



Supporting Information

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Atomically Precise Noble Metal Clusters Harvest Visible Light to Produce Energy

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Supporting Information for the paper

Supporting Information 1

Experimental Section

The Au₃₀@BSA, Au₂₅SBB₁₈ and Ag₄₄MBA₃₀ clusters were synthesized via reported procedures.^[1-4] The prepared clusters were characterized. TiO₂ nanotubes were synthesized by a hydrothermal process and photoanodes were made by doctor-blading technique. All the materials prepared were characterized adequately.

Materials and Methods

All the chemicals were commercially available and were used without further purification. Tetrachloroauric acid trihydrate (HAuCl₄.3H₂O, ≥99.9%), bovine serum albumin (BSA, Sisco Research Laboratory, India), silver nitrate (AgNO₃, 99%), 4-(*t*-butyl)benzylmercaptan (BBSH, 98%), 4-mercaptobenzoic acid (MBA, 97%) and sodium borohydride (NaBH₄, 99.99%) were purchased from Aldrich. Tetrahydrofuran (THF, AR grade), dimethylformamide (DMF, AR grade), dimethylsulfoxide (DMSO, AR grade), toluene (AR grade), citric acid and cesium hydroxide (CsOH) pellets were procured from RANKEM, India. Titanium isopropoxide (TTIP, 99.99%, Aldrich, Germany), acetic acid (99.9%, Alfa Aesar, USA), isopropyl alcohol (absolute, Alfa Aesar, USA), triton-X-100 (molecular biology grade, Aldrich, Germany), acetonitrile (99.9%, Aldrich, USA), tertiary butyl alcohol (99.9%, Aldrich, USA), fluorine-doped tin oxide (FTO, size 2 x 2 cm², sheet resistance ~22Ω) (Solaronix Switzerland), cobalt based electrolytes Co(bpy)₃(PF₆)₂ and Co(bpy)₃(PF₆)₃ (Dyesol, Australia), sodium hydroxide (NaOH, Rankem, India), hydrochloric acid (HCl, Merck, India), ethylene glycol (99.9%, Merck, India), and citric acid (99.9% Merck, India) were also used. Sinapinic acid was employed as the matrix for MALDI TOF MS. All chemicals were used as such without further purification.

Synthesis of Au₂₅SBB₁₈

Au₂₅SBB₁₈ was synthesized using our reported method.^[4] In a typical synthesis; 10 mL of HAuCl₄.3H₂O (14.5 mM in THF) was added to 15 mL of BBSH thiol (89.2mM in THF) in a round-bottomed flask with stirring at the rate of 400 rpm at room temperature (29°C). The

solution became colorless after 15 min, indicating the formation of the Au(I) thiolates. An aqueous solution of 2.5 mL of NaBH₄ (0.4 M) was added rapidly to the reaction mixture under vigorous stirring (1100 rpm), and the solution turned from colorless to black, indicating the formation of clusters. The action was allowed to proceed with constant stirring for 3h under ambient conditions and then for 3h at 45°C. The crude solution thus obtained had a dark brownish color and showed characteristic UV absorption features of Au₂₅ clusters even without any purification. The solution was left overnight to yield mono-dispersed species. Solvent was removed under vacuum, and the cluster residue was first washed with water and later precipitated with methanol. The precipitate (Au₂₅SBB₁₈) was collected after washing repeatedly with methanol and was dried.

Synthesis of Au₃₀@BSA cluster

The red luminescent Au₃₀@BSA nanocluster^[2] was prepared following a reported method by adding 10mL of aqueous solution of HAuCl₄ (6 mM) to 10mL of BSA (25 mg/mL in water) under vigorous stirring for 5min. The pH of the solution was adjusted to ~11.0 with the addition of NaOH (1mL, 1M). The reaction was allowed to take place for 24 h, after which the solution turned from pale yellow to dark orange, with deep red emission, indicating the formation of Au₃₀@BSA nanocluster. The sample was stored at 4°C.

Synthesis of Ag₄₄MBA₃₀ cluster

Ag₄₄(MBA)₃₀ cluster was synthesized using a known procedure.^[1] Initially, 128 mg of AgNO₃ was taken in a beaker containing DMSO and water (4:7 volume ratio) mixture under constant stirring. 173 mg of MBA was added to the mixture and stirring was continued. 50% CsOH was added, followed by drop-wise addition of 283 mg of NaBH₄ in 9 mL water. Slowly the color changed to deep brown and after 1 h the color became deep red, which confirmed the cluster formation. This crude cluster was now purified using DMF as described in a reported method.^[73] The purified cluster extracted in DMF showed deep red color and its unique optical features further affirmed the synthesis of Ag₄₄(MBA)₃₀.

