Surface plasmon and green light induced polymerization in mesoporous thin silica films

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ABSTRACT

The near-field of surface plasmon resonances at planar metal surfaces is confined to the nanoscale but its resonance wavelength is located in the visible light range making it interesting for confining polymer functionalization of surfaces but incompatible with the majority of polymerization reactions. Here, fluoresceine as polymerization initiator allowing dye-sensitized polymerization with green light (438 – 540 nm) is demonstrated to allow polymer functionalization of mesoporous films deposited onto planar silver metal layers. The fluoresceine-induced polymer
functionalization of mesoporous silica films is investigated with respect to the influence of irradiation power, irradiation time and its potential to generate polymer gradients. Finally, the polymer functionalization of mesoporous films upon surface-plasmon initiated polymerization is demonstrated. Polymer functionalization thereby determines pH-responsive ionic mesopore accessibility. Consequently, these results present a sound basis for further nanoscale near-field induced polymer functionalization of porous films.

INTRODUCTION

Mesoporous materials and especially polymer-functionalized mesoporous films bear potential in the field of sensors, catalysis, membrane technology, and multifunctional devices. The fabrication of nanodevices containing functional mesoporous coatings is currently limited by the local resolution of structure generation and functionalization. In the context of polymer functionalization spatial control is usually achieved using photolithography. Local resolution is limited by Abbe’s law of diffraction and the applied wavelength is mostly limited to UV-light. Higher resolution polymer structures at planar surfaces have been e.g. obtained by using activation-deactivation processes or near field modes. Near field modes are characterized by a strong confinement into nanometer dimensions and can be generated at the surface of plasmonic metal nanoparticles, metal nanostructures, and metal films. The resonance wavelength can be tuned e.g. by nanostructure size or the used metal but is usually located in the visible light or even in the infrared wavelength range. Possibly due to the spectral mismatch between near field mode wavelengths and photopolymerization wavelengths surface plasmons are not typically used in photopolymerization, but usually known for sensing applications. Surface plasmon induced polymerizations are mainly focused on nanoparticles, nanorods and 3D hybrid materials. To use this concept systematically, e.g. in microelectronics and for mesoporous film functionalization,
methods for near-field induced polymerization at planar metal films or at metal nanostructures, such as microelectrodes, are needed. Together with recent developments in photopolymerizations, which currently explore possibilities to shift the initiation wavelength towards visible light and beyond, near-field initiated polymerizations can be investigated. Recent examples of visible light compatible controlled polymerization initiation are reported for atom transfer radical polymerization (ATRP) at 380 nm, iniferter-initiated polymerizations at 460 – 530 nm and visible light mediated ring-opening metathesis polymerization (ROMP) between 450 and 480 nm. Visible light induced polymerizations can be of advantage, because side reactions originating from UV-irradiation can be avoided. Very recently, first examples of plasmon induced polymerizations are reported from grated gold surfaces by surface initiated RAFT and NMP. In addition to the before mentioned polymerization strategies, dye sensitized polymerizations are a versatile tool because they are tunable over the entire visible light spectrum from 400 nm to 650 nm, due to the broad range of applicable dyes although not offering accurate controlled polymerization conditions typically found in atomic transfer radical polymerization (ATRP), or reversible addition-fragmentation chain transfer polymerization (RAFT).

The combination of near-field modes and surface plasmons with dye sensitized polymerizations has been demonstrated for metal nanoparticles. In a previous study we showed visible light driven dye sensitized polymerizations in mesoporous silica, using 2-chlorothioxanthone, 4′,5′-dibromofluoresceine and methylene blue. Furthermore, methylene blue was applied successfully for near-field induced polymerization in mesoporous silica films at planar gold surfaces using a 633 nm He-Ne laser. To design complex and multifunctional mesopores and to broaden the applied metal films polymerization strategies using different wavelengths are required. Here, we
demonstrate the application of 4′,5′-dibromofluoresceine to initiate polymerization at 532 nm. Even at low spectral overlap a polymer functionalization is observed, indicating a strong surface plasmon enhancement of silver films at the applied wavelength.

EXPERIMENTAL SECTION

Chemicals. Tetraethylorthosilicate (98 %, reagent grade) (TEOS) and Pluronic® F127 have been purchased from Sigma-Aldrich. Dimethylaminoethyl methacrylate (DMAEMA) has been purchased from Sigma Aldrich and destabilized over a γ-alumina column, prior to use. [Bis(2-hydroxyethyl)-3-amino]propyl-triethoxysilane (65 % in ethanol) has been purchased from abcr Karlsruhe, dry Toluene (0.5 ppm residual water content) from AppliChem, and 4′,5′-dibromofluoresceine from Alfa Aesar. All chemicals have been used as received unless otherwise noted.

