The second-order nonlinearity in materials with inversion symmetry originates from both the asymmetric potential experienced by the surface/interface layer and the  
bulk multipole response beyond the electric-dipole approximation [6, 7]. Different from breaking the bulk inversion symmetry, e.g. exerting external strain [11, 12]  
or electric field [13], the second harmonic and sum frequency generation induced by the intrinsic surface nonlinearity have been developed as a non-invasive label-free  
probe. For example, second harmonic and sum-frequency  
generation spectroscopy has been developed into a viable  
surface analytical tool in detecting the arrangement, adsorption or reaction of molecules on the surface [14, 15, 9]

However, the signals from surface nonlinear effects are extremely weak even under the high-intensity pump, typically only thousands of second-harmonic photons generated from a 50-fs pulse with 500 GW/cm2 [10]. Additionally, the bulk multipole second-order effects disturb the  
deterministic study of surface properties, which has long  
been highly challenging [7, 10].  
In the past decades, cavity-enhanced nonlinear optics  
with low pump power has witnessed dramatic development in whispering-gallery (WG) microresonators, with  
the demonstration of Raman laser [16], third harmonic  
emission [17] and optical frequency combs [18]. The  
second-order nonlinear signal was also observed in cavities  
made of centrosymmetric materials [19, 20, 21, 22, 23].  
These studies, however, fail to clarify the surface secondorder nonlinear effect and to operate under low pump  
power, which presents an obstacle in surface physics and  
further applications. Here, we observe second harmonic,  
originating from symmetry breaking at the surface and  
bulk multipole response (Fig. 1a), in a silica WG microsphere under the continuous wave pump below 1 mW. A  
conversion efficiency of 0*.*049% W*−*1 benefits from doubly  
resonant enhancement of ultrahigh *Q* modes (also known  
as perfect phase matched), which is achieved by thermal effect and optical Kerr effect. We further confirm  
the second-order nonlinear signal only from the symmetry breaking at the surface, by analyzing the polarization  
dependence and the electric field distribution of the pump  
mode.  
In the experiment, a silica microsphere (diameter *∼*  
62 µm) is pumped through a tapered optical fiber (waist  
diameter *∼* 1 µm) at 1550 nm band , as shown in Fig.  
1b. To collect SH signal efficiently, a second fiber taper  
(waist diameter *∼* 0.5 µm) designed for 780 nm band is  
incorporated into the system. The intrinsic quality factor for the pumped cavity mode is 4*.*8 *×* 107. Figure 1**c**  
shows a typical SH spectrum measured from the electronmultiplying CCD (EMCCD) and the corresponding pump  
spectrum from the optical spectrum analyzer (OSA). The  
SH signal appears at 777*.*75 nm when pumped at 1555*.*14  
nm, which deviates only 0*.*023% from the expected wavelength, falling into the resolution tolerance of OSA and  
EMCCD spectrometer. Note that stimulated Raman  
scattering and parametric oscillation do not occur because their thresholds are far above the pump power in  
the experiment [16, 18]. Third harmonic generation is also  
absent due to the phase mismatch in the nonlinear optical process [17]. Moreover, SH signals arise frequently  
when cavity modes are pumped from 1545 nm to 1565  
nm, as shown in Fig. 1d. Among the occurrence of SH, a  
maximum signal power of 5 nW was observed via the signal fiber. To compare the collecting efficiency of the two  
fibers, we optimize the fiber-cavity coupling so that the  
SH signal from the pump fiber is also observable, but the  
maximum signal power is still over one order of magnitude weaker than that from the signal fiber. From either  
fibers, SH signal is absent when the pump is off-resonance  
with cavity modes, which helps to eliminate the possibility of spurious signals such as the second-order diffraction  
of the EMCCD grating.  
The doubly resonant enhancement plays a pivotal role  
in efficient SHG, which is achieved by perfect phasematching including momentum conservation and energy  
conservation [3]. The former can be fulfilled by a pair  
of modes with proper angular momentum relation *m*2 =  
2*m*1, where *m*1 (*m*2) is the azimuthal number of the pump  
(SH) cavity mode. The material and geometric dispersion  
presents a challenge on energy conservation, obstructing  
the double resonance *ω*2 = 2*ω*1 and consequently, efficient  
SHG. More accurately, the SH power can be derived from  
coupled mode equations (see Supplementary Information)  
*P*2 = 4*|g|*2*κ*2*eQ*2 2*/ω*2 2  
4*Q*2 2(2*ωp/ω*2 *−* 1)2 + 1  
16*κ*2  
1*eQ*4 1*/ω*2 4  
[4*Q*2 1(*ωp/ω*1 *−* 1)2 + 1]2 *P*1 2*,*  
(1)  
where the subscripts *j* = 1*,* 2 represent the pump cavity mode and SH mode respectively with *ωj* being the  
resonant frequency and *Qj* the loaded quality factor, *ωp*  
and *P*1 denotes the pump frequency and power respectively, *g* is the second-order nonlinear coupling strength  
between the two modes, and *κje* represents the external coupling rate. The pump power depletion is ignored  
due to the weak second-order nonlinear effect in silica.  
Equation (1) shows that ultrahigh *Q* is indispensable in  
boosting the SH power, while it also presents a challenge to achieve the double resonance due to the aggravated frequency mismatch. In order to compensate the  
dispersion, delicate geometric control of the cavity was  
proposed [22, 24, 25], but unrealistic for an ultrahigh*Q* (ultra-narrow-linewidth) microresonator. To tune the  
cavity dispersion precisely and dynamically, we leverage  
the cavity-enhanced thermal and optical Kerr effects to  
manipulate the frequencies of both pump and SH cavity  
modes.  
The mechanism of thermal and Kerr assisted phase  
matching process is illustrated in Fig. 2a. When the  
pump is weak and on resonance with the cold cavity  
mode (*ω*10), the SH mode (*ω*20) is unlikely to be on  
resonance with the SH signal due to the dispersion, as  
shown in the top panel of Fig. 2a. With a high enough  
input power, the pump mode experiences a red shift,  
*ω*1*−ω*10 = *−B*11*|α*1*|*2, where *|α*1*|*2 is the intracavity power  
of the pump mode and *B*11 denotes the coefficient. In  
this case, the wavelength of pump light should increase  
to catch the pump mode, resulting in the non-Lorentzian,  
triangular transmission shape [26], as shown in the black  
curve in Fig. 2b. The SH mode also exhibits a red shift  
from the cold cavity frequency, which can be described by  
*ω*2 *− ω*20 = *−B*12*|α*1*|*2 with the coefficient *B*12. The thermal and Kerr effects of the SH are ignored in the analysis.

