Electronic Supporting Information (ESI) for:

Microwave Assisted Fast and Facile Synthesis of SnO_2 Quantum Dots and Their Printing Applications

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Experimental section

Synthesis of SnO_2 Quantum dots: 1 mL of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] BF_4, Sigma-Aldrich, 98+%) was dried under vacuum at 80 °C for 3 h. Subsequently, 0.05 g of tin (IV) *tert*-butoxide ($Sn(OtBu)_4$, synthesized according to a reported method[S1]) was added to the dried [BMIM] BF_4 solution under Ar protection. The reaction mixture was heated in an oil bath at 45 °C for 10 min under vigorous stirring, and then a transparent solution was obtained. The transparent solution was transferred into a 10 mL glass vessel under argon gas atmosphere, and was sealed by a Teflon cap. The final reaction was carried out in a microwave oven (CEM, Discover S-Class, single mode, 2.45 GHz) at 50 W for 1 min (fixed power mode, and the temperature was set up to 180 °C; during the reaction the pressure was detected, which implied that the volatile products were generated.), and the solution was cooled down to 60 °C by a compressed air flow. A gray suspension was formed after the microwave radiation. For comparison, another reaction was conducted by oil bath heating at 180 °C for 1 hour. The products were separated by centrifugation (11000 rpm for 15 min) and washed with a mixture of water and ethanol (50 %) three times and finally dried overnight at 60 °C (for the ink-jet printing suspension, the cleaned precipitate was redispersed in water directly by ultrasonic treatment). After the drying procedure, 0.0149 g of the as-synthesized product was obtained which indicated that the production yield was 81.4%.

Characterization: Thermogravimetric analysis (TGA) of the precursor $Sn(OtBu)_4$ was carried out in the range 20 to 490 °C with a heating rate of 10 °C/min under an argon flow of 60 mL/min on a NETZSCH STA 409C/CD equipment. The phase composition of the as-prepared sample was characterized on a STOE-STADI MP X-Ray diffractometer operating in a transmission mode using Cu Kα (λ= 1.5406 Å) radiation. Fourier transform infrared (FT-IR) was measured by 5PC FT-IR Spectrometer in the range of 400 - 4000 cm^{-1}. Transmission electron microscopy (TEM) was performed on a Phillips CM 300 microscope, operating at 300 kV. Energy dispersive X-ray spectroscopy (EDX) of the as-synthesized SnO_2 QDs was characterized on a FEI Nova NanoSEM 430 microscope. UV-vis absorption spectrum and photoluminescence spectrum were recorded on Lambda 950 UV/vis spectrometer Perkin Elmer and Varian Cary Eclipse fluorescence spectrophotometer (Xenon flash lamp, excitation is 280 nm), respectively. The ink-jet printer (MD-P-802 from microdrop Technologies) was employed to print the SnO_2 QDs water dispersion on a polycarbonate foil (TP 264, provided by Bayer Materials Science AG) and a silicon chip, and the printing procedure was shown in Fig. S7. The surface of the polycarbonate substrate was sputtered with a thin gold layer and a 40 μm gap (uncovered area) at middle was reserved for printing SnO_2 "Bridge". The I-V characteristic behaviors of SnO_2 QDs bridge on polycarbonate substrate under different temperatures (RT, 80, 100, 120, 140 and 160 °C) were studied by Keithley 2400 source meter. Optical images of the printed sample were obtained on a Nikon Eclipse LV 150 optical microscope. SEM (Scanning electron microscope) images of the printed SnO_2 QDs lines were performed on a FEI Nova NanoSEM 430 microscope. Further, the gas sensing property of the printed SnO_2 QDs on a silicon chip was studied by various gases of EtOH, CH_4, NH_3 and CO (1000 ppm for each) at 200 °C on Keithley 2400 source meter. During the gas sensing measurements, 850 s was used for each response cycle (30% for gas response).