Mesoporous film preparation. First a prehydrolysis solution is prepared: ethanol (42 mL) is poured into a one-necked round flask and TEOS (53.5 mL; 50.3 g; 0.24 mol) is added under mild stirring. A freshly prepared hydrochloric acid solution [Hydrochloric acid (37 %); 0.06 mL is diluted with deionized water (4.2 mL)] is added. The one-necked flask is equipped with a reflux-condenser and the reaction mixture is heated up to 80 °C for 20 minutes. Subsequently, the solution is stirred for another 80 minutes while cooling down to ambient temperature. The solution is stored at -20 °C and used for preparation of the dip-coating solution.

Based on this prehydrolysis solution a solution for mesoporous film dipcoating (1 TEOS: 0.0082 F127: 40 EtOH: 10 H2O: 0.014 HCl) is prepared: The prehydrolysis solution (6.39 g) is poured into a glass bottle equipped with a magnetic stirrer. Ethanol (38 mL) is added to the solution under stirring (400 rpm). Pluronic® F127 (1.81 g, 0.14 mmol) is added to the solution. A freshly prepared hydrochloric acid solution consisting of hydrochloric acid (37 %; 0.016 mL) diluted with 2.8 mL
deionized water, is added to the suspension. The solution is stirred overnight prior to mesoporous film dip-coating.

For mesoporous film preparation glass substrates and silicon wafers are dipcoated using a withdrawal speed of 2 mm/s under controlled environmental conditions (50 % rel. humidity, 22 – 25 °C). Subsequently, the films are stored under these conditions for 60 minutes followed by a temperature treatment at 60 °C for 60 minutes, followed by a temperature increase to 130 °C within 10 minutes keeping 130 °C for 60 minutes. The final heating to 350 °C for 2 h using a heating rate of 1 °C/min results in template calcination.

In case of silver coated LaSF9N glasses the final temperature is adjusted to 200 °C for 2 h using a heating rate of 1 °C/min and the remaining Pluronic® F127 template is removed by a subsequent chemical extraction in absolute ethanol for 72 hours at 70 °C or in 0.01 M ethanolic hydrochloric acid solution for 24 hours as described within the literature.36

**Thermal evaporation of silver on LaSF9N glass.** Silver films for SPR experiments are prepared by thermal evaporation using a Creamet 300 V2 thermal evaporation system (Creavac, 01159 Dresden). First a 3 - 5 nm thick chromium layer is deposited, promoting silver layer adhesion, followed by a 50 nm silver layer evaporation. The metal coated LaSF9N substrates are stored under nitrogen atmosphere until further use.

**Cointitiator immobilization.** In a dried 250 mL Schlenk flask a 0.01 weight-% cointitiator solution is prepared by dissolving 0.035 mL [Bis(2-hydroxyethyl)-3-amino]propyl-triethoxysilane (0.06 mmol) in 230 mL of dry toluene. The films are placed into a heat-dried flattened Schlenk-flask under nitrogen atmosphere, covered with the cointitiator solution, and placed into a thermostat at 80 °C for five hours. Afterwards, residual unbound silane is removed by extraction in ethanol
for 1 hour. Mesoporous silica films immobilized on silver coated LaSF9N glass are functionalized for only one hour and rinsed with toluene, in order to avoid silver layer destruction.

**Dye sensitized polymerizations.** An aqueous polymerization solution containing DMAEMA (225 mg/mL; 1.43 mol/L) and 4’,5´-Dibromofluorescein (600 µg/L; 0.12 µmol/L) is prepared with a sodium hydrogen carbonate solution (0.1 mol/L) according to previous work from our group.\textsuperscript{35} The coinitiator functionalized films are placed into the solution. The solution is degassed by bubbling nitrogen for 1 minute. The samples are irradiated with the respective light sources, e.g. green laser (Laser 2000, 532 nm, 200 mW) or a lamp (LUMATEC, 460 nm - 540 nm filter, 6 mW/cm²) for the indicated reaction times and light intensities. After irradiation residual monomer is extracted in water for 30 minutes.

