Supporting Information

New ultra-violet and near-infrared blocking filters for saving energy application: Fabrication of tantalum metal cluster-based nanocomposite visible transparent and colored thin films by electrophoretic deposition

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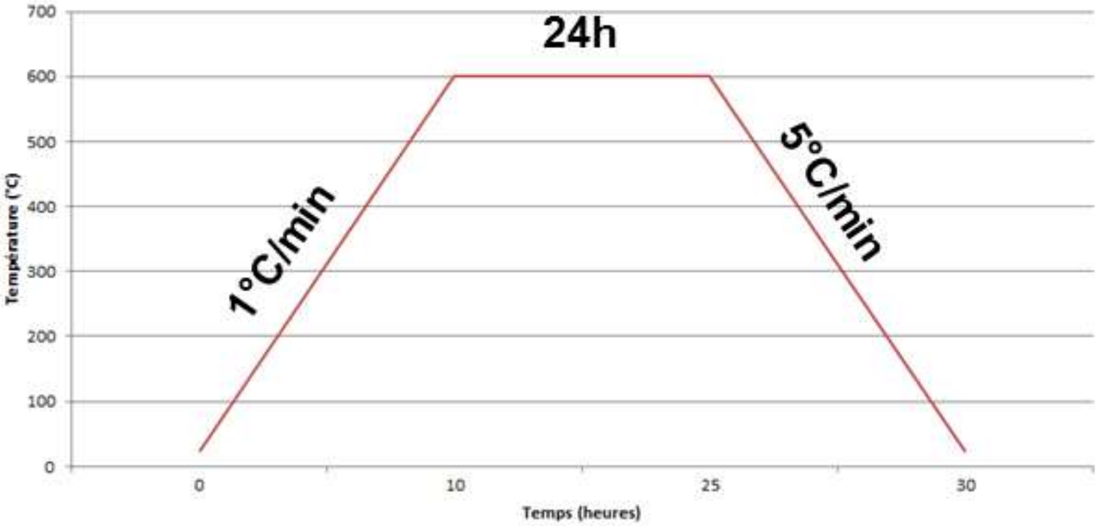
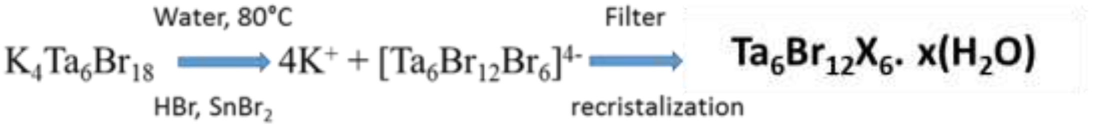
Scheme S1. Scheme of the synthesis of the KTB and TBH clusters

KTB: $4\ KBr + 14/5\ TaBr_5 + 16/5\ Ta + 0.8\ Ta \rightarrow K_4Ta_6Br_{18} + 0.8\ Ta$

In Silica sealed tube under vacuum condition



TBH:

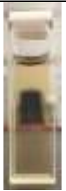


$$K_4Ta_6Br_{18} \xrightarrow[\text{HBr, SnBr}_2]{\text{Water, 80°C}} 4K^+ + [Ta_6Br_{12}Br_6]^{4-} \xrightarrow[\text{recristalization}]{\text{Filter}} Ta_6Br_{12}X_6 \cdot x(H_2O)$$

With (X = Br and/or H_2O)

Study of the EPD solutions: Various solvents such distilled water (Water Purifiers WG710, conductance $0.5.10^{-4}$ S/m at 25°C), ethanol, acetone and methyl-ethyl acetone (MEK) were tested for preparing EPD solutions. The solvents have been used without any purification. Thus we studied the dissolution of TBH (10 mg) precursor in the solvents (15 mL) and the deposition of clusters on ITO glass (Geomatec Co., LTD (Japan), 6.15-7.27 (Ohm/sq)). All the experimental parameters are reported on Tables S1 and Table S3.