Detailed discussion on FT-IR

FT-IR spectrum of the as-prepared SnO_2 QDs (Fig. S1a) displayed a broad band centered at 530 cm^{-1} which is the characteristic intrinsic vibration for SnO_2. Furthermore, some weak absorption bands at 1005, 1163, 1457 and 1569 cm^{-1} corresponding to [BMIM] BF_4 are evident indicating that the SnO_2 QDs contained residual ionic liquid.[14] However, all these absorption bands shifted to low wavenumbers compared with the ones observed from the pure [BMIM] BF_4 (Fig. S1b, 1030, 1173, 1467 and 1576 cm^{-1}), which implied that the chemical environment of the IL was changed apparently through a chemical interaction with the Sn-O units present of the surface. Previous studies showed that IL may adsorb on the surface of metal oxides through electrostatic interaction and the hydrogen bonds formed between the O^{2-} (SnO_2) and the imidazolium headgroups (proposed schematic see inset Fig. S1).[15] Further, the surface-attached IL can build a protective shell hereby imparting the stabilization and dispersion of QDs in water.[16]

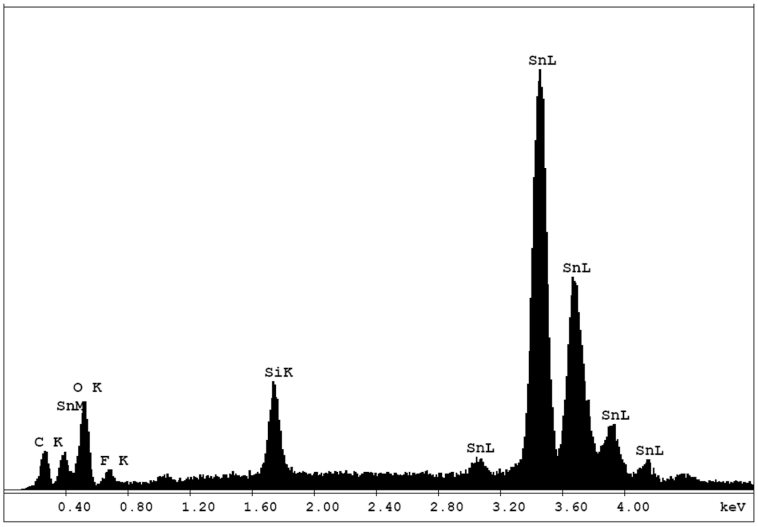

Fig. S1 EDX analysis on the as-synthesized SnO_2 QDs.

Elemental analysis on the as-synthesized SnO_2 QDs was determined by EDX (energy dispersive spectroscopy). The existing of F confirmed that there is a bit of IL remained in the final products (Si came from the substrate).