**Surface plasmon induced polymerizations.** Surface Plasmon Resonance Spectroscopy (SPR) induced polymerizations were performed in the Kretschmann configuration.\textsuperscript{37} For these measurements the sample glass slide (LaSF9N glass, Hellma Optik GmbH Jena, refractive index $n = 1.8449$, corresponding to $\varepsilon = 3.4037$) was installed into a homemade flow cell (volume ~ 40 µl) and the backside was optically (refractive index) matched with the base of the glass prism (Cargille labs, refractive index $n = 1.7000$, corresponding to $\varepsilon = 2.8900$). Monochromatic and linear, transverse-magnetic polarized (Glan-Thompson polarizer, B. Halle) laser light (Diode pumped solid state laser, Laser 2000, $\lambda = 532$ nm, 200 mW) was directed through the prism onto the sample substrate. By variation of the angle of incidence $\theta$ (two-cycle goniometer, resolution 0.005°, Huber) and detecting the intensity of the reflected laser light $I(\theta)$ with a photodiode (BPW 34B silicon photodiode, Siemens) an angular dependent spectrum was recorded in air and water or 0.1 M NaHCO$_3$-solution. SPR measurements were performed at 0.1 mW, corresponding to 100 % reflectivity. The polymerization solution, containing 4´,5´-dibromofluoresceine (600 µg/L;
0.12 μmol/L) and DMAEMA (225 mg/mL; 1.43 mol/L) was flown constantly during one experiment at a flow rate of 2 μL/min. Polymerization was performed at the indicated surface plasmon resonance angle, time and laser beam power. The laser power of the polymerization is adjusted by adjusting the angle of the first passed polarizer, according to a two polarizer system described by Malus’ law. The surface plasmon resonance angle for polymerization is determined after flooding the SPR measurement cell with the respective polymerization solution. Polymerization is carried out for the indicated times and polarizer adjustment at a fixed angle within the surface plasmon. After polymerization the measurement cell is flooded with water or sodium hydrogencarbonate solution for 30 minutes until a measurement in aqueous medium is conducted. The substrates are dried and a final measurement at air is conducted. SPR spectra are fitted to simulations via WinSpall software (Version 3.02; 2009, Restec) according to film thickness and dielectrical constant of the mesoporous silica film (one layer). The thickness of the chromium and the silver layer is determined by a separate measurement of the unmodified metal film.

**Infrared (IR) spectroscopy.** IR spectra are recorded in attenuated total reflection (ATR) mode using a Spectrum One FT-IR spectrometer from Perkin-Elmer. Corresponding spectra are recorded directly from the substrate from 4000 to 650 cm\(^{-1}\). The spectra are background corrected and normalized to the Si-O-H stretching vibrational band at 915 cm\(^{-1}\) on glass or Si-O-Si assymetric stretching vibrational bands on silver, which are observed at 1200 cm\(^{-1}\) or 1100 cm\(^{-1}\) and are assigned to cyclic Si-O-Si and Si-O-Si chains respectively.\(^{38-39}\) C=O vibrational intensity at 1728 cm\(^{-1}\) is obtained by subtraction of the baseline between 4000 and 1300 cm\(^{-1}\) from the maximum absorbance at 1728 cm\(^{-1}\).
Determination of porosity and pore volume filling fraction. The porosity and the pore filling fraction of mesoporous silica films before and after PDMAEMA functionalization are extracted from the refractive indices according to Brüggemann effective medium theory as previously described in literature.\textsuperscript{40-43} For a detailed description of the Ellipsometry measurements see the supporting information (Figures S12 to S13, Tables S1 and S2).

CO\textsubscript{2}-Plasma treatment. CO\textsubscript{2}-plasma treatment is performed with a Femto SRS plasma generator (Diener electronics, model Femto, 13.56 MHz, maximum RF power: 200 W). The samples are degassed and CO\textsubscript{2} gas is introduced. The RF generator is switched on for 12 seconds after a stable pressure of 0.3 mbar is achieved as illustrated in literature.\textsuperscript{44}

Cyclic voltammetry. Cyclic voltammograms are recorded with a Metrohm Autolab PGSTAT302N. The potentiostat is controlled by Nova 10.1 software. The measurement set up is arranged with three electrodes. A graphite counter electrode, an Ag/AgCl reference electrode (BASi RE-6) and an ITO working electrode (Delta Technologies, USA, 4-8 Ω). The maximum peak current density is obtained by dividing the maximum peak current by the ITO contact area of 0.21 cm\textsuperscript{2}. Measurements are carried out using a 0.1 molar KCl-solution containing 1 mmol/L potassium hexacyanoferrate III (K\textsubscript{3}[Fe(CN)\textsubscript{6}]) or hexaamminoruthenium-III-chloride ([Ru(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{3}). Acidic measurement conditions (pH 2) are adjusted with hydrochloric acid and basic conditions (pH 10) with sodium hydroxide solution. The cyclic voltammograms are recorded at different scanrates in the following order: 0.2 V/s, 0.1 V/s, 0.025 V/s, 0.3 V/s, 1 V/s and 0.2 V/s.
RESULTS AND DISCUSSION

