SHORT COMMUNICATION

Light Trapping to Amplify Metal Enhanced Fluorescence with Application for Sensing TNT

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Abstract Metal Enhanced Fluorescence (MEF) typically produces enhancement factors of 10 to 50. By using a polymer layer as the dielectric spacer enhancements as high as 1,600 can be observed. The effect occurs with a variety of different polymers and substrates, all of which act to trap light in the dielectric layer. This allows the fabrication of sensors with improved sensitivity as demonstrated for detection of trinitrotoluene (TNT).

Keywords Enhanced fluorescence · Polymer layer · Light trapping · TNT sensing

Introduction

Exploitation of the plasmon properties of metal nanoparticles is currently of interest. Coupling the electric field created by a plasmon to a molecule on the surface can lead to significant intensity increases in Raman spectra (surface enhanced Raman spectra, SERS) and in fluorescent spectra (metal enhanced fluorescence spectra, MEF) [1–8]. For SERS, typical enhancements can be 10^6 or greater while for MEF the enhancements are more modest, typically 10^1–10^2. We have been interested in using fluorescence methods for the detection of explosives [9]. A porous silicon (p-Si) substrate is used as the substrate for the fluorophore, which increases the surface area available to the analyte, thereby increasing the sensitivity. We presumed that adding a metal layer to the porous layer the sensitivity could be further improved by taking advantage of MEF. Optimized MEF structures require

a dielectric layer between the metal and the fluorophore and when we used a polymer as the dielectric the enhancements increased to 10^2–10^3.

We report here that using a polymer layer between a fluorophore and substrate provides an enhanced emission for a variety of polymers and substrates, including those that do not include a metal layer. The enhancement appears to arise from the ability of the dielectric layer to also act as a light trapping layer, i.e., the light makes a number of bounces between the substrate layer and the fluorophore layer, thereby being confined to the polymer layer. When the substrate contains a layer of silver nanoparticles the MEF effect is amplified cooperatively by the polymer effect. We exploit this effect to demonstrate improved sensitivity for the detection of trinitrotoluene (TNT).

Experimental Section

Silver coated porous silicon substrates, p-Si/Ag, were created by electrochemical etching [9] and reduction of silver nitrate solution on the freshly etched pores [10]. Flat silicon wafers (p-type <100>, Silicon Quest International) were first cut down to a 4×4 cm size and mounted in a Teflon etching chamber. An aqueous HF solution (100:100:90 H_2O: EtOH: HF) was poured over the wafer immediately before current was applied. Constant current was applied by a Keithley 2635A SYSTEM sourcemeter using 25 mA/cm² current for 190 s. The resulting p-Si had pores with approximately 10 μm diameter [9]. Freshly etched p-Si samples were then submerged in a 50 mM $AgNO_3$ solution for 14 min. A chosen polymer was spin-cast on the p-Si/Ag wafer at a rate of 1,200 rpm for 45 s (acceleration rate 1,296 /s/s), followed by drying in a 60 °C oven for 2 min to evaporate residual solvent. Polymer solutions used were 2 % w/v polyvinylidene difluoride, PVDF,

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in 90/10 (v/v) acetone/dimethyl formamide (DMF) mixture, 3 % w/v $[(CH_2CF_2)_{0.65}-(CHFCF_2)_{0.35}]_x$, co-polymer, in acetone/DMF, and 5 % w/v polymethylmethacrylate, PMMA, in toluene. 30 µL of the selected fluorophore (6.0×10^{-4} M of rhodamine 6G, Rh6G, dissolved in ethanol or 6.5×10^{-4} M methoxy-ethylhexyloxypolyphenylenevinylene, MEH-PPV, dissolved in methylene chloride), was applied to the p-Si/Ag/polymer samples and allowed to dry in air to complete the MEF substrates. For samples on flat Si or glass, the same coating procedure for the polymers and fluorophores was followed. The average area of the sample was 3.5 cm^2; using the densities of the fluorophores this gave an estimated thickness of 20 nm for Rh6G and 40 nm for MEH-PPV. Substrates were mounted on glass slides to fit the solid sample holder for the Horiba Fluorolog-3 instrument for fluorescence measurements and care was taken to ensure that the same spot was sampled in every measurement. The incidence angle was set to 55° from perpendicular, which was determined to provide the maximum response. For all measurements reported here, the slit width was set to 1 nm for both the excitation and emission monochromators. Reflection spectra were obtained using an Ocean Optics spectrometer with a reflectance probe at 90° incidence from the sample.

