Supplementary materials

ITO@SiO$_2$ and ITO@{M$_6$Br$_{12}$}@SiO$_2$ (M = Nb, Ta) Nanocomposite Films for Ultraviolet-Near Infrared Shielding

Wanghui Chen, [a b d] Thi Kim Ngan Nguyen, [a b d] Maxence Wilmet, [a c] Noée Dumait, [c] Ourania Makrygenni,[a b d] Yoshio Matsui, [d] Toshiaki Takei,[f] Stéphane Cordier,[c e] Naoki Ohashi, [a d] Tetsuo Uchikoshi, [a b d] and Fabien Grasset*[a d]

[a] CNRS-Saint Gobain-NIMS, UMI3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute of Material Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

[b] Fine Particles Engineering Group, Research Center for Functional Materials (RCFM), NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

[c] Univ. Rennes, CNRS, ISCR – UMR6226, 263 av. du Général Leclerc, 35042 Rennes, France

[d] RCFM, NIMS, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

[e] Research Center for Materials Nanoarchitectonics (MANA), NIMS, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

Synthesis of ITO NPs:

In a typical synthesis, InCl$_3$·4H$_2$O and SnCl$_4$·5H$_2$O were added to two bottles containing EG, forming respectively 0.5mM InCl$_3$-EG and 0.05mM SnCl$_4$-EG solutions, after continuous stirring. In order to obtain a TMAH-EG solution with concentration between 2.25 to 2.5mM, a certain volume of 25 wt.% TMAH in methanol was added to EG with vigorous string. After aging for 12 hours, the methanol was removed with a rotary evaporator at 40 °C, 13 kPa for 1.5 hours. The concentration of TMAH was determined by acid-base titration, using 10 mM HCl and NaOH aqueous solutions. The synthesis of ITO (ratio of In:Sn equal to 9:1) NPs was carried out by mixing 4.5 mL of InCl$_3$-EG, 5 mL of SnCl$_4$-EG and 10 mL of TMAH-EG solution in a 30 mL PTFE container in an ice bath. After stirring for 15 min, the PTFE container was

sealed by a stainless autoclave and transferred to an oven. The autoclave was slowly heated to 230°C and the temperature was kept constant for 96 hours. After cooling down, the dark-blue ITO slurry was separated from EG by centrifugation at 11000 rpm for 15 min, followed by washing with ethanol and DI water for 3 times. Then, ITO was stored at -4°C as an aqueous suspension. For the characterization of the synthesized materials, the ITO NPs were dried at 40°C for 12 hours. High quality aqueous solution of ITO NPs was obtained by adjusting the pH of the suspension to 12 with 28% ammonia solution, followed by ultrasonication for 1 hour.

Preparation of $K_4Ta_6Br_{18}$ and $Ta_6Br_{14}(H_2O)_4 \cdot 3H_2O$ nanoclusters

The $K_4Ta_6Br_{18}$ (KTB) compound was obtained by the reduction of tantalum pentabromide (TaBr$_5$) powder by tantalum powder in an alkaline medium (KBr) at high temperature and under an inert atmosphere. Thus, 2.97 mmol of TaBr$_5$ (Alfa Aesar, 99.9%, metals basis), 4.25 mmol of Ta (Alfa Aesar-325 mesh, Puratronics, 99.97%, metals basis) and 4.25 mmol of KBr (Acros Organics, >99%, ACS reagent) were mixed together in a glovebox (Ar atmosphere) and placed into a silica tube sealed under vacuum. The KTB phase was obtained after heat treatment at 600 °C for 24 hours in a rocking furnace. The $Ta_6Br_{14}(H_2O)_4 \cdot 3H_2O$ (TBH) powder was obtained after the dissolution of the KTB powder compound in water at 80 °C under an argon atmosphere in addition to HBr and SnBr$_2$ according to a previously reported method. After several hours of stirring, the green solution was filtered to remove any non-dissolved particles (mostly tantalum powder), then the TBH green powder was recrystallized.