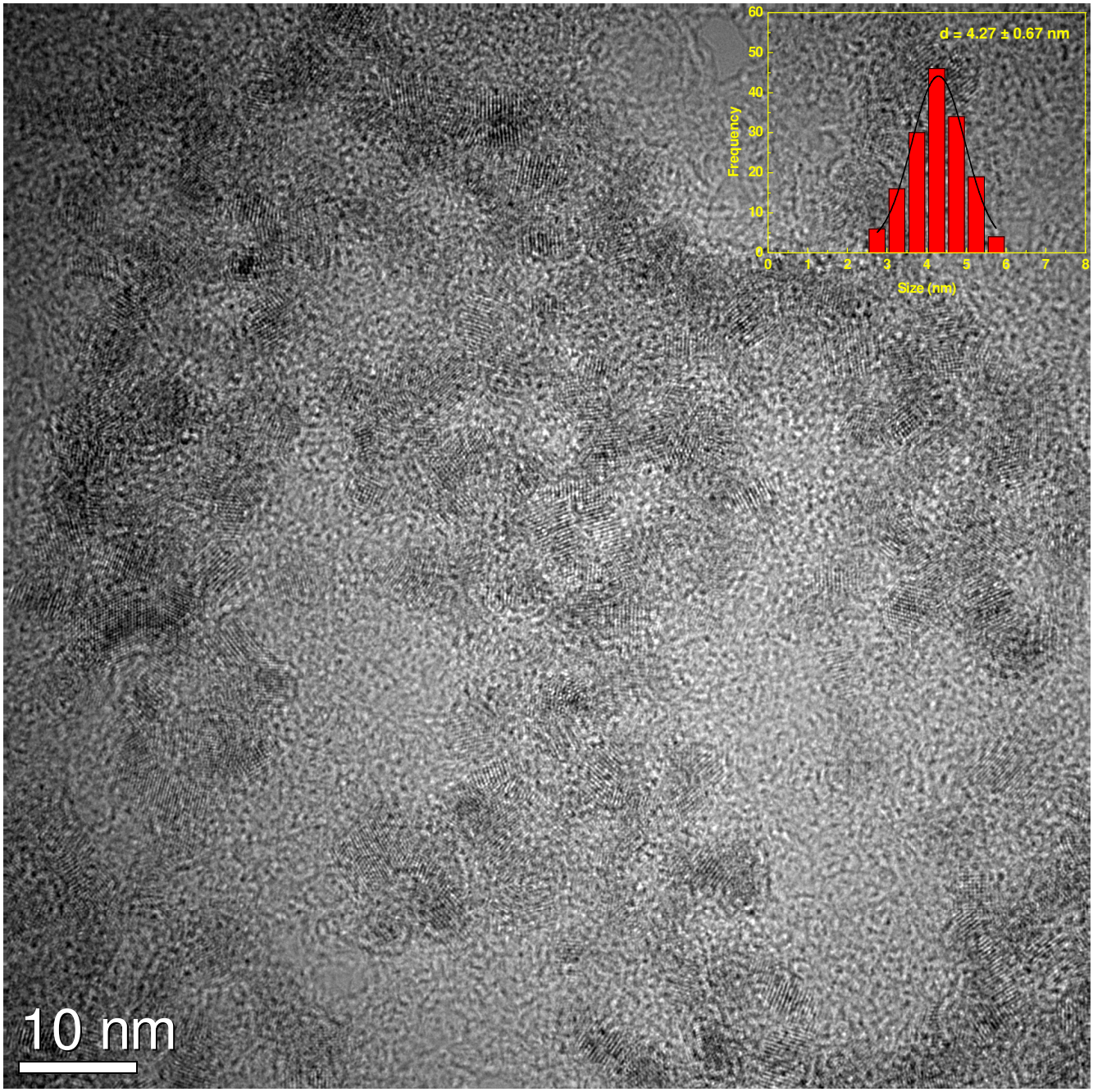

Fig. S2 HR-TEM of as-synthesized SnO_2 QDs. Inset: size distribution diagram.

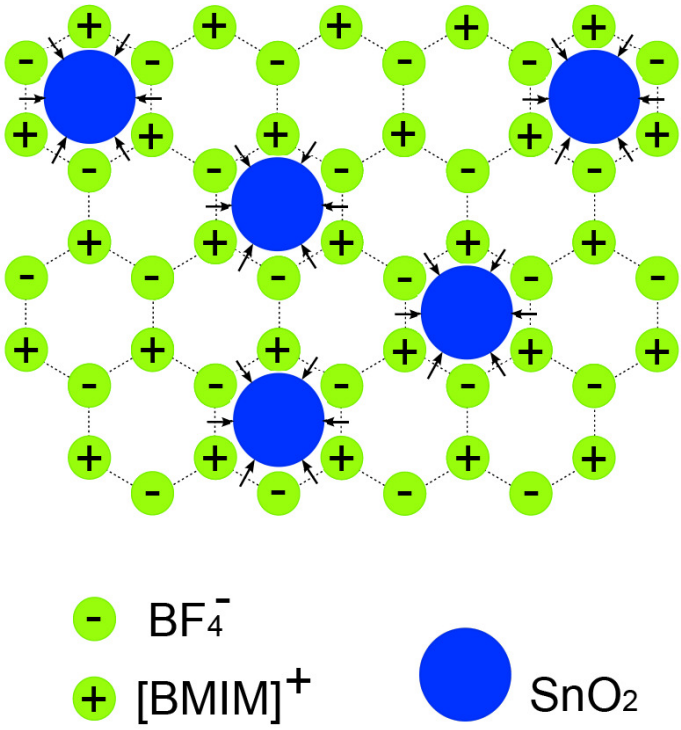

Fig. S3 Proposed 3D networks of ILs built by cations and anions, and proposed formation mechanism of SnO_2 QDs in the 3D structures of ILs.