Results and Discussion

Figure 1 shows the emission spectra for rhodamine 6G (Rh6G) on several different substrates designed with a typical
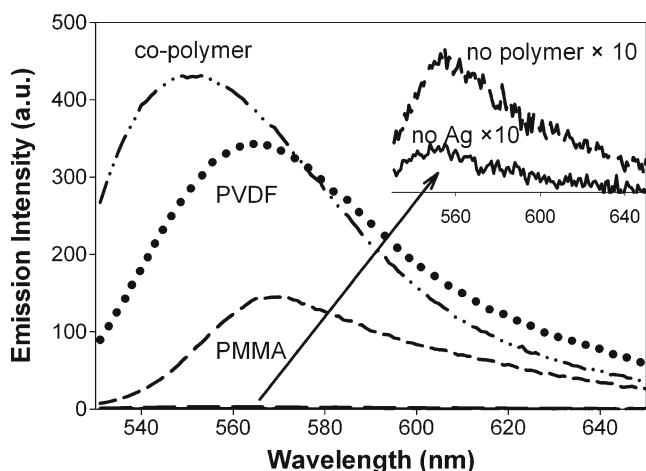
Fig. 1 Emission spectra of Rhodamine 6G coated on different polymers cast on a porous Si/Ag substrate. All spectra are referenced to the spectrum with no Ag and no polymer, p-Si/Rh6G (*solid line*). MEF samples were: no polymer, p-Si/Ag/Rh6G (*long dashed*); p-Si/Ag/PMMA/Rh6G (*short dashes*); p-Si/Ag/PVDF/Rh6G (*dotted*); and p-Si/Ag/co-polymer/Rh6G (*dot-dashed*). The *inset* shows the p-Si/Rh6G and p-Si/Ag/Rh6G spectra multiplied by 10. Excitation was at 521 nm and 1 nm slits were used for both the excitation and emission monochromator

MEF structure, i.e. substrate, Ag nanoparticle layer, dielectric layer, and fluorophore. When Rh6G is placed directly on p-Si a weak luminescence is observed with a maximum at 555 nm. When a layer of Ag nanoparticles (~100–200 nm thick islands, as estimated by AFM) is placed between the fluorophore and the p-Si the emission intensity increases by a factor of 3, which is typical for MEF with no dielectric layer. Using a transparent polymer as the dielectric spacer, giving a structure of p-Si/Ag/polymer/Rh6G, leads to dramatic enhancements, as shown in Fig. 1 (the spectra are referenced to the maximum of the p-Si/Rh6G sample). These are significantly increased compared to what is usually observed in MEF and is especially unusual since the polymer layers are ~10–20 times thicker than the usual dielectric layers used in MEF structures. There are also shifts of the wavelength maximum that are not typically seen in MEF, ranging from 553 to 570 nm.

To test the effect of different substrates, Rh6G was deposited onto polymers spin-cast onto a glass slide and a flat Si wafer. Neither of these substrates contained Ag,
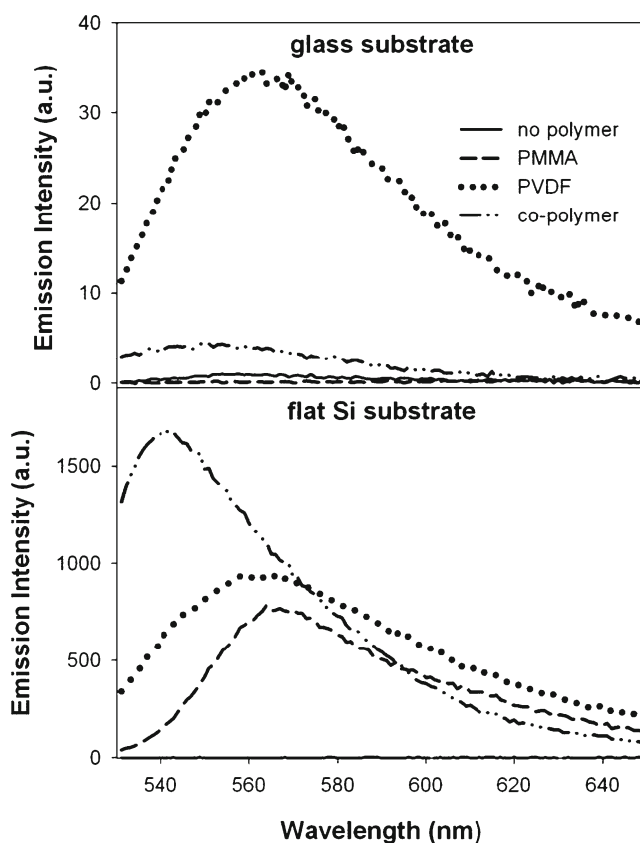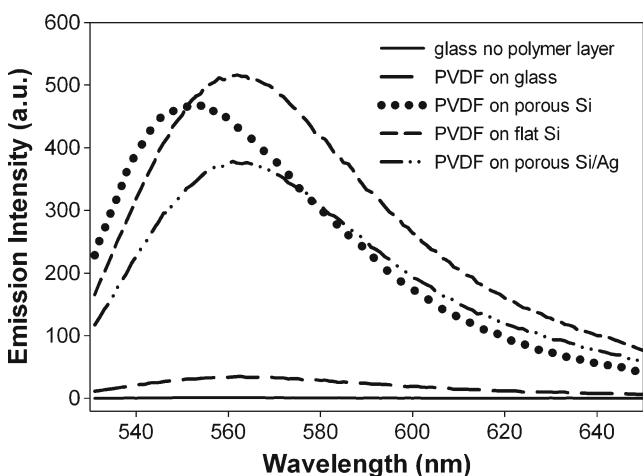