Preparation of $K_4Nb_6Br_{18}$ nanoclusters

The $K_4Nb_6Br_{18}$ (KNB) compound was obtained by reduction of the pentahalogenated precursor by metallic niobium in an alkaline medium at high temperature under neutral atmosphere. Thus, NbBr$_5$, Nb and KBr were mixed together in a glovebox and placed into a silica tube sealed under vacuum. $K_4Nb_6Br_{18}$ phase was obtained after sintering at 600 °C during 24 hours in a rocking furnace. Niobium and recrystallized KBr impurities were then removed by dissolution of synthesized powder (1.5 g) in absolute ethanol (55 mL) and filtration of the solution.

All the nanocluster powders were synthesized at the University of Rennes 1 (UMR6226 UR1-CNRS).

Microemulsion experimental condition of $ITO@SiO_2$ and $ITO@M_6@SiO_2$ nanoparticles

$ITO@SiO_2$: 0.2 mL of ITO NPs dispersion and 0.6 mL of ethanol were injected to a mixture of 3.75 mL of Brij L4 and 11.75 mL of n-heptane with mild stirring to form a reverse-

microemulsion (RM) system. The RM system went through a ultrasonication treatment for 30 min, in order to improve its uniformity. Afterwards, 0.2 mL TEOS were injected to the RM system with mild stirring to start the formation of SiO_2. This reaction lasted for 72 hours and it was terminated by vigorous stirring with 20 ml ethanol.

ITO@M_6@SiO_2: The same conditions as above were used, with only difference the replacement of ethanol in the RM system by the ethanolic solution of KNC for the $ITO@Nb_6@SiO_2$ NPs or TBH for the $ITO@Ta_6@SiO_2$ NPs. The concentration of the M_6 was varied from 2.01 to 6.79 mM.

All the products of the RM-based syntheses were collected by centrifugation and washed with water for 10 times. The resulted nanoparticles were dried at R.T. under vacuum.

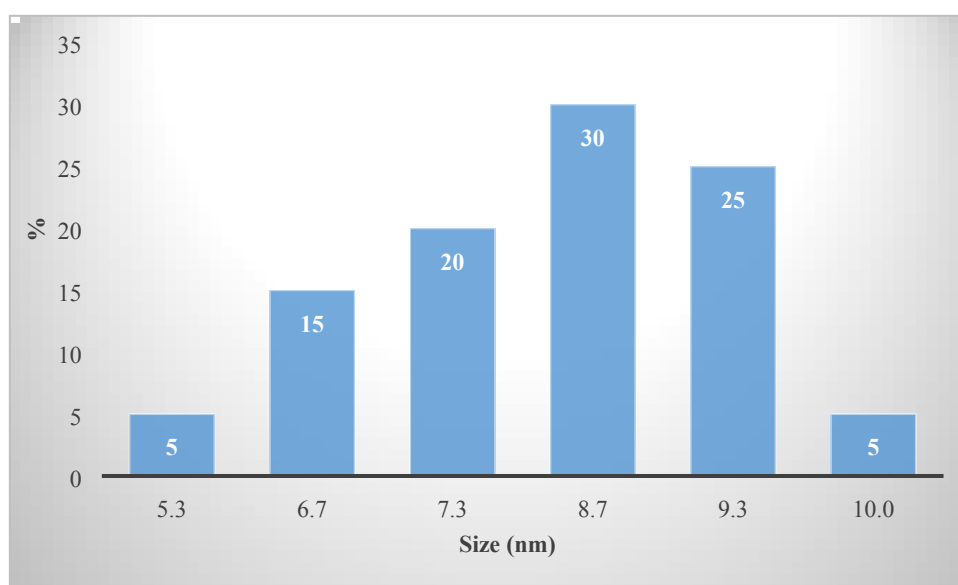All the microemulsion were synthesized at NIMS (UMI3629 LINK).

