Electronic Supplementary Material (ESI) for Nanoscale.

Fiber-optic sensor for neurotransmitter with ultralow concentration: Near-infrared plasmonic electromagnetic field enhancement using raspberry-like meso-SiO_2 nanospheres

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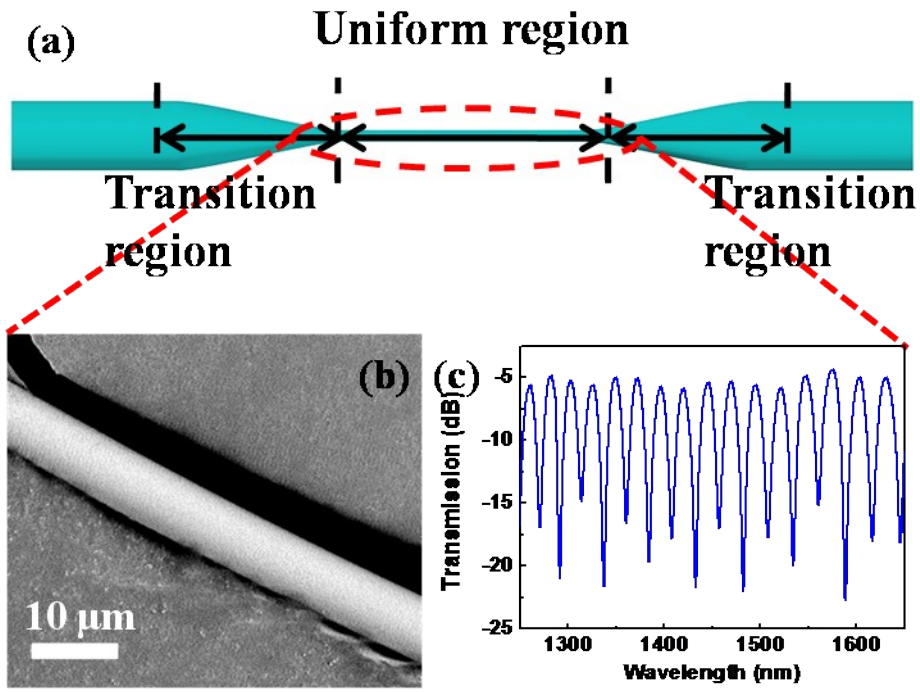

Fig. S1. (a) Schematic geometry, (b) SEM image, and (c) transmission spectrum of the silica microfiber interferometer.

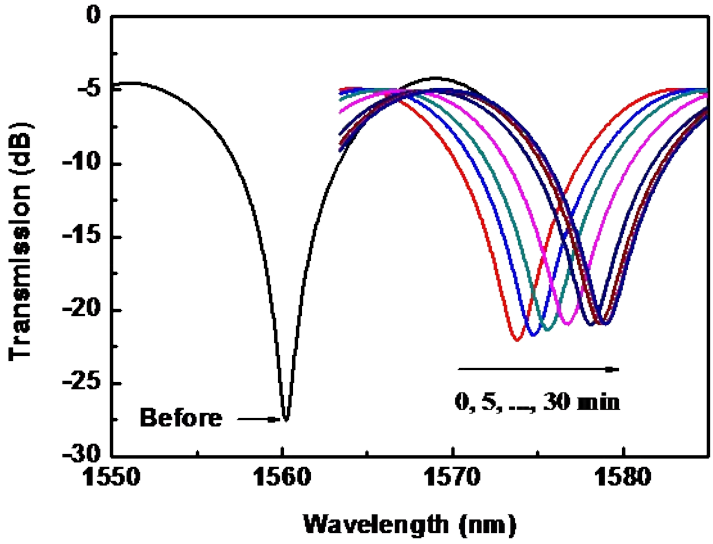

Fig. S2. Measured transmission spectra in nanospheres coating process.