Table S1. Summary the experiments of TBH cluster by Electrophoretic deposition

Solvant	**Color**	**EPD**		**Quality of the film**
		Anode	**Cathode**	
H_2O				✗
Ethanol Nacalai Tesque Inc (Japan), 99.5%				✗
Acetone Nacalai Tesque Inc (Japan), 99.5%				✓
H_2O/Acetone				✓
Acetone/PVP				✗
H_2O/Acetone/PVP				✓
MEK Nacalai Tesque Inc (Japan), 99.5%				✗
H_2O/MEK				✗

- Notice of the concentration of components:

- TBH: 0.01g
- Solvent: 15 ml
- H_2O: 0.02 ml
- PVP: 0.01g

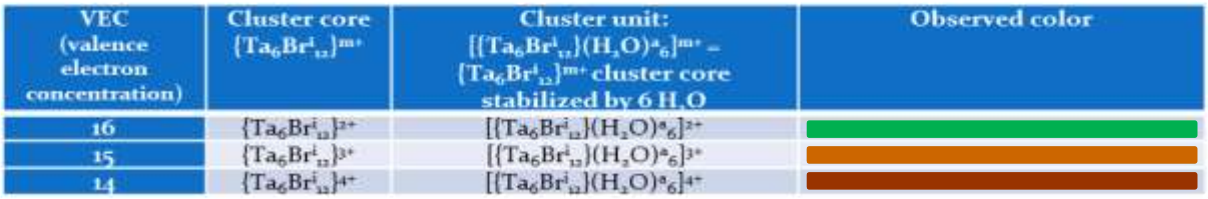
- MEK and Acetone: sonication for 30 min and stirring 24h
- Other solvents: sonication for 40 min

Table S2: Optimization of the EPD parameters for the TBH cluster thin films. Weight of TBH cluster is 10 mg.

EPD Solution	Applied voltage (V)	Deposition time (sec)	Thin film realization
10 ml Acetone	10, 15, 20, 25	30	✓
		60	✓
15 ml Acetone	20, 25	30	✓
		60	✓
0.15 ml H_2O/10 ml Acetone	8, 10, 12, 15, 18, 20, 25	30	✓
		60	✓
0.2 ml H_2O/10 ml Acetone	8, 10, 12, 15, 18, 20, 25	30	✓
		60	✓
0.25 ml H_2O/10 ml Acetone	8, 10, 12, 15, 18, 20, 25	30	✓
		60	✓
0.5 ml H_2O/10 ml Acetone	8, 10, 12, 15, 18, 20, 25	30	✓
		60	✓
0.2 ml H_2O/15 ml Acetone	15	20	✗
		30	✗
		60	✓
		90	✓
	20	20	✗
		30	✓
		60	☑
		90	✓
0.2 ml H_2O/15 ml Acetone/10 mg PVP	25	30	✓
		60	✓
		90	✓
	30	30	☑
		60	☑
		90	☑
	35	30	✓
		60	✗
		90	✗

☑ The best conditions for high homogeneity, transparence and UV-Vis absorption

Table S3.



VEC (valence electron concentration)	Cluster core $\{Ta_6Br^i_{12}\}^{m+}$	Cluster unit: $[\{Ta_6Br^i_{12}\}(H_2O)^a_6]^{m+}$ = $\{Ta_6Br^i_{12}\}^{m+}$ cluster core stabilized by 6 H_2O	Observed color
16	$\{Ta_6Br^i_{12}\}^{2+}$	$[\{Ta_6Br^i_{12}\}(H_2O)^a_6]^{2+}$	🟩
15	$\{Ta_6Br^i_{12}\}^{3+}$	$[\{Ta_6Br^i_{12}\}(H_2O)^a_6]^{3+}$	🟧
14	$\{Ta_6Br^i_{12}\}^{4+}$	$[\{Ta_6Br^i_{12}\}(H_2O)^a_6]^{4+}$	🟫

Table S4: FOM values for green-Ta_6@ITO film and green-Ta_6@PVP@ITO films after several weeks exposure in air