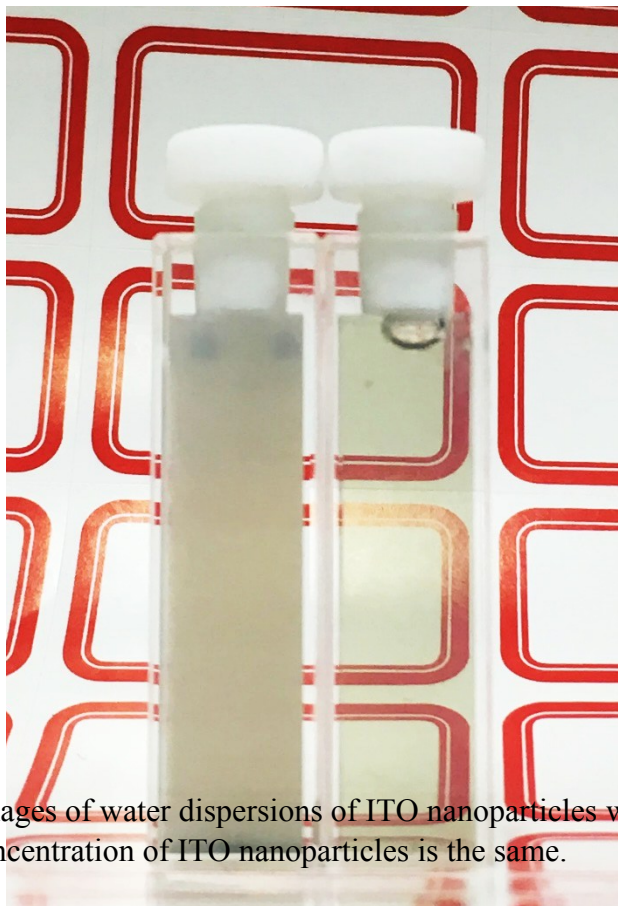**Figure S1.** The size distribution of ITO nanoparticles estimated by TEM.

Figure S2. Camera images of water dispersions of ITO nanoparticles with pH equal to 7 (left) and 12 (right). The concentration of ITO nanoparticles is the same.
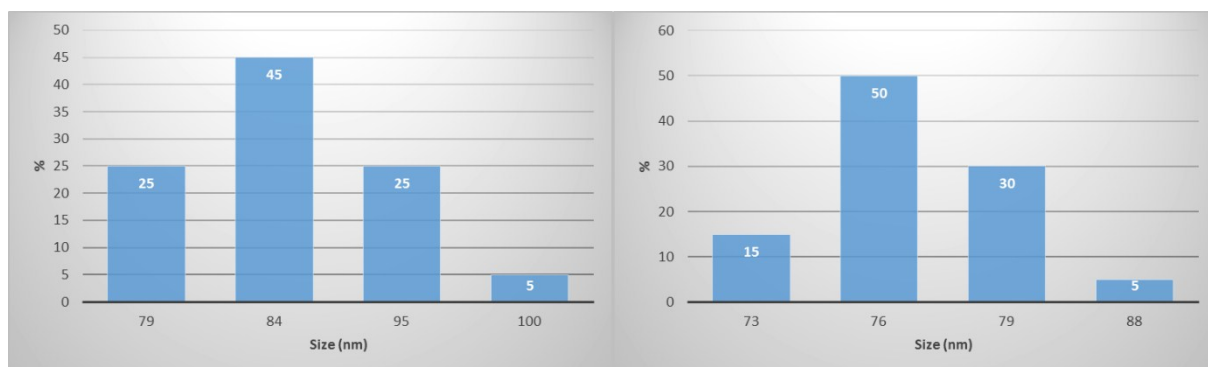