Proposed formation mechanism

At the beginning, the tin (IV) *tert*-butoxide ($Sn(OtBu)_4$) precursors were homogeneously dissolved in the 3D networks of ILs by gently heating. The precursors started to decompose and nucleate in the templates when the MW irradiation was applied to this mixture system. The size of resulted SnO_2 QDs was determined by the geometry of the ILs templates, and the narrow size distribution could be attributed to the similar size confinement of the ILs templates. Finally, a few of imidazolium cations interacted with the O^{2-} sites on the surface of SnO_2 QDs to form stabilizing shells.

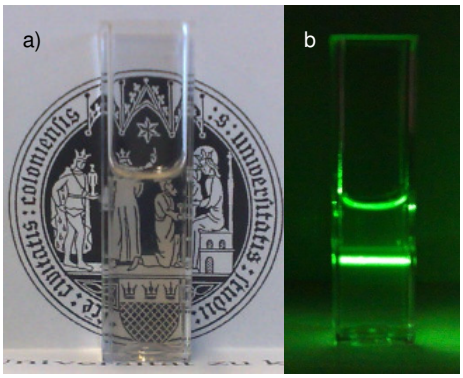

Fig. S4 a) Transparent SnO_2 QDs water solution and b) its Tyndall effect under laser irradiation.

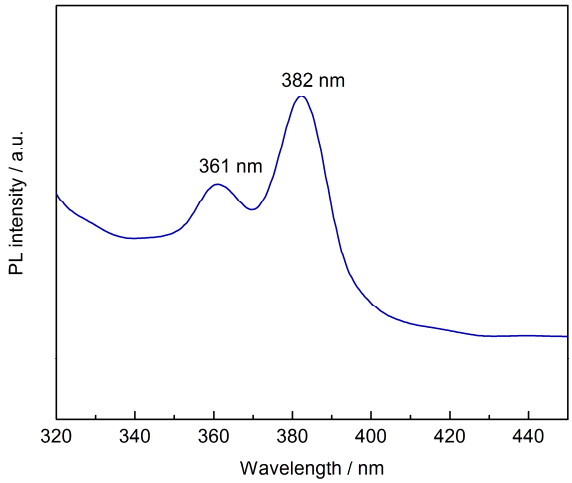

Fig. S5 PL spectrum of the as synthesized SnO_2 QDs, EX = 280 nm.

PL spectrum of the as-synthesized SnO_2 QDs is shown in Fig. S6, in where two ultraviolet emissions at 361 nm and 382 nm were observed. The emission of 361 nm is due to a typical free-exciton recombination (3.44 eV) and the emission of 382 nm (3.25 eV) is caused by defect PL. [7] Similar PL emissions were found in the extra-small SnO_2 QDs. [7]

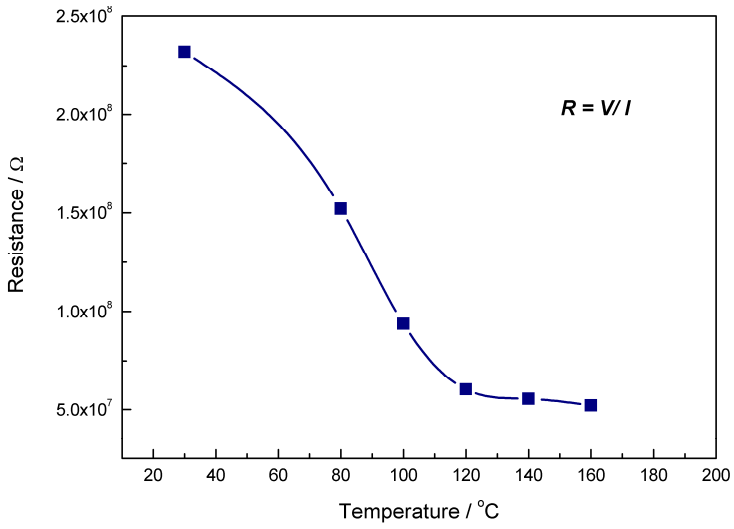

Fig. S6 Variation of the resistance of the printed SnO_2 QDs at different temperatures.