With increasing pump wavelength, the SH signal moves  
faster than the SH mode due to the temperature distribution in the cavity (see Supplementary Information). In  
the process of tuning pump light towards the pump mode  
(state 1-3 in Fig. 2a and b), the SH signal can catch the  
SH mode (*ω*2) at a certain pump wavelength. The phasematching condition is fulfilled in this case, and thus the  
SH power reaches a peak value (state 2). By increasing  
the pump wavelength furthermore, the SH signal passes  
the SH mode, and its power diminishes rapidly (state 3  
in Figs. 2a and b).  
Using the phase matching method, we measure the SH  
power by tuning the pump frequency in the range of the  
gray area (Fig. 2b) with a fixed input power, as shown in  
Fig. 2c. The dependence of SH power on pump power is  
also studied, as presented in Fig. 2d. Under each input  
power, we search for the strongest SH output by tuning the pump wavelength. Among different input power,  
a critical power manifests itself, at which both the pump  
and the SH are exactly resonant with the cavity modes. In  
this case, the SH power is able to arrives at the peak value  
in Fig. 2c, which represents the most efficient SHG with  
the pump power of 879 µW and the conversion efficiency  
of 0*.*049% W*−*1. Below the critical input power, the SH  
is off resonance within the full tuning range, resulting in  
the extremely weak SH power. Above the critical power,  
the increasing input power at a fixed frequency pushes  
the pump mode farther to the red side (the pump is not  
completely on resonance) and consequently increases the  
detuning between the pump light and the cavity. The  
resulting reduced enhancement of the pump light counteracts with the increasing input power, leading to the  
almost steady intracavity power (see Supplementary Information). The on-resonance frequency of the SH mode  
also remains unchanged so that the intracavity power and  
consequently the SH power are almost the same as well.  
It is also possible to obtain the explicit *P*2 *∝ P*1 2 dependence by introducing a new degree of freedom, such as  
a control light or a heater, to manipulate the SH mode  
frequency.  
In order to distinguish the contributions of surface and  
bulk nonlinearity, we investigate the polarization dependence in SHG. In equation (1), the nonlinear coupling  
strength from surface dipole response can be written as  
(see Supplementary Information)  
*gs*0 = 2  
*ω*2  
1  
*ω*2*n*2  
Rsurface **E***∗* 02 : χ(2) *s*0 : **E**01**E**01d**S**  
R *|***E**02*|*2d**V** (2)  
where χ(2) *s*0 represents the surface nonlinear susceptibility,  
**E**0*j*(**x**) denotes the normalized electric field, and *n* is the  
refractive index of the cavity material. The bulk multi-