Fig. 2 Emission spectra of Rhodamine 6G coated on different polymers cast on a glass substrate (*upper*) and a flat Si substrate (*lower*). All spectra are referenced to the spectrum with no polymer (*solid line*). PMMA (*short dashes*), PVDF (*dotted*), and co-polymer (*dot-dashed*). Excitation was at 521 nm and 1 nm slits were used for both the excitation and emission monochromator
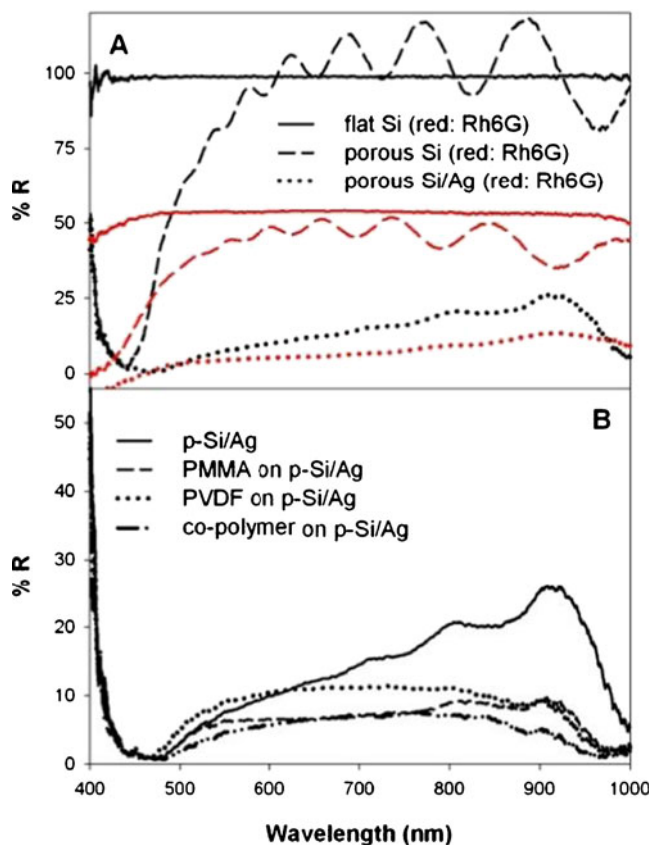
yet substantial enhancements were observed as shown in Fig. 2. Even with a glass slide substrate there is a modest enhancement, by as much as a factor of ~35 for PVDF. When the substrate is flat Si, again with no Ag, the polymers lead to enormous enhancements, as high as 1,600 for 0.3 μm thick co-polymer film. On the flat Si substrate there also is noticeable shift of the emission maximum, ranging from 560 nm for PMMA, 550 nm for PVDF, and 540 nm for the co-polymer. When Fabry-Perot modes are coupled to a plasmon resonance the absorption maximum can shift [11] and this should affect the emission maximum similarly. However, the flat Si is a semiconductor and is not expected to support a plasmon resonance in the visible region. Further, the observation of some enhancement on a glass substrate rules out any coupling to a plasmon resonance. Another possible explanation for the shift in the emission maxima is the difference in the polarity of each of the polymers. Environmental polarity is often observed to shift emission maxima in solution and that may contribute to the observed wavelength shift here, as well.

