (Au) nanoparticles have been very attractive among metal nanoparticles since they possess several interesting features such as their optical properties are tunable throughout the visible and near-IR region of the spectrum as functions of nanoparticle size, shape, aggregation state and local environment.[3,4] When Au nanoparticles are added to a dye medium, it can affect the emission of the dye in two ways. Either it can quench the emission intensity or enhance it. Recently there have been several results showing that fluorescence can be manipulated by Au nanoparticles from entire quenching to immense enhancement. The factors that affect the alteration are the size of the nanoparticle and the distance between the dye molecule and nanoparticle.[5] In previous works it is noted that fluorescence resonance energy transfer (FRET) is one of the possible reasons for fluorescence quenching of rhodamine 6G (Rh6G) by Au nanoparticles.[6,7] Because of the development in the field of nanotechnology especially in the area of Au nanoparticles, organic dyes incorporating Au nanoparticles are gaining attention. Both liquid and solid media such as films with dye-nanoparticle combination[8,9] find many tremendous applications in the field of surface enhanced Raman scattering (SERS),[10] radiative decay engineering[11] and sensing applications.[12] Even though several reports have already come up with Rh6G-Au nanoparticle combination in solid as well as liquid media showing how the particle size, concentration can affect the lasing activity of the dye,[8,9,13,14] this is the first time that one reports Rh6G-Au nanoparticle doped polymer optical fiber fabrication and its characterization such as photostability measurement.

There has already been a work by Xie *et al.*[10] that POFs with Au nanoparticles coated on the tapered part of the fiber can be used for SERS sensing of Rh6G molecule. Pettingger *et al.*[15] suggested that fluorescence quenching of the adsorbent by nanoparticles can again enhance the SERS signal. Also it is reported by Michaels *et al.*[16] that trapping the molecule, which has to be detected, between the nanoparticles makes intense Raman signals. In light of these results, dye-nanoparticle doped POF may be used to get an even higher order of magnitude SERS signal of Rh6G molecule.

In this work, we incorporate Au nanoparticles into the monomer solution, i.e. methyl methacrylate (MMA) by laser ablation synthesis in solution (LASiS). This solution containing nanoparticles is then doped with Rh6G and optical characterization is investigated. Then the monomer solution containing dye-nanoparticles is polymerized into cylindrical rods and successfully drawn to a Rh6G-Au nanoparticle doped polymer optical fiber. Photostability of the same is then measured. This work is really promising since it is a preliminary step towards the development of polymer optical fiber lasers and amplifiers incorporating noble metal nanoparticles for better operations.

Figure 1 shows the schematic diagram of the experimental setup used for the preparation of Au nanoparticles due to laser ablation of a gold plate immersed in the solution by Nd-YAG laser. A 24-Carat gold plate of $1\,g/cm^2$ is used as the substrate. The gold plate is purchased from Sigma-Aldrich. Ablation is carried out at the fundamental wavelength 1064 nm with a fluence of $10^6\,J/cm^2$, pulse width 9 ns and repetition rate 10 Hz. Lens of focal length 100 mm is used

*Supported by the DST Finland Project.

**Corresponding author. Email: sunikutty@gmail.com

© 2013 Chinese Physical Society and IOP Publishing Ltd

to focus the laser beam onto the substrate. A beaker containing both gold plate and liquid is placed at the focal point of the lens for the maximum ablation rate.

Liquid medium used for Au nanoparticle formation using LASiS is MMA so that it can be directly polymerized into a transparent rod. A gold plate in 40 ml of MMA is ablated for half an hour and the concentration of Au nanoparticles in the solution is found to be 2.3×10^{-4} M. Rh6G is doped into this solution of MMA containing Au nanoparticles. The concentration of Rh6G in MMA is fixed at a low value, i.e., 3×10^{-5} M since its solubility is less in MMA.[17] Concentration of Au nanoparticles is varied at a fixed concentration of Rh6G in the present study. A total of five samples (named R, A1, A2, A3, and A4), where R is taken as the reference, are made. A1 contains 6.7×10^{-5} M, A2 contains 3×10^{-5} M, A3 contains 6.7×10^{-6} M and A4 contains 6.7×10^{-7} M concentration of Au nanoparticles. MMA usually contains inhibitors to prevent polymerization at room temperature. Inhibitors are removed by repeatedly washing the monomer with 5% NaOH solution followed by flushing with distilled water. The remaining water is removed by adding suitable drying agents like $CaCl_2$. The monomer is purified by distillation under reduced atmosphere to get the pure MMA.[18] All chemicals in this experiment are purchased from Sigma-Aldrich, USA.