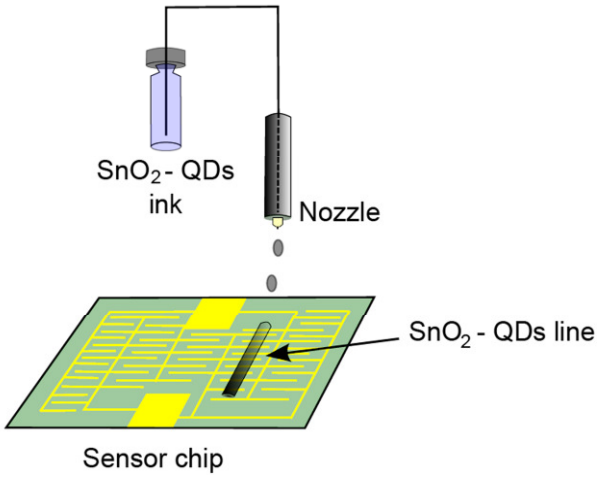

Fig. S7 Diagram of ink-jet printing process of SnO_2 QDs water suspension on silicon chip.

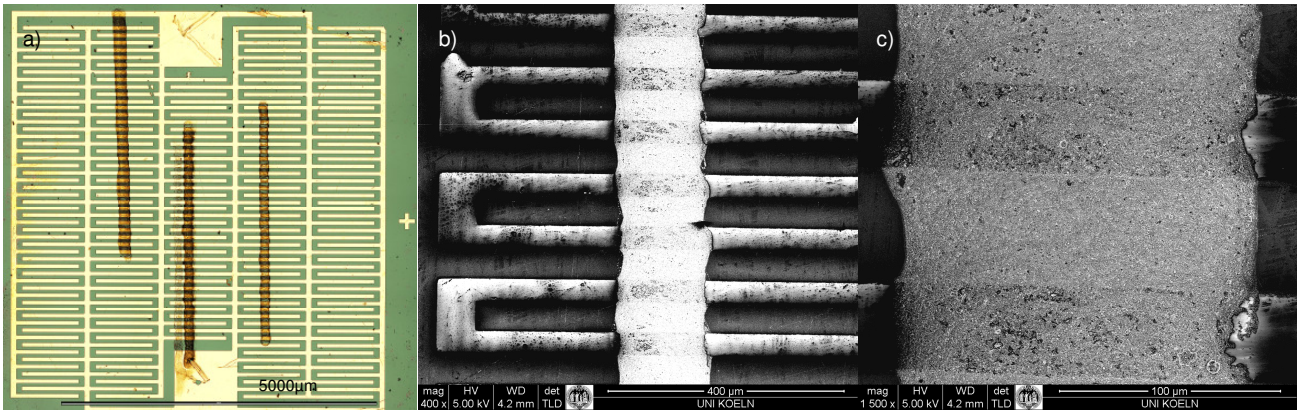

Fig. S8 a) Optical and b) , c) SEM images of the printed SnO_2 QDs wires on silicon chip.

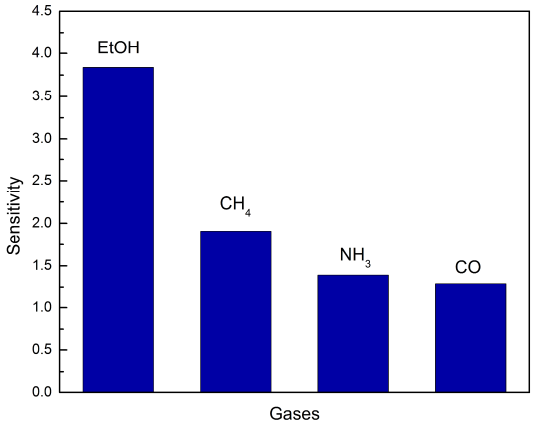

Fig. S9 Sensing selectivity of the printed sensor to EtOH, CH_4, NH_3 and CO (1000 ppm for each, under 200 ℃).

Reference

S1 M. J. Hampden-Smith, T. A. Wark, A. Rheingol and J. C. Huffman, *Can. J. Chem.*, 1991, **69**, 121.