Figure S3. Left) The size distribution of ITO@SiO$_2$; Right) ITO@Ta$_6$@SiO$_2$ nanoparticles estimated by TEM.
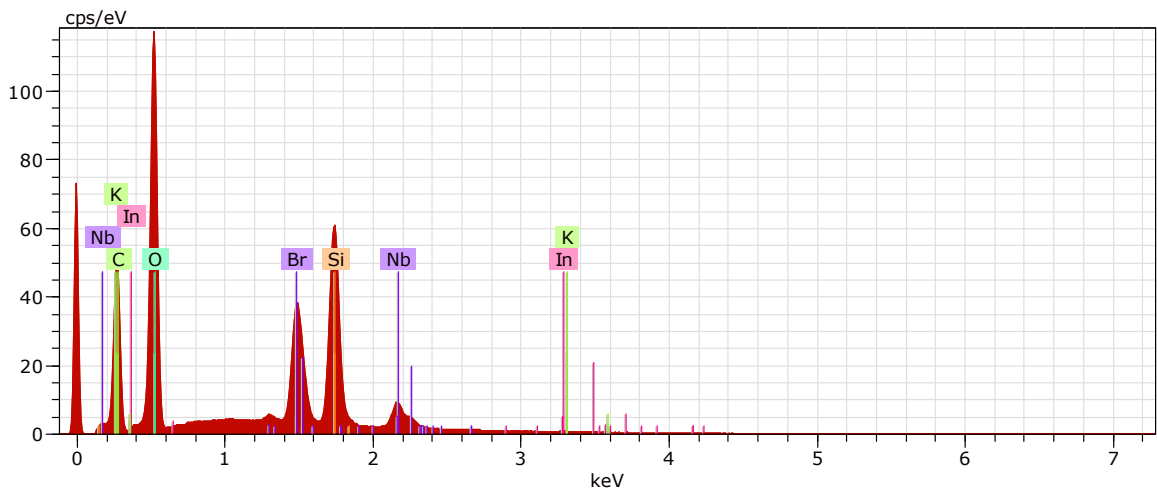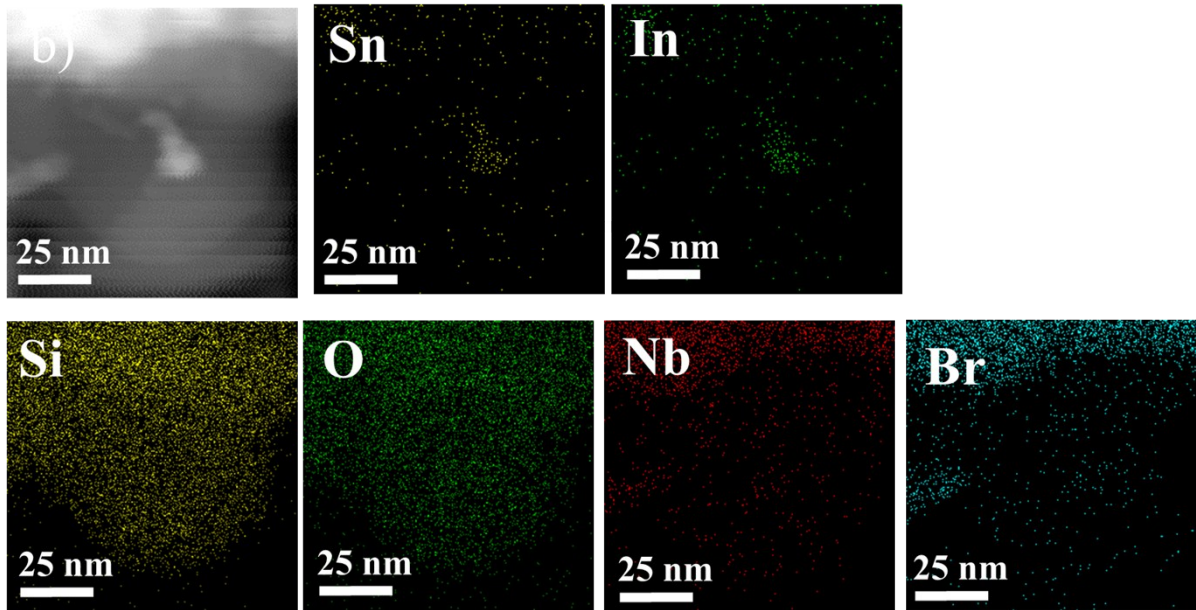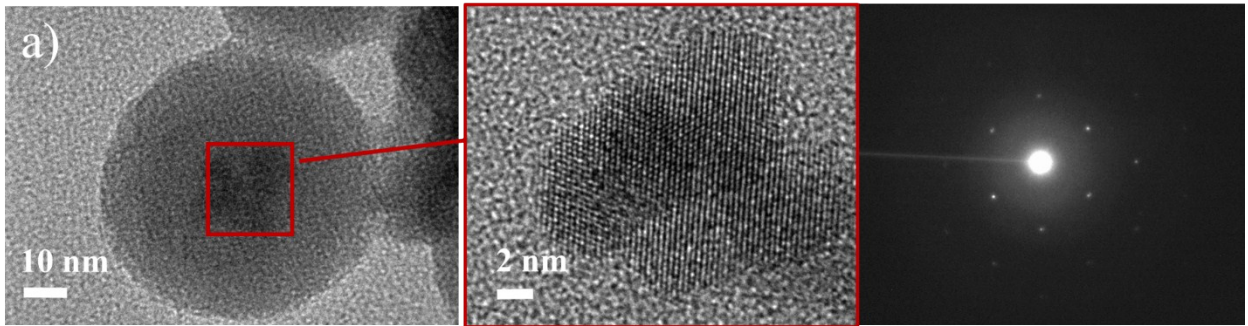
Figure S4. a) HR-TEM micrographs (FFT is on the right) and b) EDX mapping and spectra of ITO@Nb$_6$@SiO$_2$ nanoparticles.