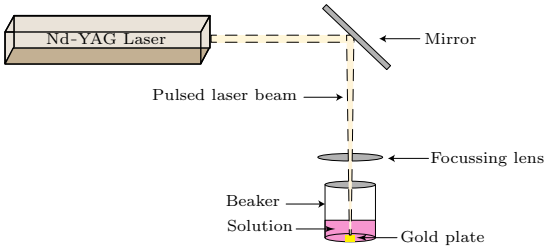


Fig. 1. Experimental setup for laser ablation.

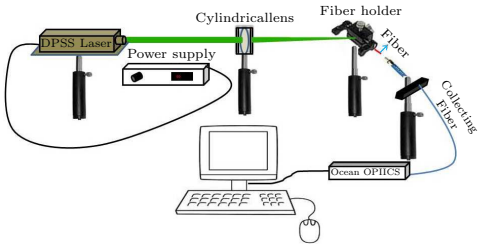


Fig. 2. Experimental setup for photostability measurement.

The solution containing Rh6G-Au nanoparticle is polymerized into a rod of diameter 1.2 cm by adding appropriate quantities of initiator and chain transfer agent. The rods were drawn into fibers of varying thickness using a conventional polymer optical fiber drawing tower.

Photostability is measured using the experimental setup shown in Fig. 2. The Rh6G-Au nanoparticle doped POF sample is placed in a fiber holder. The holder is placed at the focus of a biconvex lens of focal length 5 cm. A cw laser beam from a diode pumped solid state laser of 100 mW power is focused onto the fiber having diameter 600 μm. The fiber is transversely pumped and the fluorescence emission from the fiber is collected from the side of the fiber using a collecting fiber and intensity is recorded using a spectrometer. The experiment is repeated by noting the fluorescence intensity from the fiber in due times.

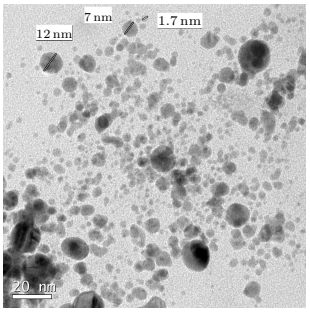


Fig. 3. TEM of Au nanoparticles in MMA produced by laser ablation.

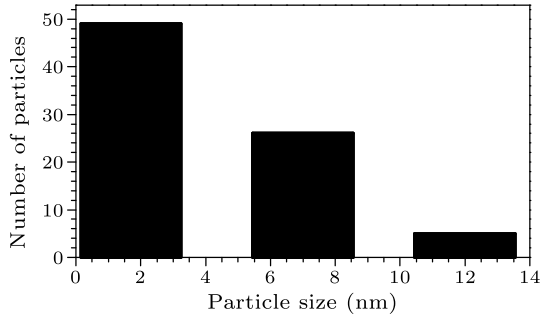


Fig. 4. Histogram of Au nanoparticles, showing the average size of the particles formed by laser ablation.

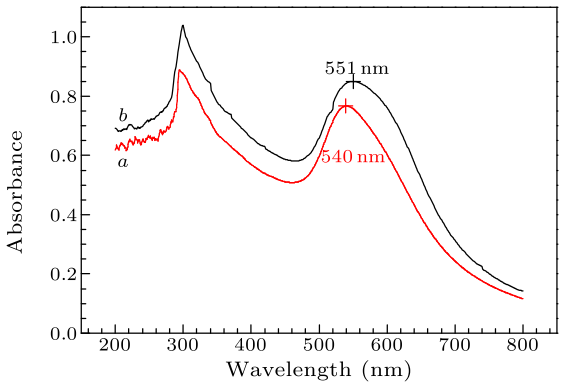


Fig. 5. Absorption spectra of Au nanoparticles in MMA: (a) taken after synthesis using LASiS, (b) taken after a month.