Figure 3 shows the emission spectra for different substrates all spin-cast with a ~0.3 μm PVDF film, normalized to Rh6G on glass with no polymer. When the substrate is glass, flat Si, or p-Si the enhancements are all comparable, ~400, relative to the glass substrates, glass/Rh6G. The enhancement more than doubles when Ag is deposited on the p-Si. This shows that the plasmon induced enhancement and the polymer amplification are cooperative.

One possible explanation for the observed enhancement effect is that the Rh6G is dissolved into the polymer layer when it is deposited. If this were to happen, then there would be less self-quenching from Rh6G and

Fig. 4 **a** Reflection spectra of flat Si substrate (*black solid line*), flat Si substrate coated with Rhodamine 6G (*red solid line*), porous Si substrate (*black dashed line*), porous Si substrate coated with Rhodamine 6G (*red dashed line*), Ag coated porous Si substrate (*black dotted line*), and Ag coated porous Silicon substrate coated with Rhodamine 6G (*red dotted line*). **b** Reflection spectra of Ag coated porous Si (*solid line*), ~310 nm PMMA on Ag/p-Si (*dashed line*), ~470 nm PVDF on Ag/p-Si (*dotted line*), and ~150 nm co-polymer on Ag/p-Si

an enhancement. This seems unlikely, however, because the solvent used to dissolve the Rh6G, ethanol, does not dissolve the polymers used here.
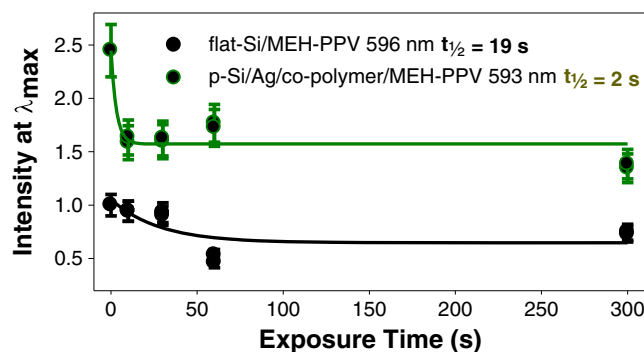
Fig. 3 Emission spectra of Rhodamine 6G cast on PVDF with different substrates. All spectra are referenced to Rhodamine 6G cast on glass with no polymer layer (*solid line*). PVDF on glass (*long dashes*), PVDF on porous Si (*dots*), PVDF on flat Si (*short dashes*), PVDF on Ag coated porous Si (*dot-dashed line*). Excitation was at 521 nm and 1 nm slits were used for both the excitation and emission monochromator

Fig. 5 Quenching of MEH-PPV at λmax (598 nm) upon exposure to TNT. *Black circles*—flat Si/MEH-PPV; *black line*—exponential fit with half-life=19 s; *green triangle*—p-Si/Ag/co-polymer/ MEH-PPV; *green line*—exponential fit with half-life 2 s. Intensities are referenced to the flat-Si/MEH-PPV value at $t=0$ s

Reflection spectra for the various layered structures were measured, as shown in Fig. 4. The effect of simply depositing Rh6G onto the substrate is shown in Fig. 4a using flat Si as the reference (using Si as the reference removed the large contribution arising from the Si reflectivity). In the absence of Rh6G, p-Si shows a fringing pattern resulting from the pore structure (~2 μm thick) but the fringing largely disappears when the Ag layer is added, indicating that the light does not pass through to the p-Si layer. The p-Si shows a resonance at 450 nm while the p-Si/Ag substrate shows minimal reflection throughout the visible region. Upon addition of Rh6G, reflection drops considerably in all cases and does not show any feature that could be assigned to the absorption maximum expected for Rh6G at 521 nm. The featureless response is assigned to diffuse reflection of the rough Rh6G surface since the Rh6G layer is too thin (20–40 nm) to exhibit a fringing pattern. Figure 4b shows the reflection spectra of different polymers, with no Rh6G, coated onto p-Si/Ag. The polymers, which are all transparent, all reduce the reflectivity compared to the bare p-Si/Ag, showing that the polymers trap the light within the polymer layer of the structure.