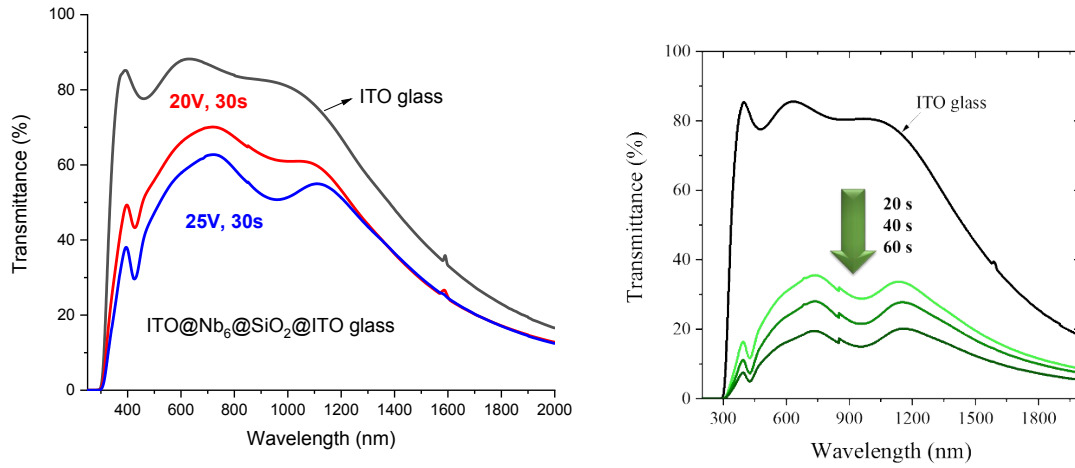
Figure S5. Transmission UV-Vis-NIR spectra of films based on ITO@Nb$_6$@SiO$_2$ NPs coated on ITO-glass by: Left) varying the voltage (20V and 25V) (time is fixed at 30 s) using a solution with concentration equal to 0.8 g/L solution; Right) by varying the time (voltage is fixed at 20 V) and using a solution with concentration equal to 2.5g/L (right).