Absorption spectra of the samples are recorded by using a Jasco UV-ViS NIR Spectrophotometer. The fluorescence spectrum of the Au doped in the solution of Rh6G in MMA is recorded by using a Varian Cary Eclipse Fluorometer. Transmission electron microscopy is obtained with a 300 kV high-resolution transmission electron microscope (FEI, Model: 30 G2 S-twin). Time-resolved fluorescence measurements are carried out using a Horiba Jobin Yuvon Fluorocube-01-NL fluorescence lifetime system. A picosecond diode laser (469 nm) is used as the excitation source, and a highly integrated picosecond PMT module is used as the detector. The instrument response

function of the experimental setup is limited by the FWHM of the excitation laser pulse and is 18 ns for the 469 nm source. The lamp profile is recorded by placing a dilute scattering solution (Colloidal Silica/Ludox in water) in place of the sample. Decay curves are analyzed by a nonlinear least-square iteration procedure using the F900 decay analysis software. The quality of the fit is accessed by the chi square (χ^2) values and distribution of residuals. Temperature is controlled by the quantum northwest (TC125) instrument.



Fig. 6. Au nanoparticles prepared by LASiS in MMA. All the samples are irradiated for 5 min showing the consistency of the yield of nanoparticles.

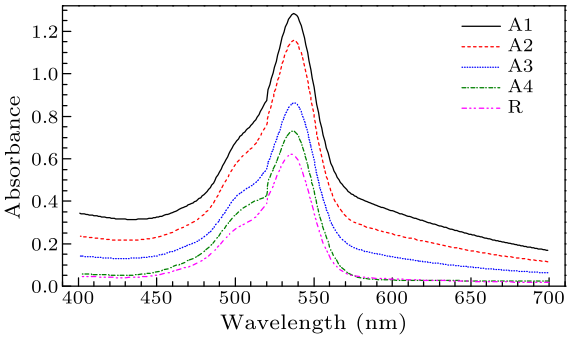


Fig. 7. Absorption spectra of Rh6G with and without Au nanoparticles.

Figure 3 shows the transmission electron microscopic image (TEM) of laser ablated Au nanoparticles in MMA. Spherical nanoparticles of varying sizes are found in the solution. The size variation is due to the high value of laser fluence used for ablation. Figure 4 shows the histogram of Au nanoparticles in MMA. It is inferred that the average size of laser ablated Au particle is 1.5 nm. Also it is found from the absorption spectra (Fig. 5) that the SPR peak of Au nanoparticles in MMA is at 540 nm. The nanoparticles so formed in MMA by LASiS are found to be stable for weeks and after a month a shift of 11 nm in the SPR peak is found, as shown in Fig. 5. As shown in Fig. 6, LASiS results in the synthesis of Au nanoparticles in MMA which is violet in appearance.

Firstly the optical characterization of Rh6G-Au nanoparticles in MMA is carried out using the absorption and fluorescence spectra shown in Figs. 7 and 8. It is found from the absorbance that as the concentration of Au nanoparticles in the solution is increased, the total absorbance of the Rh6G-Au nanoparticle system is increased. This is because both Au nanoparticles and Rh6G absorb around 540 nm, and as the concentration of Au is increased, more absorption for the system and so high absorbance appear. However, the reverse is observed in the case of the fluorescence spectrum. The reason is found to be because of fluorescence resonance energy transfer (FRET) from Rh6G to Au nanoparticles.[6,7]

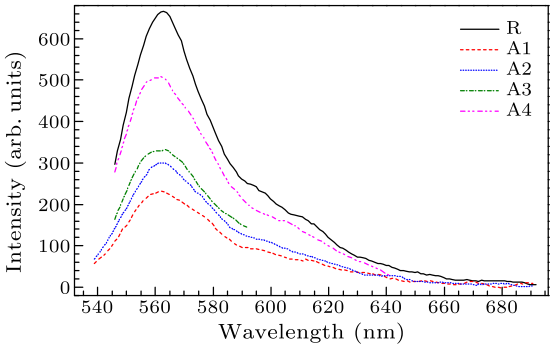


Fig. 8. Fluorescence spectra of the sample solutions excited at 500 nm.