pole nonlinear polarization in silica can be expressed as  
**P**bulk = *γ∇*(**E** *·* **E**) + *δ*(**E** *· ∇*)**E** [8], where *γ* and *δ* are  
the nonlinear coefficients. The first term **P**bulk  
*γ* represents a longitudinal wave which can excite SH only at the  
surface. Therefore **P**bulk  
*γ* can contribute to an effective  
surface susceptibility[7] χ(2) *s* = χ(2) *s*0 + χ(2) *s,γ*, corresponding to an effective coupling strength of *gs*. The coupling  
strength induced by the second term **P**bulk *δ* can be written  
as  
*gb* = 2  
*ω*2  
1  
*ω*2*n*2  
*δ* R **E***∗* 02 *·* (**E**01 *· ∇*)**E**01d**V**  
R *|***E**02*|*2d**V** (3)  
Thus the total second-order nonlinear coupling strength  
*g* = *gs* + *gb*, as shown in Fig. 3a.  
The effective surface susceptibility tensor χ(2) *s* contains  
three non-zero components χ*⊥⊥⊥*, χ*kk⊥* and χ*⊥kk* [7],  
where *⊥* denotes the electric field direction perpendicular  
to the surface and *k* corresponds to the parallel direction.  
First, χ*⊥kk* can be ignored in studying SHG due to the  
non-degeneracy of transverse magnetic (TM) and transverse electric (TE) pump modes. Second, χ*⊥⊥⊥* (χ*kk⊥*)  
plays a major role when TM (TE) mode is pumped, which  
only generates the TM polarized second harmonic in both  
cases. TM modes are preferable in surface induced SHG  
because χ*⊥⊥⊥* is larger than χ*kk⊥* [27]. Considering the  
bulk nonlinear response induced by **P**bulk *δ* , the coupling  
strength *gb* relies on the specific field distribution in the  
cavity and the generated SH exhibits the same polarization as the pump mode. Note that for TE polarization,  
the field direction is along the polar direction, so that  
the polar symmetry of modes prohibits the excitation of  
SH modes with an even polar distribution from **P**bulk *δ* .  
While the TM pump modes, with electric field along the  
radial direction, can excite second harmonic without the  
above restriction. Because of a stronger confinement in  
the radial direction than the polar direction and thus a  
larger divergence for most of the modes, TM modes tend  
to link with a larger *gb* than TE modes. Consequently,  
from both the surface and the bulk second-order nonlinearity, TM pump modes can generate stronger SH signals  
statistically. In the experiment, TM or TE modes from  
1545 nm to 1565 nm are pumped separately by adjusting  
the polarization of the pump light. The TM pump modes  
exhibit larger SH power, as shown in Fig. 3b and c, which  
agrees with the theoretical analysis.  
The polarization dependence can be utilized to identify  
the surface nonlinearity from the bulk nonlinear response  
of both **P**bulk  
*γ* and **P**bulk *δ* . The former can be removed  
by selectively pumping a TE polarized mode since χ(2) *s,γ* is  
absent in the susceptibility χ*kk⊥* [7]. The latter can also  
be discerned from the surface nonlinear response with a  
fundamental TE pump mode (angular number *l*1 = *m*1),  
where SHG from **P**bulk  
*δ* is forbidden by the selection rule  
and the even polar field distribution of the SH mode  
(see Supplementary Information). In the measurement,  
a surface-only second harmonic is obtained deterministically by employ a fundamental TE pump mode at 1553.07  
nm, as shown in the left inset in Fig. 3c. Here the fundamental TE pump mode is confirmed experimentally by  
measuring the transmission while scanning the relative  
angular position of the pump fiber and the cavity, as illustrated in the Fig. 3c. Additionally, **P**bulk *δ* can also be  
eliminated by measuring the polarization of the SH signal  
[SI].  
With the second-order nonlinearity demonstrated  
above, sum frequency generation (SFG) also arises, assisted by a Raman signal. Shown in Fig. 4 is a sumfrequency signal (804*.*67 nm), with the corresponding  
pump (1550*.*88 nm) and the stimulated Raman scattering (1674*.*22 nm). The deviation of the sum-frequency  
wavelength from the expected value (804*.*63 nm) is much

smaller than the resolution of the spectrometers.  
For the first time, to the best of our knowledge, the second harmonic from breaking of inversion symmetry at the  
surface is deterministically observed in a silica microresonator without the influence of bulk multipoles. This  
work opens up a new direction to focus on the surface  
nonlinearity with double resonance enhancement, where  
the detectable SH signal under submilliwatt pump power  
demonstrates the potential of studying surface properties  
and detecting molecules with ultrahigh sensitivity. Additionally, the phase-matching method we used does not  
rely on the specific geometry and material of the cavity, making it possible to extend the surface SHG into  
other microcavity systems such as microtoroid, microdisk  
and microring with different centrosymmetric materials  
like Si and Si3N4. Combining with the ultralow operating power and simplicity of measurement, the extension  
to other microcavity systems also enables a type of novel  
label-free biological molecule sensing, which can potentially be integrated on a chip. In quantum optics applications, this work also represents a remarkable step towards  
the second-order nonlinearity mediated squeezing and entangled pair generation.

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