Plasmonic Enhanced Burst Release from Electrospun Fibers Exposed to Light

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Incorporation of metallic nanoparticles (NPs) in polymer matrix has been used to enhance and control dissolution and release of drugs[3-4], for targeted drug delivery,[5] antimicrobial agents,[6] localized heat sources,[7-8] and for unique optoelectronic applications[10]. Gold NPs in particular exhibit a plasmonic response that can be utilized for photothermal applications. In our work, we have incorporated ~3-nm-diameter colloidal gold (Au_c) NPs into electrospun polyethylene glycol (PEG) fibers to utilize the nanoparticle plasmonic response for enhanced localized heating of the polymer (Fig 1A, B). The plasmonic response of gold NPs involves conduction electrons on the particle surface, which oscillate at resonance with incident light.[11] In the photothermal process used, resonant light excites a surface plasmon on the gold NP, and absorbed energy is converted to heat due to electron-photon collisions. Photothermal heat generation is efficient and conducive to polymer melting[7] for the release of treatment contained in drug-release fibers. Reflectivity of the resulting gold colloid/PEG (Au_c/PEG) composite fibers was measured, revealing the greatest absorption at 504 nm wavelength. This result was slightly blue shifted from the Au_c alone or Au_c/PEG straight polymer, which both exhibited the greatest response at 522 nm (Fig 1C). From the reflectivity measurements collected, theoretical energy absorption was calculated in the case that Au_c/PEG was interrogated with white and green light (Fig 2). Theoretical calculations showed a significant energy absorption efficiency enhancement of 9.6 % under white light illumination and 38.3 % under green light illumination when compared to polymer fibers without Au_c. Such results are promising for white or green light illumination of drug-containing polymer fibers with embedded gold NPs to allow efficient and localized polymer melting for burst release of treatment. Future work aims to improve Au_c/PEG fiber structure through blended polymer preparation. In our laboratories, blended polymers are used to control release of antibiotic treatments contained in coaxial fibers that release upon contact with a physiological environment. Through blending of Au_c/PEG with polycaprolactone (Fig 3), we aim to create multi-functional drug release fibers capable of burst release initiated by interrogated light or slow release upon exposure to a living system. The near 40 % enhancement of photon to thermal energy conversion translates to a portable drug delivery system that is 40 % smaller or has a 40 % longer lifetime, both desirable results for portable, on-demand drug delivery.

[1]Yazhou et al., *Polymer Journal*, 43, pp. 478-483 (2011), [2]Perni et al., *Biomaterials*, 30(1), pp. 89-93 (2011), [3]Ulbrich et al., *Chemical Reviews*, 116(9), pp. 5338-5431 (2016), [4]Palza, *International Journal of Molecular Science*, 16(1), pp. 2099-2116 (2015), [5]Maity et al., *Polymer*, 52, pp. 1674-1685 (2011), [6]Govorav et al., *Nano Today*, 2(1), pp. 30-38 (2007), [7]Zhang et al., *Scientific Reports 7*, 46682 (2017), Li et al., *Nano Reviews* (2010), [8]Amendola et al., *Journal of Physics Condensed Matter*, 29(20) (2017).

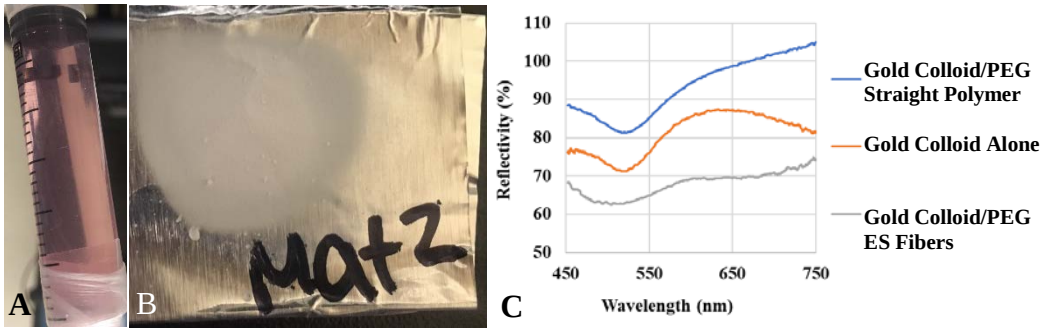

Fig 1. A Prepared PEG dissolved in gold colloid (gold NPs suspended in deionized water) prior to electrospinning (58 wt%). **B** Mat of gold colloid/PEG fibers after electrospinning. Electrospinning of this material resulted in electrospinning as well as electrospraying. Future work will aim to improve fiber structure through polymer blending. **C** Reflectivity data showing the greatest absorption of gold colloid/PEG straight polymer and gold colloid alone at 522 nm. Gold colloid/PEG electrospun into fibers had a slightly blue shifted peak absorption at 504 nm. Background was taken on PEG alone prepared at the same wt % in deionized water.

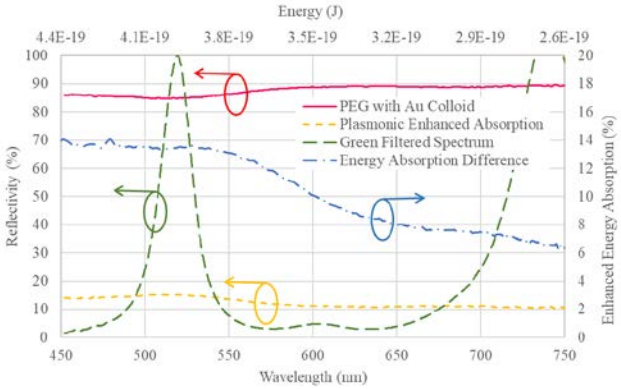

Fig 2. Reflectivity measurements were used to calculate the theoretical energy absorption for gold colloid/PEG interrogated with white and green light. Theoretical calculations showed a significant energy absorption efficiency enhancement of 9.6 % under white light illumination and 38.3 % under green light illumination when compared to PEG fibers without gold colloid. Energy absorption efficiency enhancement was calculated using a trapezoidal integration of the energy absorption difference curve.

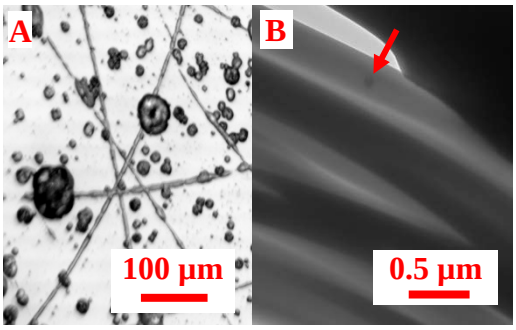

Fig 3. A Micrograph of electrospun PEG fibers embedded with gold NPs. Fiber structure observed was inconsistent and intermingled with electrosprayed droplets. **B** Coaxial, polycaprolactone fibers electrospun to carry viruses (red arrow) which kill bacteria. Through blending of polycaprolactone with PEG, we have fabricated fibers which release these viruses slowly over time upon exposure to a physiological environment. Future work aims to blend the gold colloid/PEG with polycaprolactone to create multi-functional fibers which release slowly over time when exposed to a physiological system, or burst release upon illumination with light.