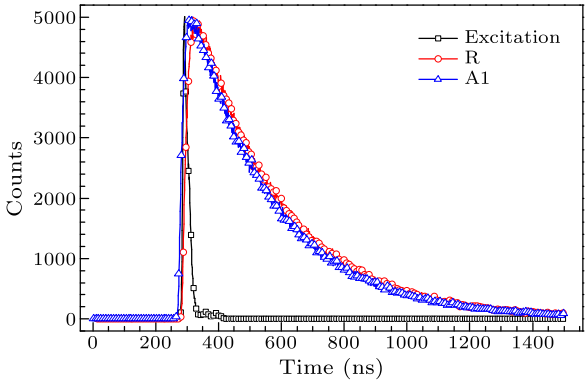


Fig. 9. Decay curves of sample solutions R and A1.

Since FRET quenching affects the lifetime of the dye, time resolved fluorescence spectra are taken for the samples R and A1. The spectrum is illustrated in Fig. 9. The decay curves are fitted with a biexponential decay function with an iterative reconvolution program (F900) maintaining the χ^2 between 1 and 1.2 as a measure of goodness of fit. From Table 1 it is found that the reduction in lifetime is only 3% and this is because in FRET the rate at which energy is transferred depends upon the magnitude of spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the quantum yield of the donor, the relative orientation of the donor and acceptor transition dipoles, and the distance between the donor and acceptor molecules.[19] The rate of energy transfer is small in Rh6G-Au nanoparticle pair in MMA and there may be other types of non-radiative decay paths giving rise to entire quenching.

Table 1. Calculations of lifetime measurements.

Sample	T_1 (ns)	T_2 (ns)	B_1 (normalised)	B_2 (normalised)	τ (ns)
R	3.51	5.04	0.8379	0.1619	3.76
A1	3.37	4.92	0.8148	0.1852	3.66

Also quantum yields of Rh6G in MMA in the presence and absence of Au nanoparticles are calculated using the comparative method. Reference fluorophore is taken as Rh6G dissolved in distilled water whose quantum is already known. Calculated quantum yield of samples R and A1 are 0.85 ns and 0.17 ns, respec-

tively.

Now with these inferences we polymerized five samples. Optical characterization such as absorption spectra and fluorescence spectra of the rods is also taken and found to be almost similar to that of Figs. 7 and 8. However, for sample A4 there is a very slight enhancement in fluorescence intensity as shown in Fig. 10. This enhancement is because when the monomer solution is polymerized into a solid medium such as a rod, the spacing between Rh6G and Au nanoparticles is changed to favor the metal enhanced fluorescence.

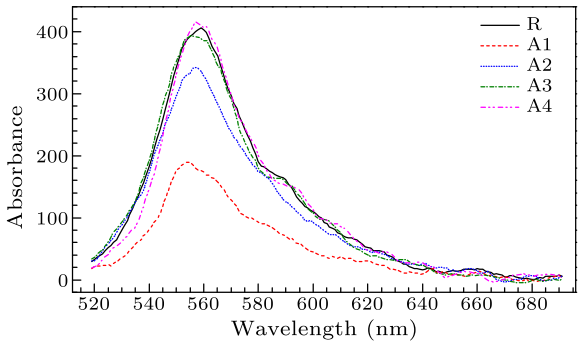


Fig. 10. Fluorescence spectra of Rh6G-Au nanoparticle doped polymer rods.

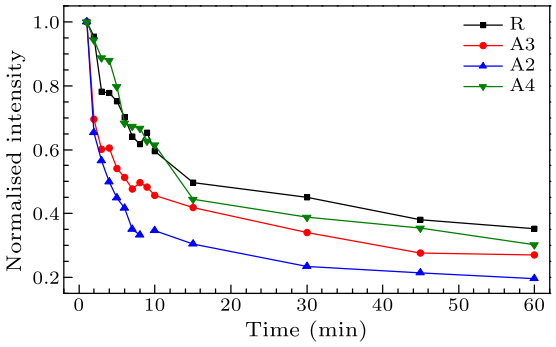


Fig. 11. Photostability of Rh6G-Au nanoparticle doped POF.