Name	x	y	z	Tvis	Tsol	Tvis/Tsol
green-Ta6@ITO 20V 60s after several weeks	0.342	0.363	0.295	52.74	42.83	1.23
green-Ta6@PVP@ITO 30V 30s after several weeks	0.291	0.362	0.346	59.33	47.58	1.25
green-Ta6@PVP@ITO 30V 60s after several weeks	0.282	0.381	0.338	50.53	41.27	1.22
green-Ta6@PVP@ITO 30V 90s after several weeks	0.287	0.383	0.330	48.90	39.14	1.25

Table S5: L*a*b colour space values

Name	L*	a*	b*
ITO 6-7 Ω/sq	94,917	-2,430	4,052
Brown-Ta6@ITO film	78,099	-0,940	19,438
green-Ta6@ITO 20V 60s	76,162	-6,667	10,961
green-Ta6@PVP@ITO 30V 30s	83,259	-19,283	6,114
green-Ta6@PVP@ITO 30V 60s	76,250	-30,877	10,437
green-Ta6@PVP@ITO 30V 90s	75,288	-29,910	11,186
Ideal blocker	95,996	-0,044	0,075

Table S6: L*a*b colour space values after several week exposure in air

Name	L*	a*	b*
green-Ta6@PVP@ITO 30V 30s after several weeks	81,454	-22,486	6,410
green-Ta6@PVP@ITO 30V 60s after several weeks	76,342	-31,493	9,801
green-Ta6@PVP@ITO 30V 90s after several weeks	73,584	-35,087	10,769
green-Ta6@ITO 15V 60s after several weeks	84,048	-4,054	8,896
green-Ta6@ITO 20V 60s after several weeks	77,317	-0,738	14,282

Calculation of color coordinates:

The color coordinates (x, y, z) 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 an reference illuminant I(λ) giving the following equations:[S2]

$$X = \frac{1}{N} \int \bar{x}(\lambda) \times T(\lambda) \times I(\lambda)\, d\lambda \qquad \text{Eq. S1}$$

$$Y = \frac{1}{N} \int \bar{y}(\lambda) \times T(\lambda) \times I(\lambda)\, d\lambda \qquad \text{Eq. S2}$$

$$Z = \frac{1}{N} \int \bar{z}(\lambda) \times T(\lambda) \times I(\lambda)\, d\lambda \qquad \text{Eq. S3}$$

$$N = \int \bar{y}(\lambda) \times I(\lambda)\, d\lambda \qquad \text{Eq. S4}$$

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:

$$X = \frac{1}{N} \sum_i \bar{x}_i \times S_i \times I \qquad \text{Eq. S5}$$

$$Y = \frac{1}{N} \sum_i \bar{y}_i \times S_i \times I_i \qquad \text{Eq. S6}$$

$$Z = \frac{1}{N} \sum_i \bar{z}_i \times S_i \times I_i \qquad \text{Eq. S7}$$

$$N = \sum_i \bar{y}_i \times I_i \qquad \text{Eq. S8}$$

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

$$x = \frac{X}{X + Y + Z} \qquad \text{Eq. S9}$$

$$y = \frac{Y}{X + Y + Z} \qquad \text{Eq. S10}$$

$$z = \frac{Z}{X + Y + Z} \qquad \text{Eq. S11}$$

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

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

FOM values: The efficiency as saving energy of the prepared Ta_6-based UV and NIR filters 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]

$$T_{vis}= \frac{\int_{300}^{1200} T(\lambda) \times X(\lambda)\, d\lambda}{\int_{300}^{2500} X(\lambda)\, d\lambda} \qquad \text{Eq. S12}$$

$$T_{sol}= \frac{\int_{300}^{2500} T(\lambda) \times X(\lambda)\, d\lambda}{\int_{300}^{2500} X(\lambda)\, d\lambda} \qquad \text{Eq. S13}$$

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:

$$T_{sol},\ T_{vis}= \frac{\sum_{i} Ti \times X}{\sum_{i} X_{i}} \qquad \text{Eq. S14}$$

Figure S1. (a) UV-vis-NIR spectra of ITO substrate and green-Ta_6@ITO films prepared according to various water content (b) SEM images of the surface of the green-Ta_6@ITO films prepared according to various water content (c) XRD patterns of different Ta_6-films compared with that of the TBH precursor powder. Green-Ta_6@ITO (big particles) and green-Ta_6@ITO were prepared from solutions containing 0.050 and 0.015 mL of water per mL of acetone respectively (10 V and 60 s). Brown-Ta6@ITO film was obtained without addition of water (10 V and 60 s).

