Supporting Information

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Thermoplasmonic-Activated Hydrogel Based Dynamic Light Attenuator

*Filippo Pierini, Alexa Guglielmelli, Olga Urbanek, Pawel Nakielski, Luigia Pezzi, Robert Buda, Massimiliano Lanzi, Tomasz A. Kowalewski, and Luciano De Sio**

Supporting information 1

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The stability of the P(NIPAm-*co*-NIPMAm) /GNR samples after a prolonged storage time in water was verified by performing a detailed characterization of the morphological and optical properties. Four identical samples (see Materials and methods for technical details) were fully immersed in distilled water and investigated at t= 0 days, t= 1 day, t= 30 days, t= 45 days by a: i) field emission scanning electron microscope (FE-SEM); ii) UV-Vis spectrophotometer; iii) pump-probe optical setup. More details on these techniques are reported in the Experimental section.

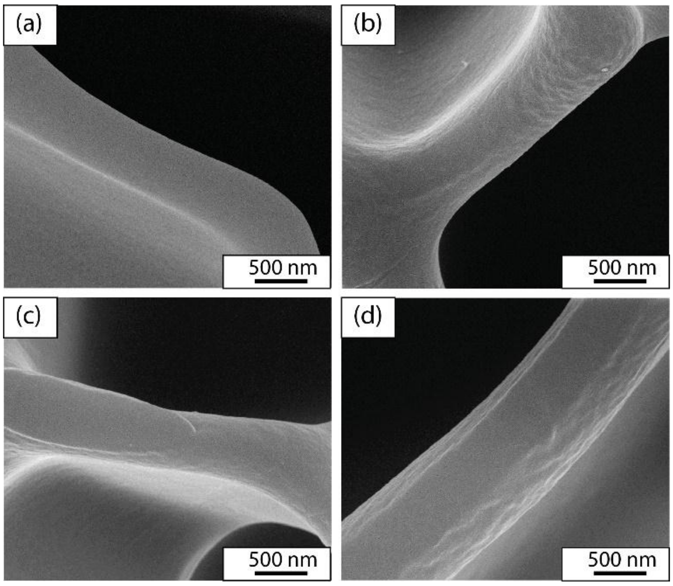

Figure S1. FE-SEM analysis of the samples at different hydration times: t= 0 days (**a**), t=1 day (**b**), t=30 days (**c**), t=45 days (**d**).

Figures **S-1(a-d)** clearly show that the prolonged immersion in water does not affect the morphology of the P(NIPAm-*co*-NIPMAm) film. Indeed, no presence of structural defects is visible at this level of magnification, thus highlighting the extraordinary capability of the P(NIPAm-*co*-NIPMAm) material to retain its morphological properties even after 45 days of continuous hydration.

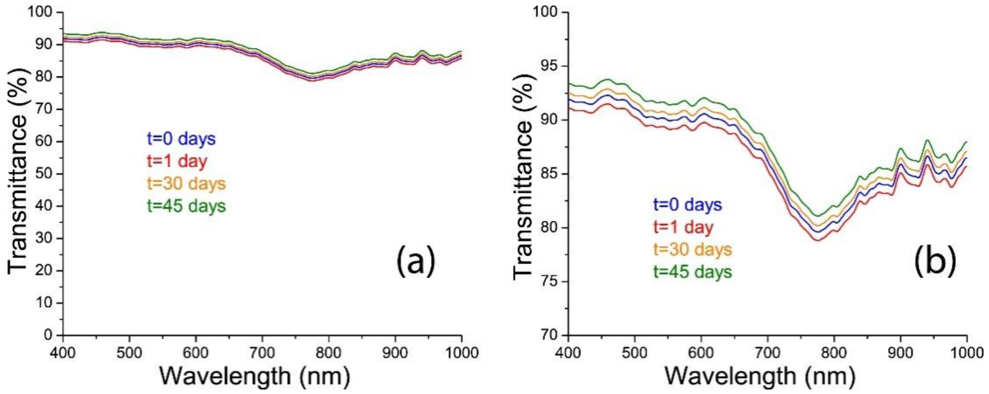

Figure S2. Spectral response of the samples at different hydration times (**a**) along with a detailed view of the same graph (**b**).