Calculation of color coordinates:

The color coordinates (x, y, z) are calculated thanks to the procedure defined by the International Commission on Illumination (CIE 1931). Thus, we used the CIE standard illuminant D65, corresponding roughly to the average midday light in Western Europe / Northern Europe and the standard colorimetric observer for the 10° field obtained from the combined measurements of Stiles and Speranskaya.[S1]

The spectral transmittance spectrum of the sample T(λ) is multiplied by the spectral power distribution of a reference illuminant I(λ) giving the following equations:[S2]

$$X = \frac{1}{N} \int \bar{x}(\lambda) \times T(\lambda) \times I(\lambda) \, d\lambda$$

Eq. S1

$$Y = \frac{1}{N} \int \bar{y}(\lambda) \times T(\lambda) \times I(\lambda) \, d\lambda$$

Eq. S2

$$Z = \frac{1}{N} \int \bar{z}(\lambda) \times T(\lambda) \times I(\lambda) \, d\lambda$$

Eq. S3

$$N = \int \bar{y}(\lambda) \times I(\lambda) \, d\lambda$$

Eq. S4

Where $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the CIE standard observer functions (10 degree). The integrals are computed over the visible spectrum (from 360 nm to 830 nm). We used the common reference D65. In practice, the functions found in these integrals exist either from empirical experiment or by measurement. Therefore, there are not mathematical equations representing them. Instead, they exist as discrete samples and so the integrals are replaced by summations:

$$X = \frac{1}{N} \sum_i \bar{x}i \times Si \times I$$

Eq. S5

$$Y = \frac{1}{N} \sum_i \bar{y}i \times Si \times Ii$$

Eq. S6

$$Z = \frac{1}{N} \sum_i \bar{z}i \times Si \times Ii$$

Eq. S7

$$N = \sum_i \bar{y}i \times Ii$$

Eq. S8

Then, given an XYZ colour whose components are in the nominal range [0,1]:

$$x = \frac{X}{X + Y + Z}$$

Eq. S9

$$y = \frac{Y}{X + Y + Z}$$

Eq. S10

$$z = \frac{Z}{X + Y + Z}$$

Eq. S11

The L*a*b coordinates were obtained by using this conversion equation:

$$L^\star = 116\, f\left(\frac{Y}{Y_n}\right) - 16$$
$$a^\star = 500\left(f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right)$$
$$b^\star = 200\left(f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right)$$

FOM values: The efficiency of the prepared M_6-based UV and NIR filters as saving energy was estimated *via* the determination of the different figure of merit (FOM) values such T_{vis}, T_{sol}, T_{vis}/T_{sol}. The solar transmittance T_{sol} is the integrated spectral transmittance of a window weighted with the normalized solar energy distribution spectrum. The visible transmittance T_{vis} is calculated in a similar way, but the solar transmittance is now weighted with the photopic response of the human eye. For more reliability, we include the equation leading to our figure of merit (FOM) values. T_{vis} and T_{sol} can be calculated by the following formula:[S3]

$$Tvis = \frac{\int_{300}^{1200} T(\lambda) \times X(\lambda) \, d\lambda}{\int_{300}^{2500} X(\lambda) \, d\lambda}$$

Eq. S12

$$Tsol = \frac{\int_{300}^{2500} T(\lambda) \times X(\lambda) \, d\lambda}{\int_{300}^{2500} X(\lambda) \, d\lambda}$$

Eq. S13

where T is the transmission spectrum as measured and X represents the Air Mass 1.5 (AM 1.5), which is equivalent to the spectrum of solar radiation after passing through 1.5 times the perpendicular atmospheric thickness in T_{sol}, or the human eye spectral response in T_{vis}. The CIE Colorimetric System (the CIE 1931 with 10° Standard Observer from 1964 and D65 source) was used for color analysis.

For the same reason as above, integrals were replaced by summations giving the following equations:

$$Tsol, Tvis = \frac{\sum_i Ti \times X}{\sum_i Xi}$$

Eq. S14

Nom	X	Y	Z	x	y	z	u'	v'	L	u	v	T_L/T_E
ITO@Nb6@SiO2 20V 20s 0.8 g/L	0,585	0,612	0,524	0,340	0,356	0,304	0,206	0,486	82,470	9,181	17,478	1,11
ITO@Nb6@SiO2 20V 20s 1 g/L	0,394	0,411	0,297	0,357	0,373	0,270	0,211	0,497	70,266	12,306	24,705	1,07
ITO@Nb6@SiO2 20V 20s 2.5 g/L	0,260	0,272	0,177	0,366	0,384	0,249	0,213	0,503	59,196	11,631	25,657	1,05

[S1] a) W. S. Stiles, J. M. Burch, *Optica Acta* 1959, *6*, 1; b) N. I. Speranskaya, *Opt. Spectroscopy,* 1959, *7*, 424; c) D. B. Judd, *in Proc.CIE Symposium on Advanced Colorimetry*, CIE Central Bureau, Vienna, Austria, 1993, pp. 107 – 114 ; d) P. W. Trezona, *Color Research and Application,* 2001, **26**, 1.

[S2] B. J. Lindbloom, Site gathered the useful color information, http://www.Brucelindbloom.com, accessed: February, 2017.

[S3] G. B. Smith, C. A. Deller, P. D. Swift, A. Gentle, P. D. Garrett, W. K. Fisher, *J. Nanopart. Res.,* 2002, **4**, 157.