To test the utility of the enhanced fluorescent signal, samples were prepared using MEH-PPV on flat Si and p-Si/Ag/co-polymer substrates to be used for TNT sensing. MEH-PPV has been previously shown to be effectively quenched by nitroaromatics [9], while Rh6G has not been shown to interact with TNT in the gas phase. The p-Si/Ag/co-polymer/MEH-PPV structure showed a fluorescence enhancement compared to flat-Si/MEH-PPV, but the enhancement at the emission maximum (598 nm) was only about 2.5 times. It is not clear why the enhancement is so much less than observed with Rh6G, but may be related to the overlap of the excitation wavelength (495 nm) and the resonance observed in the p-Si. Some of the excitation light is undoubtedly lost into the tail of the p-Si absorption.

Figure 5 shows the effect of exposing flat-Si/MEH-PPV and p-Si/Ag/co-polymer/MEH-PPV samples to TNT. The decay of the emission maximum is plotted as a function of exposure time to vapors of TNT (formed from the natural vapor pressure of TNT at room temperature, which is in the ppb range [12]). Both samples exhibit a quenching of about 60 % of the initial signal in less than 100 s. For comparison, MEH-PPV coated onto p-Si also shows about a 60 % quench but requires ~300 s to reach this value. Notably, in the p-Si/Ag/co-polymer/MEH-PPV sample this quenching occurs significantly faster: the half-life for the flat-Si/MEH-PPV sample is 19 s while the half-life for the p-Si/Ag/co-polymer/MEH-PPV sample is only 2 s, nearly an order of magnitude improvement.

Conclusions

In conclusion, we have shown that by adding a light trapping layer to a MEF structure can increase the fluorescence signal intensity by a factor of several hundred to over 1,000. Further, when the light trapping layer is used in a TNT sensor, the exposure time to reach maximum quenching is reduced, an important quality required for improved sensors. Work to better understand the influence all of the parameters in the structures is underway.

References

1. Geddes CD, Lakowicz JR (2002) Metal-enhanced fluorescence. J Fluoresc 12:121–129
2. Geddes CD, Cao H, Gryczynski I, Gryczynski Z, Fang J, Lakowicz JR (2003) Metal-enhanced fluorescence (MEF) due to silver colloids on a planar surface: potential applications of indocyanine green to in vivo imaging. J Phys Chem A 107:3443–3449
3. Parfenov A, Gryzcynski I, Malicka J, Geddes CD, Lakowicz JR (2003) Enhanced fluorescence from fluorophores on fractal silver surfaces. J Phys Chem B 107:8829–8833
4. Lakowicz JR (2005) Radiative decay engineering 5: metal-enhanced fluorescence and plasmon emission. Anal Biochem 337:171–194
5. Aslan K, Leonenko Z, Lakowicz JR, Geddes CD (2005) Fast and slow deposition of silver nanorods on planar surfaces: application to metal-enhanced fluorescence. J Phys Chem B 109:3157–3162
6. Deng W, Goldys EM (2012) Plasmonic approach to enhanced fluorescence for applications in biotechnology and the life sciences. Langmuir 28:10152–10163
7. Gill R, Tian L, Somerville WRC, Le Ru EC, van Amerongen H, Subramanian V (2012) Silver nanoparticle aggregates as highly efficient plasmonic antennas for fluorescent enhancement. J Phys Chem C 116:16687–16693
8. Guzatov DV, Vaschenko SV, Stankevich VV, Lunevich AY, Glukhov YF, Gaponenko SV (2012) Plasmonic enhancement of molecular fluorescence near silver nanoparticles: theory, modeling, and experiment. J Phys Chem C 116:10723–11073
9. Levitsky IA, Euler WB, Tokranova N, Rose A (2007) Flourescent polymer—porous silicon microcavity devices for explosives detection. Appl Phys Lett 90:041904/1–041904/3
10. Zeiri L, Rechav K, Porat Z, Zeiri Y (2012) Silver nanoparticles deposited on porous silicon as a surface-enhanced Raman scattering (SERS) active substrate. Appl Spectrosc 66:294–299
11. Saison-Francioso O, Lévêque G, Akjouj A, Pennec Y, Djafari-Rouhani B, Szunerits S, Boukherroub R (2012) Plasmonic nanoparticles array for high-sensitivity sensing: a theoretical investigation. J Phys Chem C 116:17819–17827
12. Oxley JC, Smith JL, Luo W, Brady J (2009) Determining the vapor pressures of Diacetone diperoxide (DADP), and Hexamethylene triperoxide diamine (HMTD). Propellants Explos Pyrotech 34:539–543