**Figure 1.** a) Scheme showing dye sensitized laser induced polymerization of dimethylaminoethylacrylate (DMAEMA) with 4’,5’-dibromofluoresceine on coinitiator-functionalized, CO\textsubscript{2}-plasma treated mesoporous silica films on glass substrates. b) ATR IR spectra of an unfunctionalized mesoporous silica film (black), a coinitiator functionalized mesoporous silica film (red) and a mesoporous silica film after dye sensitized polymer functionalization (blue). 
The dye sensitized polymerization is conducted by visible light irradiation of a coinitiator functionalized mesoporous silica film in a solution containing DMAEMA (1.4 mol/L), 4’,5’-dibromofluoresceine (1.2 mmol/L) in sodium hydrogencarbonate solution (0.1 mol/L).

In order to investigate the potential of fluoresceine dye sensitized polymerizations (see also Figures S1 to S7 for general details) for near-field mode initiated polymerization in mesoporous films at 532 nm, a polymerization is carried out using coinitiator functionalized, CO\textsubscript{2}-plasma treated mesoporous silica films. The coinitiator [Bis(2-hydroxyethyl)-3-amino]propyl-triethoxysilane is grafted to the mesopore wall and initiates the polymerization after radical generation in a redox reaction with the dye triplet state.\textsuperscript{14} The CO\textsubscript{2} plasma treatment destroys organic moieties and thus the grafted coinitiator at the external planar mesoporous film surface. This results in polymer functionalization exclusively within the mesoporous film. The energy and time dependence of mesoporous film polymer functionalization was analyzed. It has to be noted
that the energy dependence and especially the minimal energy per time at which polymerization is observed is a determining parameter for near-field induced polymerizations.\textsuperscript{14,45} To investigate the potential for local resolution, the resulting polymer amount is analyzed at the laser focused spot as well as in 5 mm and 10 mm distance using infrared spectroscopy monitoring the 1728 cm\textsuperscript{-1} polymer C=O stretching band intensity within normalized (915 cm\textsuperscript{-1} Si-O-H vibrational band)\textsuperscript{46} ATR-IR spectra (Figure 1). The presence of the C=O stretching band at 1728 cm\textsuperscript{-1} in ATR-IR spectra after 4’,5’-dibromofluoresceine sensitized polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) illustrates successful PDMAEMA functionalization. Under the applied conditions, polymer functionalization of the mesoporous silica films is already induced at a laser beam power of 0.1 mW (532 nm wavelength; laser spot diameter approximately 1.5 mm) using 4’,5’-dibromofluoresceine (Figure 2 a) for a polymerization time of 30 minutes. At an applied power of up to 0.3 mW (Fig. 2 a, blue box), polymer functionalization has been limited to the laser focused spot for polymerization times of up to 30 minutes (see also Figure S8). The largest observed polymer amount which could still be confined to the laser focused spot (C=O stretching band intensity of 0.006 at 1728 cm\textsuperscript{-1}) is observed for an irradiation time of up to 60 minutes at the relatively low laser power of 0.3 mW (Figure 2 b). A prolonged irradiation time of 120 or even 240 minutes is accompanied by polymer formation at 5 mm and even 10 mm distance from the laser focused spot (Figures S9 – S10). Correlating the obtained ATR-IR results to pore filling studies (Figure S12 – S13, including Tables S1 and S2, supporting information) indicates that under the applied conditions discussed in Figure 2 no highly filled mesopores are obtained and pore filling upon irradiation with 0.3 mW are in the range of ~ 30 vol%. The mesoporous film thickness before and after polymerization as detected by ellipsometry does not change significantly (Figure S13, a), indicating that the polymerization exclusively occurred within the mesopores and
not on the surface of the film. This, in turn, can be attributed to the CO$_2$ plasma treatment, which efficiently destroyed the co-initiator located at the external mesoporous film surface (Figure S13). An increasing C=O vibrational band intensity at 1728 cm$^{-1}$ corresponds to an increase in mesopore volume filling fraction. Thus, a pore volume filling of up to 30 vol % corresponding to an IR C=O vibrational band intensity at 1728 cm$^{-1}$ of 0.009 relative to the Si-O-H vibrational band intensity at 915 cm$^{-1}$ is observed.