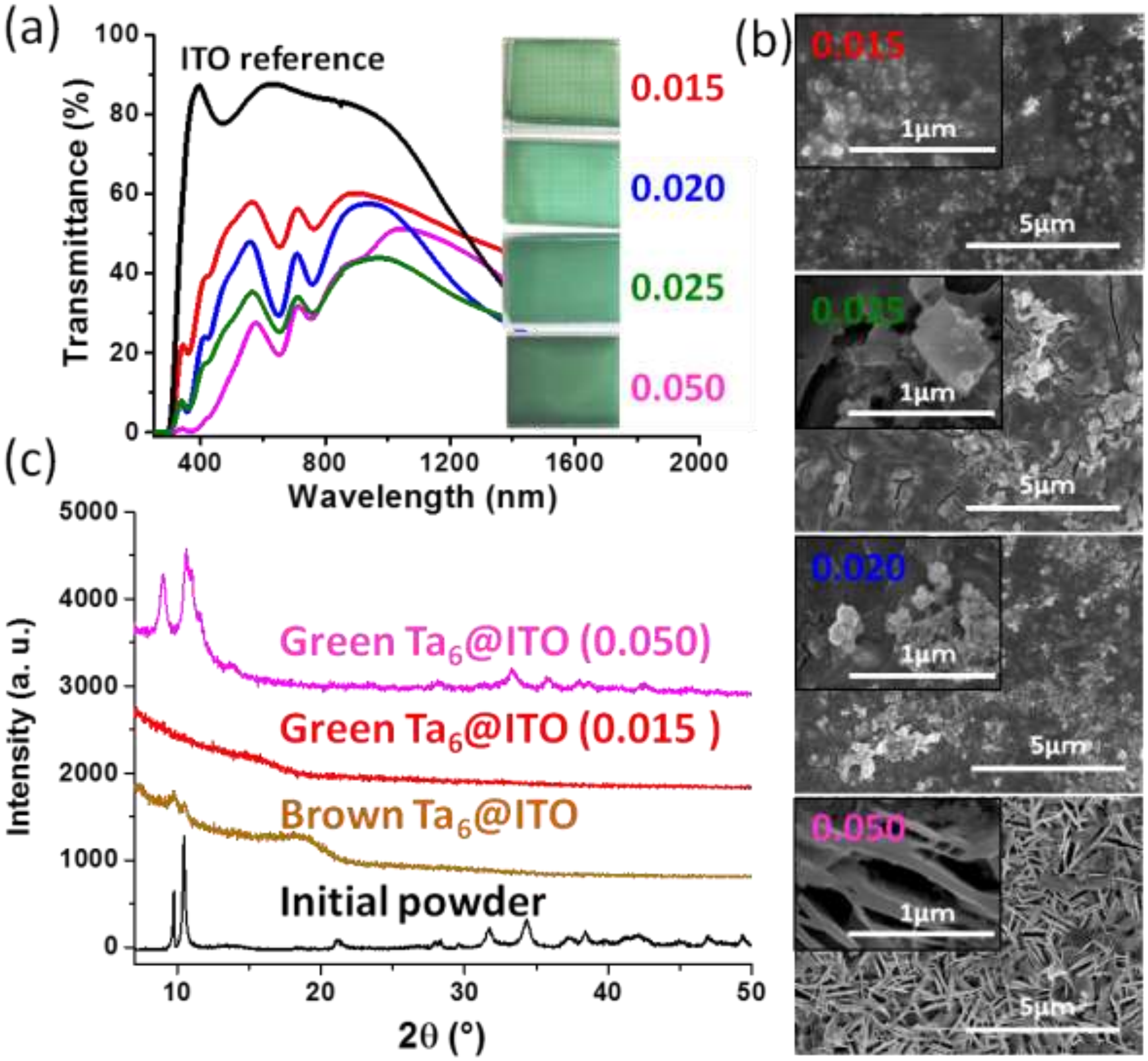
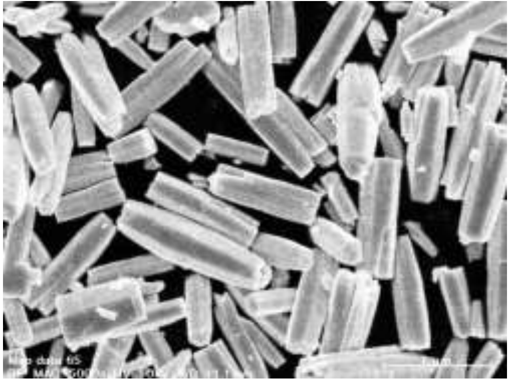


