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A miniaturized photoreactor based on a hollow-core metal cladding waveguide

Tian Xu [a], Liming Huang [a,1], Danzhu Wei [a], Yonglong Jin [a], Jinhuai Fang [a], Guoqiu Yuan [a,*], Zhuangqi Cao [b], Honggen Li [b]

[a] Physics Department, Nantong University, Jiangsu, No. 999 Tong Jin Road, Nantong 226007, PR China
[b] Department of Physics, Shanghai Jiao Tong University, No. 800 Dong Chuan Road, Shanghai 200240, PR China

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ABSTRACT

We present a novel reactor based on the ultrahigh order modes in a hollow-core metal cladding waveguide (HCMW). Aqueous Fe^{2+}/Fe^{3+} salt solutions in the hollow-core act as the HCMW guiding layer. Light power is induced into the guiding layer using the free-space coupling technique. A series of enhanced power points, considered to be optical trapping points, are formed because of the excitation of the ultrahigh-order modes. It is demonstrated that, at these optical trapping points, crystalline magnetite $\gamma-Fe_2O_3$ is synthesized after the deionized water is photolyzed into OH^-. The magneto-optical effect of this $\gamma-Fe_2O_3$ is explored for potential applications.

Recently, many new photoreactors have been developed for photocatalysis, liquid waste treatment, and other applications [1,2]. Using a reactor to facilitate electrosteric stabilization of colloidal polymer particles can greatly shorten the reaction time or improve the reproducibility of the reaction [3]. The TiO_2-coated optical fiber photoreactor (OFR), which involves a strict evanescent wave mechanism for light propagation, has been used for *in situ* remediation of contaminated subsurface environments [4]. Use of a reactor coated waveguide in an attenuated total reflection (ATR) mode has been proposed to use light energy more efficiently or enhance quantum efficiency for the photocatalytic oxidation of formic acid in water [5]. In an ATR mode of propagation, incident light upon the silica/TiO_2/water interface is totally reflected back into the silica. At each reflection, the film absorbs a portion of the UV light (310–380 nm) that has greater energy. Here, we present a novel reactor based on the ultrahigh order modes in a miniaturized hollow core metal-cladding waveguide (HCMW) stirred by a low-power laser. In contrast to the usual photo-reactor, three major benefits can be summarized as follows. First, the HCMW structure can be triggered by a 100 mW laser. Secondly, the HCMW structure provides an extremely large reaction area, since the whole guiding layer region will have a similar enhanced intensity due to the excitation of several oscillating modes instead of evanescent waves. Third, the HCMW structure enables excitation of guided modes with orthogonal polarizations (TE or TM).

The HCMW structure in Fig. 1 is composed of three parts: (i) A sample cell about 5 mm in radius and 0.7 mm in depth fabricated from the precise placement of two identical C-shaped glass gaskets; (ii) a thin silver film (about 30 nm) coated on the top side of a thin glass slab for better coupling; (iii) a relatively thick gold film (200 nm) deposited on a thick glass slab to prevent light leakage. To ensure parallelism, the three parts of the HCMW structure are attached by optical cement. The top silver film serves as a coupling layer as well as a metal cladding, the glass slab (0.5 mm) and the solution injected from the inlet of the sample cell (0.7 mm) work as a guiding layer, and the base gold film acts as a substrate of the waveguide. In this paper, the subscripts 1, 2, 3, and 4 represent the free space, silver layer, guiding layer, and gold substrate, respectively. h_2, h_3, and h_4 are the thickness of each film, respectively. Here, the thickness of the guiding layer $h_3 = h_{glass} + h_{solution}$. In our experiment, the solution (about 250 μL aqueous Fe^{2+}/Fe^{3+} salt solution) was made by dissolving 34 mg $FeCl_3 \cdot 6H_2O$ and 29 mg $FeCl_2 \cdot 7H_2O$ (purchased from Slnopharm Group Co. Ltd.) in 100 mL deionized water, and was injected into the sample cell of HCMW by a micro-injector. The HCMW was settled on a goniometer as shown in Fig. 2. A 100 mW collimated light beam emitted from a diode laser at wavelength of 780 nm (AUT-FSL-780-100T, Shanghai Haoliang Optoelectronic Equipment Co., Ltd.) was incident upon the upper silver layer after passing

* Corresponding author. The author contributed equally to this work.
E-mail address: yuanguoqiu@gmail.com (G. Yuan).
[1] The author contributed equally to this work.

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through one polarizer and two apertures (the diameter of the apertures was 2 mm, and the distance between them was 0.2 m). The reflected light was detected by a photodiode (PD). Homemade software allowed us to carry out angular scanning. The intensity of the reflected beam varies with the incident angle and forms a series of sharp dips in the reflection spectrum at the extremely small phase-matching resonance angles, as shown in the inset of Fig. 3, indicating that the energy of the light source has been coupled to the ultrahigh-order modes in the HCMW structure [6–10].

Subsequently, one reflection dip was selected as shown in Fig. 3, and the incident angle was adjusted at the minimum of the dip, where maximum energy can be coupled. After the laser had been coupled into the HCMW for two hours, the solution in the sample cell was rinsed and cleaned with 10 mL deionized water twice to scour off Cl^- and SO_4^{2-}. High resolution transmission electron microscopy (HRTEM, Tecani G2 F20 S-TWIN) demonstrated that the product in the sample cell was composed of Fe and O, and the iron oxides were a nano-scale mixture of crystalline and amorphous form as displayed in Fig. 4. The measured lattice spacing of the iron oxide was 0.2692 nm (Fig. 4(b)), which is in accordance with the distance of 0.27 nm between two {310} crystal planes in maghemite ($\gamma-Fe_2O_3$). [11] The mixture of crystalline position and amorphous forms (Fig. 4(a)) illustrates that the higher the light intensity, the better the crystallization of $\gamma-Fe_2O_3$. This result further confirms the existence of optical trapping [9,12,13] at the crystalline position. An experiment without the HCMW structure (by removing the upper silver film of the HCMW) was also carried out, and the magnetic product was not found.