An increasing laser irradiation power (e.g. 18.4 mW (Figure 2 c) or 140 mW (Figure 3 b) results in increasing polymer amount as well as it leads to polymer functionalization at a larger distance from the laser spot. The measured C=O vibrational band intensity of 0.006 at 1728 cm$^{-1}$, 60 min 0.3 mW within the laser spot corresponds to 50 % of the maximum C=O vibrational band intensity of 0.012 at 1728 cm$^{-1}$ obtained for an irradiation power of 18.4 mW and identical irradiation time of 60 minutes in the laser spot (compare Figures 2 b and 2 c). Consequently, applying an irradiation power of 18.4 mW (Figure 2 c) leads to almost two times higher polymer amount in the mesopores corresponding to a pore filling of ~50 vol%. An even further increasing irradiation power of 140 mW (Figure 3 b) for 60 minutes shows a further increase in the C=O stretching band intensity by a factor of two, indicating highly filled mesopores (pore filling > 90 vol%, Figure S13, b). At the same time increasing irradiation power leads to a loss of local resolution. For example, polymer is generated even at 10 mm distance from the laser spot after irradiation at 18.4 mW for only 10 minutes reaction time (Figure 2 c), as evidenced by the presence of the CO stretching band of the polymer (Figure 2 a). Under the applied conditions irradiation power of 18.4 mW or higher do not result in laser spot limited polymer functionalization even for short irradiation times of 10 minutes (Figure 2 c).
Most probably increasing irradiation power results into an increasing number of excited dye molecules, which induces an increasing number of radicals to initiate the polymerization at the pore wall surface but as well an increasing number of radicals in solution diffusing away from the laser spots. In order to achieve a laser spot limited polymer functionalization in x-y direction a locally limited radical concentration and diffusion time and thus short polymerization times seem to be favorable. If larger polymer amounts are required and laser power is increased the polymerization time has to be even further reduced (compare e.g. Figure S11).

In summary, the highest polymer amount exclusively located within the laser spot (~30 vol% pore filling) were obtained for low irradiation power (0.3 mW) and reaction times up to 60 minutes. With increasing laser power of 18.4 mW, a maximum pore filling of ~50 vol% was achieved for 60 minutes reaction time while the polymer functionalization could not be limited to the laser spot under the applied experimental conditions. The highest pore filling was obtained using 140 mW irradiation for 60 minutes resulting in highly filled pores within the laser spot (Figure S11, Figure 3b).
**Figure 2.**

**a)** Power dependence of PDMAEMA polymerization under irradiation with a 532 nm laser (approximate spot diameter 1.5 mm) monitored by plotting the C=O vibrational band intensity at 1728 cm\(^{-1}\) of an IR spectrum normalized to the Si-O-H band at 915 cm\(^{-1}\) vs the polarizer angle from ATR-IR measurements for a fixed irradiation time of 30 minutes. The polarizer angle is used to adjust the laser power (magenta dots). The color correspond to the location of the laser spot (black) as well as 5 mm (red) and 10 mm (blue) distance from the laser spot. Error bars are based on three independent polymerization reactions.

**b, c)** Time dependence of PDMAEMA functionalization as detected by the C=O vibrational band intensity at 1728 cm\(^{-1}\) for **b)** low (blue}
box, 0.3 mW, approximate spot diameter 1.5 mm) and c) high laser beam power (green box, 18.4 mW, approximate spot diameter 1.5 mm).
Figure 3. a, b) ATR IR spectra of a mesoporous silica film supported on indium tin oxide (ITO) coated glass substrates after dye sensitized polymer functionalization. A coinitiator functionalized and CO$_2$-plasma treated mesoporous silica film in solution containing DMAEMA (1.4 mol/L), 4',5'-dibromofluoresceine (1.2 mmol/L) in sodium hydrogen carbonate solution (0.1 mol/L) was irradiated with a green laser (Laser 2000, 532 nm, 200 mW, 1.5 mm approximate spot diameter) for 60 minutes. a) Irradiation at 0.5 mW for locally resolved polymer functionalization at the laser spot (black), 1 mm lower position (blue), 1 mm to the right (cyan blue), 1 mm to the left (magenta) and 5 mm higher position than the laser focused spot (olive green) b) Irradiated with 140 mW and IR spectra recorded at the laser spot (black), 5 mm higher position (red), 2 mm lower position (blue), 2 mm to the right (cyan blue), 2 mm to the left (magenta) and 10 mm higher position than the laser focused spot (olive green). c-e) Cyclic voltammograms recorded with a scan rate of 0.2 V/s of a mesoporous silica film (black), a coinitiator functionalized and CO$_2$ plasma treated mesoporous silica film (red), a mesoporous silica film after polymerization with 0.5 mW at the laser focused spot (blue) and after polymerization with 140 mW at the laser focused spot (cyan blue). c) Cyclic voltammograms for [Ru(NH$_3$)$_3$]$^{3+/2+}$ at pH 10 d) for [Ru(NH$_3$)$_3$]$^{3+/2+}$ at pH 2 e) for [Fe(CN)$_6$]$^{3-/4-}$ at pH 10 and f) for [Fe(CN)$_6$]$^{3-/4-}$ at pH 2.