Figure S2. SEM image of TBH powder



Raman spectroscopy.

Raman spectra of TBH powder and Ta_6@PVP@ITO film were recorded at room temperature and compared with data reported by Preetz et al.[S4] for $Ta_6Br_{14}.8H_2O$ (recorded at 80 K). They have shown that main typical frequencies of the M_6X_{12} cluster core units in $Ta_6Br_{14}.8H_2O$ are: two Ta_6-Br^aphase-vibrations (ν_{12}: 103 cm^{-1} ; ν5: 125 cm^{-1}), the symmetric metal-metal vibration located around 177 cm^{-1} (ν_1) and the Ta-Br^i vibration at 228 cm^{-1} (ν_2). It turns out that experimental spectrum of crystalized TBH powder and amorphous film exhibit similar characteristics with main bands at ν_{12} = 102 cm^{-1}; ν_5 = 123 cm^{-1}; ν_1 = 174 cm^{-1}; ν_2 = 223 cm^{-1} and at ν_{12} = 102 cm^{-1}; ν_5 = 119 cm^{-1}; ν_1 = 169 cm^{-1}; ν_2 = 225 cm^{-1} respectively (Figure S3). In first approximation, these bands are in good agreement with spectrum reported by Preetz et al.. Only a new band appears at 117 cm^{-1} in the case of bulk TBH powder, which can be explained by different apical ligand in our compound than Preetz's compound (H_2O instead of Br). The difference between powder and films can be explained mainly by the dissolution process for EPD (crystal bulk powder to amorphous thin film), the exchange of apical ligand and obviously the presence of PVP binder in the film. A complete understanding of Raman spectra are in progress.

