Electronic Supplementary Information

Third-order nonlinear optical vitreous material derived from mesoporous silica incorporated with Au nanoparticles

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Experimental Information

SBA-15 was synthesized following the published procedure using the triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av}=5800, Aldrich) as a template in acid conditions[1]. According to published procedure[2], a typical synthesis of Au NPs/SBA-15 is below. 5.0 g calcined SBA-15 was dried at 200 °C in vacuum for 12h to remove residual water. After cooling to room temperature, the sample was suspended in 250 ml of toluene solution containing 1.5 g of mercaptopropyltrimethoxysilane (MPTMS, 95%, Aldrich) and stirred at 70 °C for 24h. The resulting materials were filtered, washed with toluene, acetone and deionized water, and then dried to remove the remaining solvent under vacuum. These 5.0 g functionalized SBA-15 powders were added into 50 ml of 0.25 mM $HAuCl_4$ (Au=0.0025g) aqueous solution and continuously stirred for 30 min, subsequent mixed with a proper quantity of sodium citrate aqueous solution (molar ration Na citrate/Au=20). After filtration and drying, these reduced powders were suspended in 100ml of $NaBH_4$ solution ($NaBH_4$/Au=10) and stirred for 20 h at 60°C. The suspension was filtered, washed with ethanol two times and dried for 30 h in vacuum.

As-prepared 0.6g of powders were loaded in a cylindrical graphite die with an inner diameter of 12 mm and sintered in vacuum in a Spark Plasma Sintering (SPS) apparatus (Dr. Sinter 725, Sumitomo Coal Mining Co. Ltd., Japan). A heating rate of 100°C min^{-1} and a uniaxial pressure of 50MPa were applied. Finally the samples were obtained at 1020 °C with a holding time of 3 min and total sintering time is 10min.

Characterizations

X-ray powder diffraction (XRD) patterns were collected on a Rigaku D/Max-2550 PC diffractometer equipped with a Cu Kα X-ray source. Transmittance and absorption spectra in the UV-Vis range were recorded with a Perkin Elmer Lambda-950 spectrometer. Transmission electron micrographs (TEM) and Energy Dispersive X-Ray Spectroscopy (EDX) analyses were taken on JEOL JEM-2010 microscope operating at 200 kV. The sintering sample was mechanically broken and the pieces were grinded to be powder. Then, the grinded powder was dispersed in alcohol through ultrasonic irradiation and dropped onto a carbon-coated copper grid for TEM analysis. The nonlinear optical properties of Au NPs/glass were measured by Z-scan method with a 76MHz repetition rate and 200 fs pulse width mode-locked Ti:Sapphire laser (Coherent Mira 900D). The third-order nonlinear optical susceptibility $\chi^{(3)}$ values of the sample can be calculated according to literature[3].

Graphics

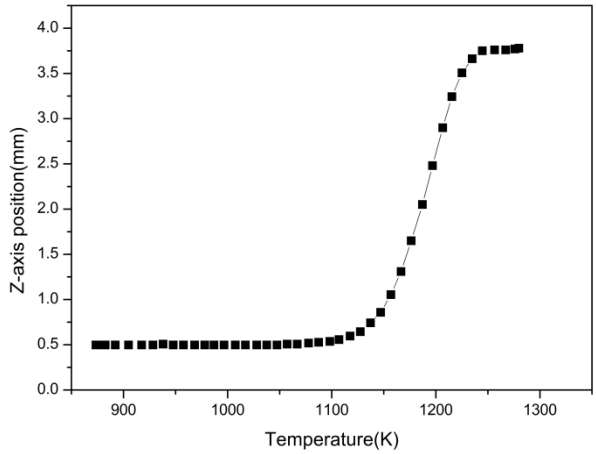

Fig.S1 Normalized shrinkage curve depending on elevated temperature in SPS sintering

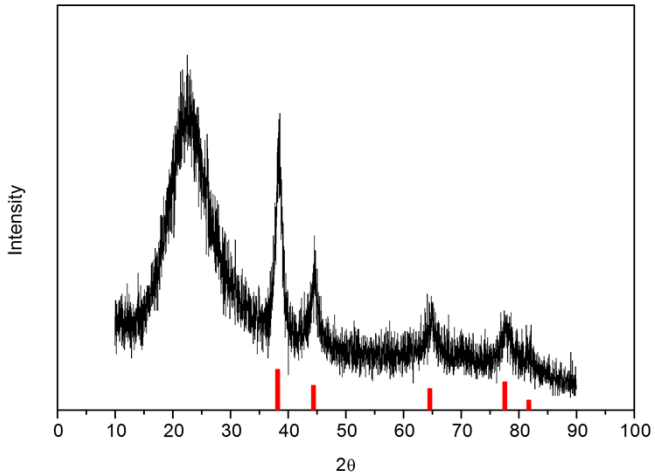

Fig.S2 Wide-angle XRD pattern of Au NPs/SBA-15 powder. The vertical red bars represent diffraction data from PDF card No. 04-0784 of fcc Au

A broad peak occurs at 21.6° is identical with that of sintered glass which is the sign of amorphous phase. However, different to the XRD pattern of already prepared silica glass containing Au NPs in Figure 2b, more than three obvious peaks can be recognized easily because the Au dosage is much higher in powder (2wt%) than in glass (0.05wt%). The high dosage in powder aims at confirming presence and crystalline form of Au. These peaks are assigned to face centered cubic Au due to PDF card No. 04-0784. The grain size of Au NPs in composite powder is calculated by Scherrer Equation to be 7.3 nm which is in agreement with our judgment about the size of Au NPs (in the range of 3-10nm).

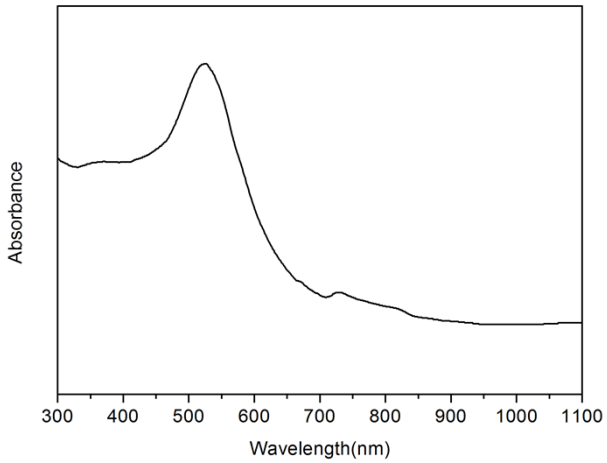

Fig.S3 UV-Vis absorption spectrum of Au NPs/SBA-15 powder

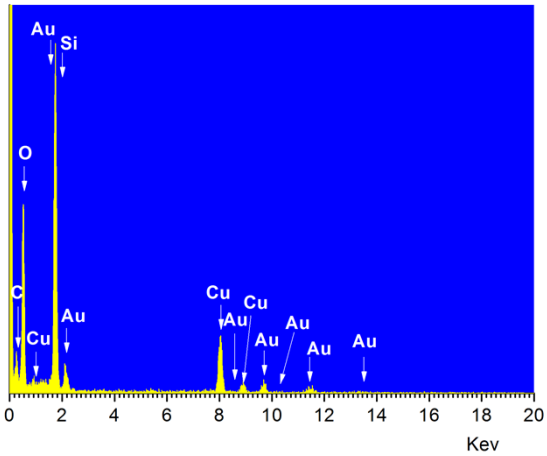

Fig.S4 EDX spectrum taken on the dark spherical spots in Fig 4a. Note that the Cu signals come from the copper grid.

Notes and references

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