To investigate the influence of the obtained polymer amount variation and localization the ionic mesopore accessibility is characterized. Therefore, the polymerization conditions are adjusted such that this area is entirely modified with PDMAEMA (Figure 3 a, b). Two mesoporous films are characterized. One irradiated with 0.5 mW within the laser spot (Figure 3 a) and one irradiated with 140 mW within the laser focused spot (Figure 3 b). Upon irradiation with 0.5 mW within the laser spot (Figure 3 a) the maximum C=O vibrational band intensity at 1728 cm$^{-1}$ on coinitiator
functionalized and CO$_2$-plasma treated mesoporous silica films is three times lower than after irradiation with 140 mW (Figure 3 b). In case of the laser spot limited polymerization achieved upon irradiation with 0.5 mW for 30 minutes (Figure 3 a) a polymer pore filling of approximately 30 vol% at the laser spot region is obtained. In case of irradiation with 140 mW for 60 minutes (Figure 3 b) a polymer gradient in pore filling from highly filled mesopores at the laser spot to 30 vol% at 5 mm and to 10 vol% at 10 mm distance is obtained (compare Figure S11). The achieved polymer amounts are in good agreement with the results shown in Figure 2 b) and c) considering energy and time dependence.

Ionic mesopore accessibility of these samples is characterized within an area of 0.21 cm$^2$ (diameter 5.2 mm) using cyclic voltammetry. The charged probe molecules are detected at an ITO electrode below the mesoporous film in case these are able to access the mesopores. The unmodified mesoporous silica film (Fig. 3 c-f black) shows the expected pre-concentration of positively charged [Ru(NH$_3$)$_3$]$^{3+/2+}$ ions at pH 10, reflected by an increase in maximum peak current and peak broadening (Figure 3c, black) as compared to mesopores at a neutral pH (Figure 3d, black). This preconcentration at basic pH results from electrostatic attraction by the deprotonated silanol groups at the mesopore wall. It has to be noted that recent studies emphasize the role of mesoporous film instabilities at basic pH especially together with applying potentials.$^{47}$ To avoid misinterpretations arising from such detrimental effects relatively short measuring times have been maintained during cyclic voltammetry measurements.

Subsequent functionalization with the coinitiator and PDMAEMA leads to partial shielding of the deprotonated silanol groups. Consequently, at basic pH pore accessibility for [Ru(NH$_3$)$_3$]$^{3+/2+}$ is electrostatically less favored as compared to unfunctionalized mesoporous silica films resulting in a decreasing peak current density (Figure 3 c). Functionalization with PDMAEMA additionally
introduces pH-responsive, positive charges further hindering mesopore accessibility for \([\text{Ru(NH}_3\text{)}_3]^{3+/2+}\) at acidic pH. Interestingly, no complete ion exclusion is achieved for \([\text{Ru(NH}_3\text{)}_3]^{3+/2+}\) at pH 10 even after PDMAEMA functionalization (Figure 3c, cyan). This result indicates the dominating role of the remaining silanol groups in the area with low PDMAEMA pore filling where the polymer is not able to overcompensate the negative silanol-based charges at the pore wall as well as remaining unfunctionalized mesopores next to the laser spot region. This indicates the potential of gradients for transport control.

Conversely, \([\text{Fe(CN)}_6]^{2/-3-}\) is excluded from mesopores in case of unmodified negatively charged silica at basic pH and becomes increasingly electrostatically attracted upon functionalization with positively charged co-initiator and PDMAEMA (Figure 3e, black). As a result an increase in maximum peak current density \((j_p)\) proportionally reflects increasing polymer amount with increasing irradiation power. Polymerization under 140 mW irradiation (Figure 3b) results in factor 2-3 higher amounts of PDMAEMA within the area of the CV measurement cell as compared to irradiation using 0.5 mW (Figure 3a). This increase in polymer amount is reflected in the CV measurements, which show an increase in the electrostatic pre-concentration of \([\text{Fe(CN)}_6]^{2/-3-}\) by a factor of ~2.5 at pH 2 as well as at pH 10.