The spectral response (**Figure S-2a**) confirms that the transmission properties of the samples are not affected by the prolonged hydration. As such, the change in the transmittance is less than 2-3% (**Figure S-2a**) and this small change can be ascribed to the intrinsic experimental error of the utilized optical setup. This result clearly evidences that there is no evidence of critical instability of P(NIPAm-*co*-NIPMAm) material after prolonged storage times in water.

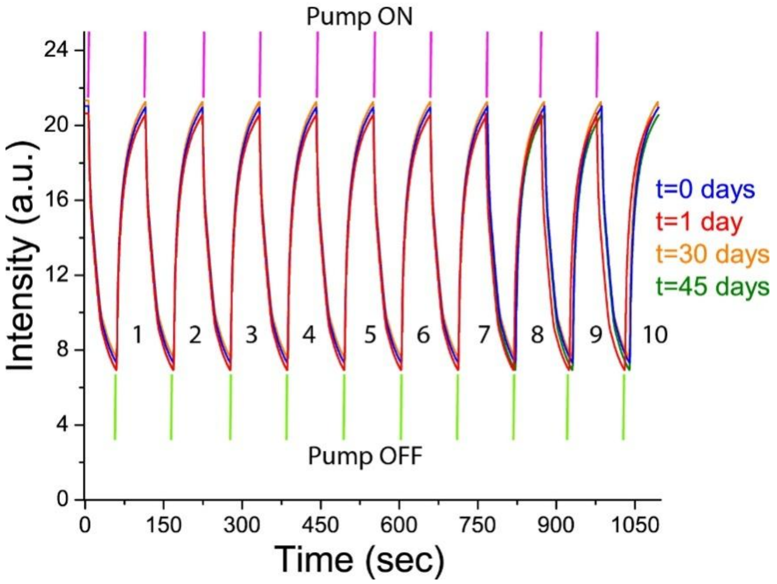

Figure S3. Reversible change of the transmitted intensity of the samples induced by cycling (from 0 to 10) the pump beam ON and OFF.

Photo-switching experiments (by cycling the sample up to 10 times) at each hydration time were conducted using the all-optical setup described in the Experimental Section. Figure **S3** shows an excellent reversibility of the transmitted intensity and no change in the optical properties in terms of response times and optical contrast is observed for all the investigated samples. It is worth pointing out that the small offset between the four curves reported in Figure **S3** can be attributed to the experimental difficulty to set the same initial intensity value for each measurement.

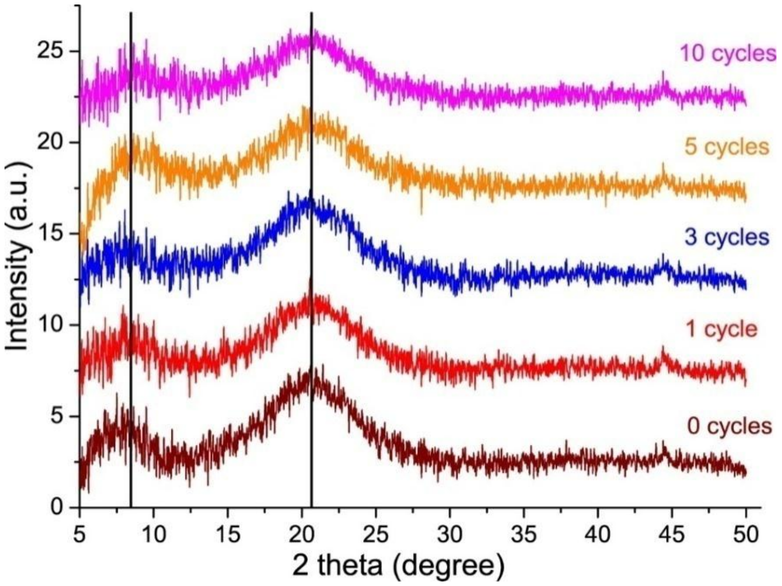

Figure S4. Wide angle X-ray scattering (WAXS) analysis of the of the samples at different cycles of photo-switching experiments.