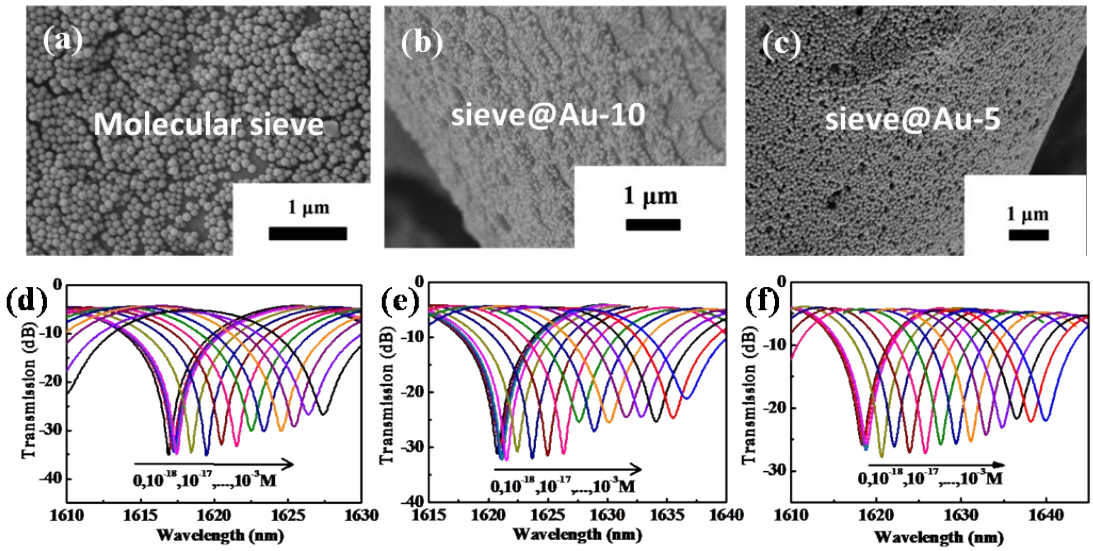

Fig. S3. SEM images of the proposed sensors and their experimental transmission spectra versus GABA solutions. ((a, d) Molecular sieve; (b, e) Sieve@Au-10; (c, f) Sieve@Au-5. The concentrations of solution are range from 0 to 10^{-3} M.)

Selectivity of sensor. (The sensor employed here was sieve@Ag-10.)

The size selectivity of the proposed biosensor is presented in Fig. S4. CTAB is a 16-carbon molecular with hydropjilic end adhereing on the surface of inner SiO_2. It

played role as the soft template to direct the formation of the mesoporous structure on the shell by co-assembly with the dissolved silica species.[49] For the reason that CTAB chain curled up in the process of outer SiO_2 forming, the pore volume would be more suitable for the molecular with slightly smaller size, such as dopamine with 8 carbons.[50] In detecting process, GABA molecular with four-carbon attached on the microsphere surface and entering into the nanopore on it.[51] Owning suitable pore size, the GABA molecular stayed in the pores without exiting, which endowed the detecting with stability (Fig. S4a). Consequently, the GABA concentration information can be captured by the tapered microfiber and translated into obvious interferometric fringe shift in the transmission spectrum (Fig. S4b). By contrast, molecular with smaller size (Cu^{2+}) also attached on the molecular sieve surface and entered into the nanopores. However, with the much smaller size, they exited the nanopores after entering (Fig. S4a). A similar result has been proved by Yuan and his coworkers.[49] In the case of molecules with larger sizes, they were disable to enter the nanopores (Fig. S4a). In these cases of target molecule with dismatched sizes, only unstable surface attachment took place between targets and raspberry-like molecular sieve arrays, and no obvious wavelength shifts were observed (Fig. S4b).

To further confirm the specificity for GABA, the detection reactivity to different potentially size-based substances (with sizes similar to GABA) were chosen in control experiments. Molecules with smaller size like urea, glucose and molecules with larger size like BSA were employed to determine the selectivity of sensor (The concentrations of these species were: urea 10^{-3} M, glucose 10^{-3} M, BSA 10^{-6} M, and

GABA 10^{-11} M.) (Fig. S4c). The results indicated that only GABA induced a dramatic increase in optical signal response (~8.69 nm) of the sensor, while the other 3 substance solutions showed no significant wavelength shift effect (BSA: 0.79 nm; urea: 0.11 nm; glucose: -0.36 nm). Furthermore, in the mixture with GABA and all the interfering molecules above, the sensor also displayed an obvious optical signal response which could be attributed to the presence of GABA.

Therefore, with highly uniform channels, large surface area and narrow pore-size distribution, the moleclar sieve caught GABA molecules and presented molecular size selectivity.