Increasing amount of PDMAEMA, achieved upon irradiation with higher power of 140 mW, leads to exclusion of positively charged \([\text{Ru(NH}_3\text{)}_3]^{3+/2+}\) at pH 2 in case a critical polymer amount is grafted and all pores are functionalized (Figure 3d, cyan). At pH 2 and thus in the presence of protonated coinitiator and PDMAEMA negatively charged \([\text{Fe(CN)}_6]^{2/-3-}\) probe molecules are increasingly pre-concentrated within the mesopores with increasing PDMAEAMA pore-filling (Figure 3f). Hence, higher peak current densities as compared to pH 10 are observed indicating the remaining influence of Si-O⁻ negative charges at pH 10.
In summary, increasing polymer pore filling and varying gradients by tuning irradiation power and time is possible and results in gradual control of ionic pore accessibility. To achieve polymer functionalization of mesoporous films with nanoscale local limitation we investigate near-field modes originating from thin metal films as light source for polymerization initiation. In this context, we investigate polymer functionalization of mesoporous films initiated by surface plasmons at a wavelength of 532 nm.

**Figure 4. a, b)** Exemplary surface plasmon resonance spectra of two individual polymerization experiments recorded in air before (black and magenta) and after plasmon induced polymerization (blue and dark yellow) in cointiator-functionalized mesoporous silica films supported on a thin silver film. Dotted lines show measurements, solid lines represent fits. $\theta_{pol}$ shows the chosen plasmon resonance angle for the polymerization in presence of monomer dye solution. The respective polymerization angle is illustrated by a vertical black line inside the SPR spectra. **c)** ATR IR spectra of cointiator-functionalized mesoporous silica films on silver supports before polymerization (black and magenta spectra) and after polymerization next to the plasmon
resonance reflectivity minimum with a green laser (532 nm; &lt;0.1 mW blue; 0.018 mW dark yellow; encoupled power: 2 % blue and 8 % dark yellow) (blue and dark yellow spectra). The irradiation time for polymerization was fixed to 30 minutes. d) and e) SEM cross-section measurements of mesoporous silica films deposited on silver coated LASF9N glass and transferred onto silicon wafers. d) SEM cross-section of a coinitiatorfuntionalized mesoporous silica film before surface plasmon induced polymerization and e) after surface plasmon initiated 4′,5′-dibromofluoresceine sensitized polymerization of DMAEMA at the beginning of the plasmon for 30 minutes.