Further, the rods are drawn and the photostability of the fibers is recorded. For the measurement, fibers with the same diameter are taken from all sets (R, A2, A3 and A4). Figure 11 shows the photostability curves of all the fibers. It is found that for samples A2 and A3, the photostability is less in comparison with the bare Rh6G sample (R). This is because of the small size of the Au nanoparticle generated in MMA as well as the high concentration of Au.[13] However, for sample A4, since it exhibits a slight MEF when it is in the rod form/fiber, its SPR locally enhances the upcoming field from the laser radiation and so it shows a better stability up to 5 min compared to sample R. However, since the strength of MEF is low, it starts getting deteriorated in its stability as time goes on (as shown in Fig. 9). A similar result was also observed earlier.[9] Anyway, the detailed mechanism behind the phenomena needs to be studied.

We have successfully incorporated Au nanoparticles directly into MMA solution by laser ablation synthesis in solution technique. Formation of spherically shaped nanoparticles in the solution is confirmed from TEM and absorption spectra. Average size of the nanoparticles is found to be 1.5 nm and the surface plasmon resonance peak of Au nanoparticles is at 540 nm. Rh6G is added into the solution containing Au nanoparticles. It is found that fluorescence of Rh6G in MMA is quenched by the presence of laser ablated Au nanoparticles due to FRET. Further confirmation of FRET is carried out by taking lifetime measurements and quantum yield. We then polymerize the monomer solution containing Rh6G-Au nanoparticles into rods. Optical characterization is performed using fluorescence spectra as well as absorption spectra. The result seems to be similar to that of the solution except that for sample A4, there is a slight enhancement in fluorescence when polymerized. Photostability of Rh6G-Au nanoparticle doped POFs is studied using a cw laser. It is found that photostability of POFs containing Rh6G-Au nanoparticles deteriorates compared to the bare Rh6G doped POFs. However, for sample A4, photostability enhancement is observed for five minutes. We vary concentration of Au nanoparticles in MMA even below the concentration of A4. There is no photostability enhancement observed. Thus it is necessary to increase the size of the nanoparticles in the monomer solution as shown in a previous study.[8] However, we have opened a new area of polymer optical fiber incorporating metal nanoparticles for the first time so that other metal nanoparticles such as silver and copper can be easily incorporated with fiber for various applications.

The first author would like to thank NIIST, Trivandrum and Spectroscopy/Analytical Test Facility, IISc, Bangalore for providing the facility for taking TEM and lifetime measurements. The first author extends her gratitude to Dr. Thomas Lee S (technical consultant, Tech Mahindra, Bangalore) and Dr. Jyotsna Ravi (AkzoNobel, Bangalore) for their constant support and encouragement. The author also wishes to thank Sooraj S, Animesh Aaryan and Jaison Peter for their help during the work.

References

[1] Arrue J et al 2011 *Polymers* **3** 1162
[2] Kuzyk M G et al 1999 *Chem. Phys.* **245** 533
[3] Kabashin A V et al 2003 *J. Phys. Chem.* B **107** 4527
[4] Murphy C J et al 2005 *J. Phys. Chem.* B **109** 13857
[5] Kang K A et al 2011 *J. Nanobiotechnol.* **9** 16
[6] Karthikeyana B 2010 *J. Appl. Phys.* **108** 084311
[7] Sen T et al 2007 *Appl. Phys. Lett.* **91** 043104
[8] Popov O et al 2006 *Appl. Phys. Lett.* **89** 191116
[9] Dong L et al 2012 *Opt. Lett.* **37** 34
[10] Xie Z et al 2009 *Opt. Commun.* **282** 439
[11] Aslan K et al 2005 *Curr. Opin. Biotechnol.* **16** 55
[12] De M et al 2008 *Adv. Mater.* **20** 4225
[13] Dong L et al 2011 *J. Eur. Opt. Soc.-Rapid Publ.* **6** 11019
[14] Dong L et al 2012 *IEEE J. Quantum Electron.* **48** 1010
[15] Pettingger B et al 2000 *Electrochemistry* **68** 942
[16] Michaels A M et al 2000 *J. Phys. Chem.* B **104** 11965
[17] Achammakurian et al 2002 *Laser Chem.* **20** 99
[18] Rajesh M et al 2007 *Appl. Opt.* **46** 106
[19] Lakowicz J R 2006 *Principles of Fluorescence Spectroscopy* (New York: Kluwer)