The most conventional method for obtaining Fe_3O_4 or $\gamma-Fe_2O_3$ is by co-precipitation. This method involves mixing Fe^{3+} and Fe^{2+} ions in a 1:2 molar ratio in highly basic solution at room temperature or at elevated temperature. Highly basic solutions or OH^- is necessary for synthesizing Fe_3O_4 or $\gamma-Fe_2O_3$. Why does the HCMW reactor allow the synthesis of magnetic fluid in aqueous Fe^{3+}/Fe^{2+} salt solutions without alkaline conditions, and why does the optical trapping effect occur in the HCMW structure? Owing to the advantage of the free-space coupling technique [14], HCMW with a relatively thick (submillimeter scale) optical waveguide can support a large amount of reflection dips, and so called ultrahigh-order guided modes can be excited at the extremely small phase-matching resonance angles [6–10]. Those modulus coefficients are $m > 1000$. The optical energy is mainly confined in the guiding layer (including the glass slab and the solution), where appears the oscillating field of guided modes. Compared with the power confined in the guiding layer, the power confined in the metal claddings approaches zero. Therefore, the sample in a HCMW is different from that in conventional waveguides and the surface plasmon resonance (SPR) structure, where an evanescent field exists. The light (blue line) coupled in the guiding layer of the HCMW propagated along the "Z" path shown in Fig. 5 because of total reflection between the guiding layer and cladding. The traveling wave is therefore along the z-axis. Moreover, a standing wave exists along the x-axis due to the overlaying of incident and reflected waves in Fig. 5. The red points of periodic and strong power, which are considered to be the optical trapping points, appear in the sample cell as shown in Fig. 5.

Maghemite crystallized in these trapping points, while out of them was $FeO(OH)_x$ with amorphous form. The amorphous material was unstable intermediate of iron oxides. Thus, the optical field in the HCMW is anisotropic and the energy of each optical trapping point in the HCMW structure is sufficient for promoting the photolysis of H_2O. Therefore, the mechanism of the reaction should be

$$H_2O \xrightarrow{\text{photoionization}} O_2 + 4e^- + 4H^+, \quad (1)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-, \quad (2)$$

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O, \quad (3)$$

$$4Fe_3O_4 + O_2 \longrightarrow 6\gamma - Fe_2O_3. \quad (4)$$

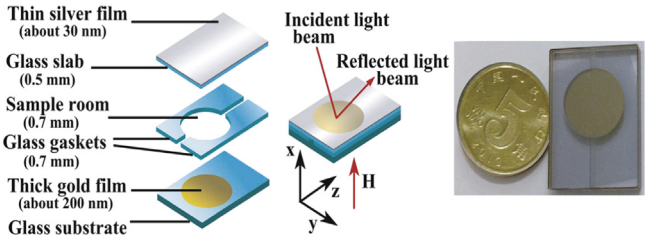

Fig. 1. Schematic structure of the symmetrical metal-cladding waveguide (HCMW).

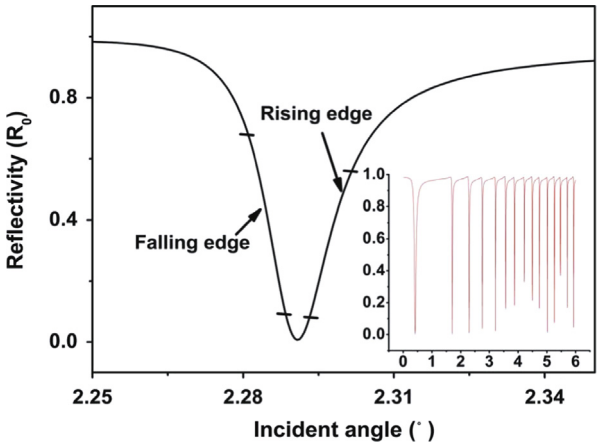

Fig. 3. Reflection spectrum of the ultra-high modes in a HCMW structure with the following parameters: $\lambda = 780$ nm, $\varepsilon_2 = -26.3 + 1.4693i$, $\varepsilon_{glass} = 2.25$, $\varepsilon_{solution} = 1.8225$, $\varepsilon_4 = -24.1 + 1.7230i$, $h_3 = 1.2$ mm, $d_2 = 30$ nm. The inset is the reflectivity for incident angles of 0–6 degrees.

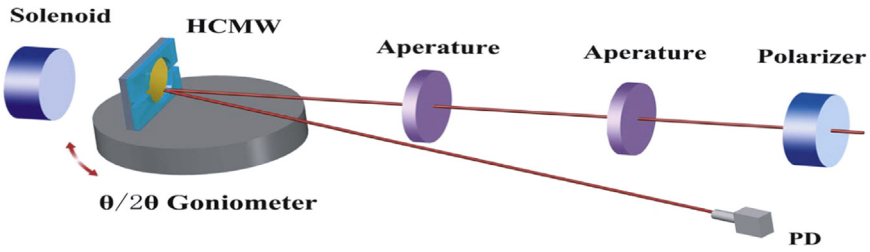

Fig. 2. Schematic diagram of the experimental setup.