Figure S3. Raman spectra of TBH powder and Ta-@PVP@ITO film

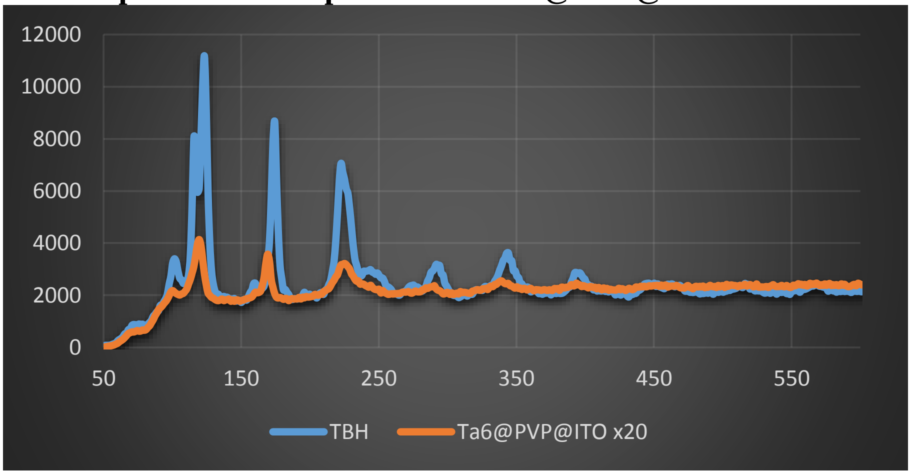
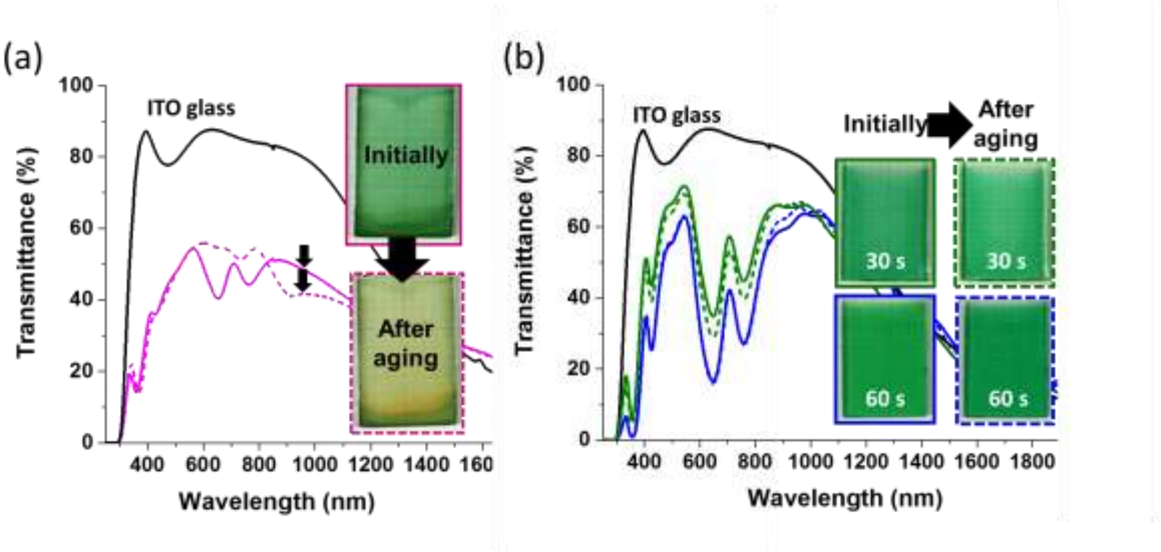


Figure S4. (a) Photographs and UV-vis-NIR spectra of ITO substrate and green-Ta_6@ITO film (20 V and 60 s) before and after aging several weeks (b) Photographs and UV-vis-NIR spectra of ITO substrate and green-Ta_6@PVP@ITO (30 V, 30 s and 60 s) before and after aging several weeks. Straight lines on UV-vis-NIR spectra and dash lines are corresponding to fresh sample and after several weeks of storing in air respectively.



HAADF-STEM observations. Scanning transmission electron microscopy (STEM) images were taken using a Cs-corrected JEOL JEM2100F microscope operating at 200 kV. It is equipped with a field-emission electron gun and incorporates multiple additional functions such as an energy-dispersive spectrometry (EDS) and a high sensitivity Z-contrast high angular annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis. A sample was prepared by direct deposition of powder (scratch from thin film) on carbon-activated copper grids. Thanks to the HAADF-STEM mode image in high resolution (FigureS3), it is clearly possible to observe the Ta_6 clusters inside the PVP matrix. As it can be observed, the cluster units, represented by light spots, are relatively well dispersed inside the PVP binder. Ta and Br elements have been clearly detected by EDS and are well distributed in the PVP matrix (Figure S4). A Br/Ta ratio of 2.13 (0.2) was estimated, which is closed to the theoretical value of Ta_6Br_{12}.