To transfer the fluoresceine dye sensitized polymerization to initiation by surface plasmons, mesoporous silica films are deposited onto silver coated LaSF9N glass substrates. Surface plasmon resonance (SPR) spectroscopy is performed in the Kretschmann configuration using the same green laser (Laser 2000, 532 nm, 200 mW) as above. The power of the irradiation beam is adjusted to below 0.1 mW, below the threshold to induce polymerization solely under laser irradiation. Surface plasmon induced polymerization can be carried out within the reflectivity minimum but as well works if carried out at an angle next to the minimum and thus at lower energy (Figure 4). The corresponding SPR spectra recorded in air before and after the polymerization as well as the SPR spectrum in water are shown in Figure 4 a) and b). Exemplary IR spectra, normalized to the highest band, either the asymmetric Si-O-Si stretching vibrational band at 1100 cm\(^{-1}\) for Si-O-Si chains or to the asymmetric Si-O-Si stretching vibrational band at 1200 cm\(^{-1}\) for cyclic Si-O-Si species,\(^{39}\) are depicted in Figure 4 c. Upon polymerization the C=O stretching band intensity at 1728 cm\(^{-1}\) increases to 0.04 (Figure 4 c blue and dark yellow spectra). The presence of a polymer on the substrate indicates that the enhancement of the surface plasmon (Figure S19-S22) seems to be sufficient to initiate a polymerization, although only a small ratio (8 % in case of Figure 4 b)
based on the measured reflectivity reduction at the chosen angle as compared to the measured reflectivity at total internal reflexion) (See also Figures S17 – S18) of the initial laser beam power of 0.018 mW (Figure 4 b) irradiated onto the prim is coupled into the silver film an available to excite the surface plasmon. The initial SPR spectra in contact with air before polymerization are comparable for both investigated films (Figure 4 a black, Figure 4 b magenta) showing a resonance angle around 55° and 57° as well as an incoming leaky optical waveguide mode. Fitting the SPR spectra to the waveguide mode at 22° and the surface plasmon at 55 – 57° (Figure 4 a,b black and magenta spectrum) a film thickness of 230 - 245 nm and refractive index of 1.311 – 1.335 before polymerization is determined. After having been in contact with polymerization solution under surface plasmon irradiation a film thickness and refractive index in contact with air of 143 – 163 nm and 1.4 are determined (Figure 4 a, blue). As two parameters are used to fit the surface plasmon spectrum, two sets of parameters can be obtained for the spectrum after polymerization (Figure 4 b, dark yellow): Either a thickness of 205 nm and a corresponding refractive index of 1.2 or a thickness of 49 nm and a refractive index of 1.4. In case of successful PDMAEMA functionalization, as indicated by ATR-IR (Figure 4 c), the refractive index would be expected to increase as compared to the unfunctionalized mesoporous film. This, in turn, results in a shift of the surface plasmon to higher resonance angles assuming constant film thickness. In contrast to this expectation the surface plasmon resonance angle not always shows this expected shift and sometimes even shifts to lower resonance angle as observed in Figure 4 b (magenta, dark yellow). Based on the SPR spectra after polymerization the film thickness is expected to be below 200 nm as no leaky optical waveguide mode is observed any more (Figure 4 a, b, blue and dark yellow spectra). It has to be noted that unambiguous fitting of film thickness and refractive index is only possible in case of at least one present leaky optical waveguide mode together with the surface
As the SPR spectra after polymerization do not unambiguously show refractive index and film thickness increase but infrared spectroscopy suggest PDMAEMA functionalization, we hypothesize that mesoporous silica film degradation due to the combination of plasmon irradiation and contact with the applied basic polymerization solution. This is supported by SEM images of a following polymerization experiment for 30 minutes at the beginning of the surface plasmon resonance (next to the plasmon resonance minimum angle) (Figure 4 d, e Figure S15, S16), showing film thickness decrease but apparently intact mesoporous film structure (no cracks) of the remaining film after two hours contact to the applied polymerization solution without irradiation. Interestingly etching processes have recently been used to allow ultrathin mesoporous film generation. Following this logic the combination of ultrathin (~ 30 nm film thickness, Figure 4 e) polymer-functionalized mesoporous films can be prepared in a one step process by combining a basic polymerization solution and plasmon irradiation. This indicates that polymerization times as short as possible would be favorable.

Furthermore, it is remarkable that the surface plasmon induced 4´-5´-dibromofluoresceine dye sensitized polymerization at 532 nm is already initiated at the beginning of the surface plasmon coupling (reflectivity decrease) and does not require irradiation at the surface plasmon resonance angle (minimum reflectivity of SPR spectra). This especially holds true as the spectral overlap between 4´-5´-dibromofluoresceine absorption and laser wavelength (Figure S1) is relatively low. This observation notably indicates a significant enhancement as supported by theoretical estimations (Figure S19-S22). This is in agreement with reported enhancement factors as e.g. for planar silver irradiated with 633 nm enhancement factors of up to 80 are determined in literature corresponding to theoretical estimation (Figure S22). Plasmon propagation in x-y direction has to be assumed in the range of below 20 µm.
CONCLUSION

Visible light-induced functionalization of mesoporous films at 532 nm with millimeter scale gradients has been demonstrated using fluoresceine-dye sensitized polymerization. The polymer amount deposited within the mesopores can be controlled by the irradiation power and irradiation time. The varying polymer amount can be used to alter the mesopore accessibility for ions, as detected by cyclic voltammetry using [Fe(CN)$_6$]$^{3-}/^{3-}$ and [Ru(NH$_3$)$_3$]$^{3+/2+}$ probe molecules. Near field induced polymerization has been achieved at 532 nm using planar silver metal layers in the Kretschmann configuration and fluoresceine dye sensitized polymerization. Polymer functionalization of mesoporous coatings on silver layers can be achieved already using very low energy coupling next to the plasmon minimum reflectance and tested laser power of 0.018 mW although the overlap between laser wavelength and dye absorption is relatively low indicating the highly efficient effect of the near field enhancement. It has to be noted that silica mesopores experience film etching (film thickness reduction) under plasmon irradiation in contact with basic polymerization solution. This as well supports the observation of a field enhancement and demonstrates that this approach can be used to generate ultrathin polymer functionalized mesoporous films in a one step process by combining a basic polymerization solution and plasmon irradiation. On the other hand polymerization conditions as well as mesoporous film composition and with this stability have to be optimized in case etching is to be avoided.

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ASSOCIATED CONTENT

The Supporting Information is available.

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The authors declare no competing financial interest.
REFERENCES