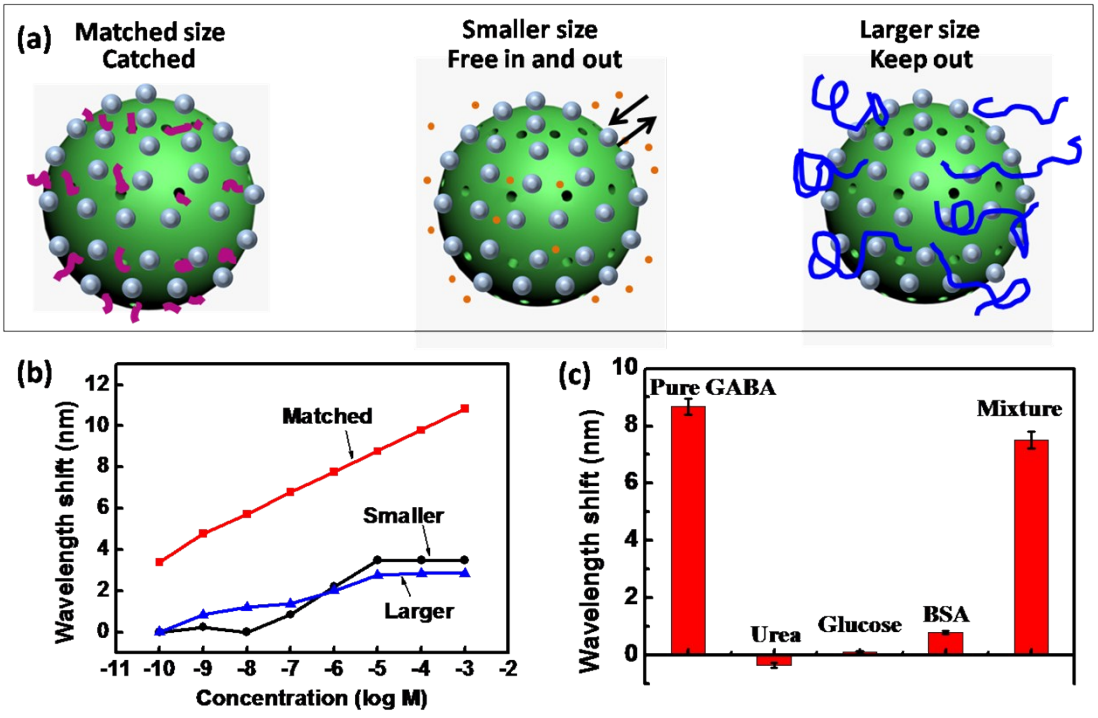

Fig. S4. (a, c, e) The schematic of molecular adsorbing process and (b, d, f) corresponding wavelength shift of proposed sensor (with sieve@Ag-10 coating) versus (a, b) matched size molecular, (c, d) smaller molecules, and (e, f) larger molecules. For all the cases, the concentrations of solution are ranged from 0 to 10^{-3} M. Comparison of optical response of fiber-optic sensor to 10^{-11} M GABA and other potential interferents: 10^{-6} M BSA, 10^{-3} M urea, 10^{-3} M glucose, and a mixture of 10^{-11} M GABA, 10^{-6} M BSA, 10^{-3} M urea, 10^{-3} M glucose under the same experimental condition.

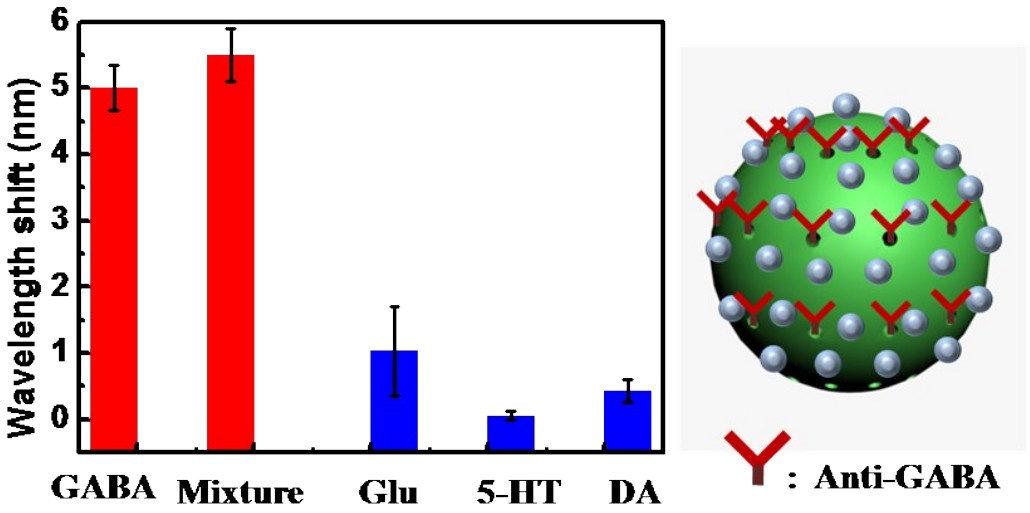

Fig. S5. Comparision of optical response of the sensor functionalized by anti-GABA modified raspberry-like meso-SiO_2 raspberry-like nanospheres (anti-GABA modified Sieve@Ag-10). (Concentrations: GABA: 10^{-12} M; glucose: 10^{-3} M; 5-HT: 10^{-6} M; DA: 10^{-6} M; mixture: including of all these contents.).