Figure S5. HAADF-STEM images of a Ta6@PVP@ITO thin film at different magnifications

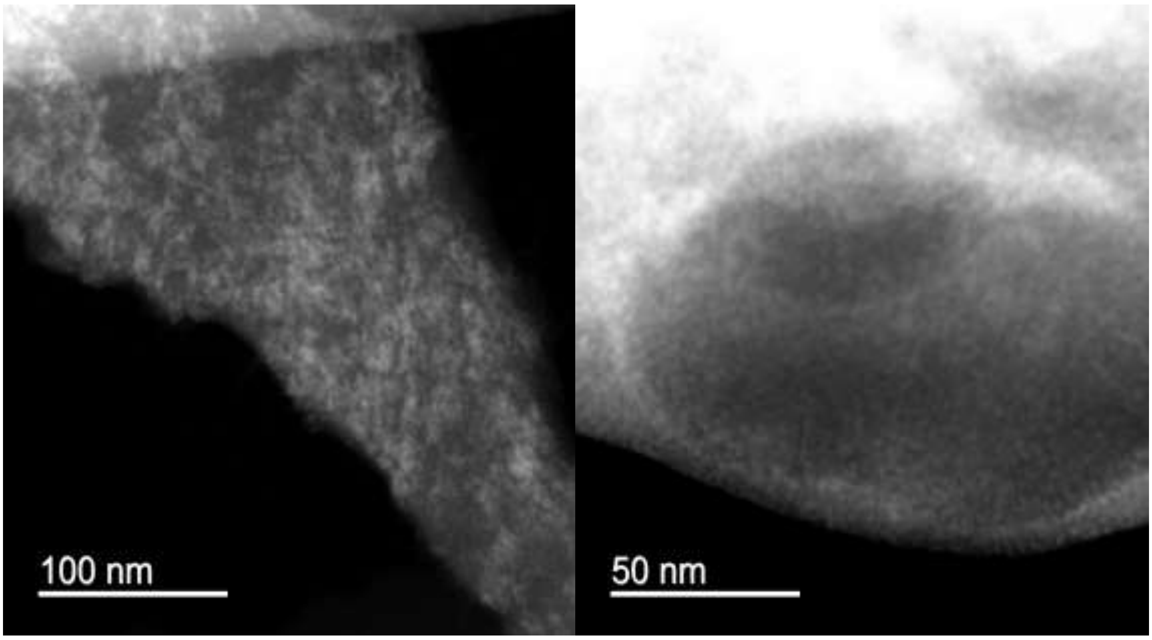


Figure S6. EDX-STEM analysis of Ta6@PVP@ITO thin film

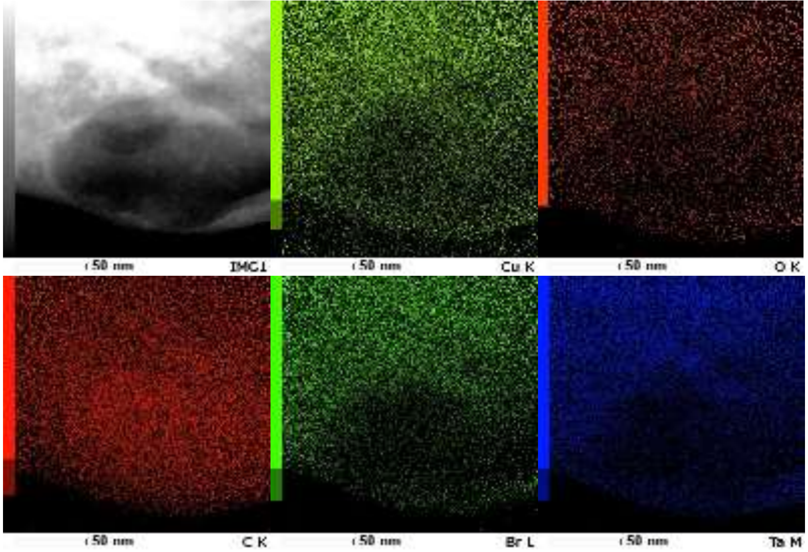


Figure S7. Photographs of highly transparent thin films deposited on 4x5 cm ITO substrates.

[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.

[S4] K. Harder, W. Preetz, *Z. anorg. allg. Chem.* 1990, ***591***, 32.