In order to investigate the chemical structure of the P(NIPAm-*co*-NIPMAm) material and detect any potential change in matrix structure after different irradiation cycles, wide angle X-ray scattering (WAXS) analysis was performed by means of a Bruker D8 Discover diffractometer. Measurements were carried out in reflection mode, using Bragg-Brentano geometry in the angular range (2 theta) between 5 and 50 degrees, with a step of 0.02 degrees. The time of data accumulation at a particular angular point was 1.0 s. Figure **S4** (wine curve) shows the WAXS diffractogram of the sample before any photo-thermal experiment. The sample exhibits two wide peaks centered at 8°and 21° which can be attributed to the amorphous structure of the polymer.[1] Further measurements performed on the same sample after some cycles of illumination show identical WAXS patterns, thus confirming that there has been no change in the structure of the P(NIPAm-*co*-NIPMAm) material. It is worth mentioning that the WAXS characterization does not show any peak related to the presence of GNRs because the utilized concentration is under the limit of detection of the instrument.

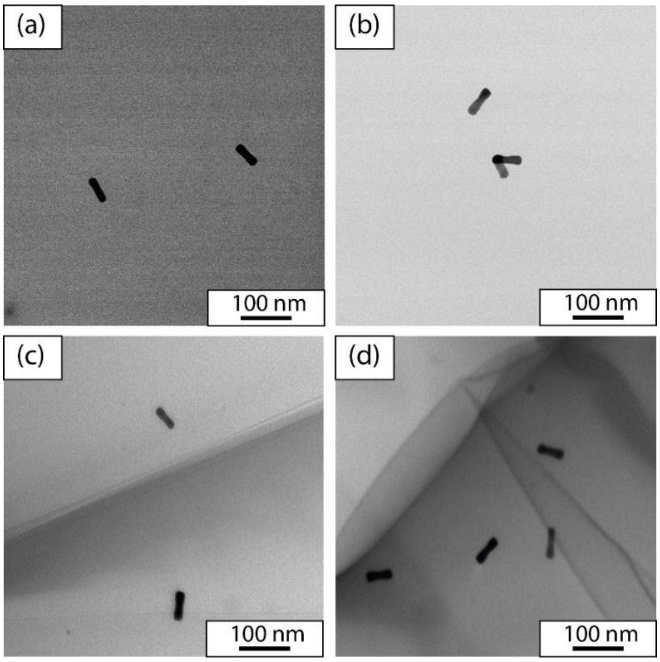

Figure S5. Transmission electron microscope (TEM) analysis of the samples after different cycles of photo-switching experiments: (**a**) - 0 cycles; (**b**) - 1 cycle; (**c**) - 5 cycles; (**d**) - 10 cycles.

Samples were inspected by TEM (see the Experimental Section for technical details) in order to verify if the light-induced thermal heating can produce detectable changes (reshaping) of GNRs. Figure **S5** confirms that even after cycling the samples up to 10 times (Figure **S5-d**), the shape of GNRs turns out to be very similar to the one observed before the photo-switching experiments (Figure **S5-a**). This is a clear evidence that GNRs are stable under the resonant light beam illumination and the reshaping process of GNRs is completely absent.

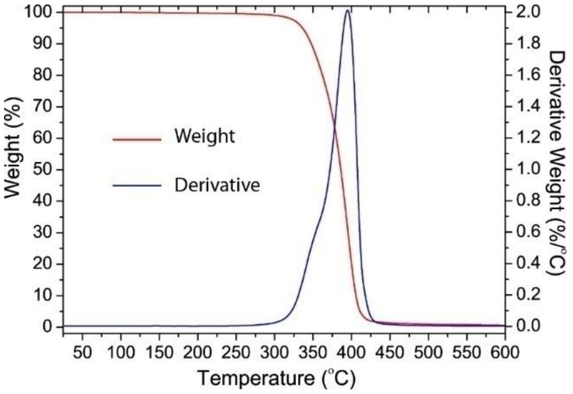

Figure S6. Thermogravimetric analysis of the sample reporting the weight loss (red curve) and its derivative (blue curve).

Lastly, in order to stress out the excellent stability of the P(NIPAm-*co*-NIPMAm)/GNRs samples, a thermogravimetric analysis (TGA) was performed. TGA was carried out by using a TA Instruments SDT Q600 to investigate the thermal stability of the plasmonic hydrogel. The TGA analysis was performed placing around 5.0 mg of sample in an Al_2O_3 pan. The test was carried out by increasing the temperature from 25 °C to 600 °C at a rate of 10 °C/min under a nitrogen flow (100 ml/min) and weighing the sample simultaneously. Figure **S6** shows that the sample is completely stable up to 300 °C. After that point, there is a noticeable weight loss (red curve) which is evidenced by the increasing of its derivative (blue curve).

References

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Supporting information2

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The response function of an ellipsoidal nanoparticle (NP) is related to the extinction cross section through its polarizability tensor α. In the framework of the Gans theory[1], α can be expressed as:

$$\alpha_{||,\perp} = 3\varepsilon_h V_{NR} \frac{\varepsilon_n + \varepsilon_h}{3\varepsilon_h + 3L_{\perp,||}(\varepsilon_n - \varepsilon_h)} \tag{1}$$

where ε_n and ε_h are the dielectric functions of the NP and its surrounding medium, V_{NR} is the NP volume, and:

$$L_{||} = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right) \tag{2}$$

$$L_{\perp} = \frac{1 - L_{||}}{2} \tag{3}$$

$$e^2 = 1 - \frac{b^2}{a^2} \tag{4}$$

a and *b* are the long and short axes of the NP, respectively. In order to take into account the real geometry of the NP (in terms of shape and aspect ratio), equation 1 was modified by adding few correction terms[2]. The modified equation for α turns out to be:

$$\alpha_{||,\perp} = 3\varepsilon V_{NR} \frac{\frac{1-0.1(\varepsilon_n+\varepsilon_h)\theta^2}{4}}{\frac{3\varepsilon_h+3L_{\perp,||}(\varepsilon_n-\varepsilon_h)}{\varepsilon_n-\varepsilon_h} + \frac{\Xi_1(0.1\varepsilon_n+\varepsilon_h)\theta^2}{4} + \Xi_2\varepsilon_h^2\theta^4 + \frac{2i\Xi_3\sqrt{\varepsilon_h^3}\theta^3}{3}} \tag{5}$$

where $\theta=2\text{л}\omega/c$ (ω is the frequency of the incident radiation and c is the speed of light). Equation 5 describes the polarizability tensor for a single NP. It is worth remembering that in the experiments we are in presence of several NPs (randomly oriented). In order to take into account the presence of several NPs, it is mandatory to utilize the average absorption cross section $\langle C_{abs} \rangle$for a 3D configuration, as reported in[3] . In the actual case, it is possible to simplify the geometry assuming a 2D configuration (NPs are close to the surface). So that, the average absorption cross section can be written as:

$$\langle C_{abs} \rangle = k\Im\left(\frac{1}{2}\alpha_{\perp} + \frac{1}{2}\alpha_{||}\right) \tag{6}$$

where $\alpha_{\perp}, \alpha_{||}$ are the parallel and perpendicular polarizabilities of a single NP and K is the wave vector. By implementing a fitting procedure, the obtained parameters are:

$$\Xi_1 = 1.8, \qquad \Xi_2 = 5.5, \qquad \Xi_3 = 2.3 \tag{8}$$

thus, ensuring an excellent agreement with the experimental results reported in Figure 6.

References

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[2] G. Lamri, A. Veltri, J. Aubard, P.-M. Adam, N. Felidj, A.-L. Baudrion, Beilstein Journal of Nanotechnology 2018, 9, 2657.H. Kuwata, H. Tamaru, K. Esumi, K. Miyano, Applied Physics Letters 2003, 83, 4625.
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