Synthesis of TiO₂ nanoparticles (TiO₂ NPs)

The TiO₂ NPs synthesized from titanium(IV) isopropoxide (TTIP) were used as a source material for the synthesis of TiO₂ nanotubes (NTs) by adopting a reported hydrothermal procedure.^[5] Briefly, 10 mL of TTIP was added drop-wise into 20 mL of distilled ethanol in a dried beaker under constant stirring. Then, 5 mL of double distilled water was added drop-wise and the resultant milky white suspension was stirred for 15 min. The formed TiO₂ NPs were washed several times with double distilled water and dried in a vacuum oven at 100°C for 3 h.

Synthesis of TiO₂ NTs

TiO₂ NTs were generated through a simple hydrothermal method reported already.^[6] In short, 1 g of the as-prepared TiO₂ NPs were treated with 25 mL of 10 M NaOH solution under constant stirring for 30 min to form a milky white suspension, which was transferred to a Teflon-lined autoclave, sealed and kept at 120°C in a muffle furnace for 24 h. After the treatment, the generated precipitate was separated from the suspension, treated with HCl (pH = 1.6) and washed thoroughly with double distilled water several times until the suspension become neutral. Finally, the TiO₂ NTs were separated through centrifugation, dried at 100°C for 3 h and subjected to calcination at 400°C for 3 h.

TiO₂ colloidal solution for electrospraying

The colloidal solution containing TiO₂ NPs for electrospraying was prepared using the following protocol. TTIP (20 mL) and glacial acetic acid (2.5 mL) were added to 25 mL isopropyl alcohol. This solution was subjected to a continuous stream supply (till the total volume of the solution become 25-30 mL). This resulted in rapid hydrolysis of TTIP leading to the formation of a thick TiO₂ colloid. This thick colloid was ground with 50 mL water using a mortar and pestle, and subsequently autoclaved at 180°C for 3 h. 20 mL of the autoclaved solution was added to a mixture of 2.5 mL acetic acid, 10 mL isopropyl alcohol and 5 drops of triton-X-100 and sonicated thoroughly for 1 h before electrospraying.

Synthesis of liquid polymer

The liquid polymer used for the TiO₂ paste preparation was synthesized using a reported procedure.^[7,8] Ethylene glycol (8.15 g) was taken in an RB flask and heated to 80°C in an oil

bath. At 80°C, 1.42 g of TTIP was added and stirred well. Once TTIP was completely dissolved, 6.3g of citric acid was added and the temperature was raised to 100°C. The mixture was kept at the same temperature under slow stirring for about 5 h. The resulting clear polyester was kept overnight for cooling down to room temperature.

Fabrication of quantum cluster-sensitized solar cell (QCSSC)

FTO glass plate was cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol. A compact TiO₂ blocking layer was first deposited onto the surface of a pre-cleaned FTO substrate by spray pyrolysis deposition (SPD) on a hot plate at 100°C. 100 mg of the prepared TiO₂ nanotube was mixed with 100μL of the polyester and sonicated for 12 h to make a fine paste of the right rheology. The paste was doctor-bladed on the FTO substrate which was pre-coated with a thin layer of TiO₂ colloid using SPD. Two different thicknesses of about 12 and 18 μm of TiO₂ film were deposited using SPD method. The doctor-bladed FTO plates were kept in an oven at 80°C for drying. The dried samples were kept in the furnace for annealing at a temperature of 450°C for 3 h. After annealing, the samples were treated with 30 mM TiCl₄ at 80°C for 30 min, washed with water and ethanol, and annealed again at 450°C for 3h.

Sensitization of cluster onto TiO₂ film

The annealed TiO₂ electrode was immersed into the cluster solution and kept at room temperature for 24h, followed by thorough washing with distilled water. The electrode turned light pink in color as the clusters were adsorbed onto TiO₂. The cluster-modified TiO₂ working electrode and the Pt-deposited FTO counter electrode were sandwiched together by a 50 μm spacer. A redox electrolyte of Co(bpy)₃(PF₆)₂/Co(bpy)₃(PF₆)₃ was introduced between the two electrodes. A drop of electrolyte solution (solid electrolyte of 0.22 M Co(bpy)₃(PF₆)₂, 0.033M Co(bpy)₃(PF₆)₃, 0.1M LiClO₄ and 0.5M 4-tert-butylpyridine in acetonitrile) was placed between the two electrodes, which were then finally sealed.

Characterization

Absorption spectra of clusters were recorded in the UV–Vis range with the PerkinElmer Lambda 25 UV–Vis absorption spectrophotometer. Scanning electron microscope (SEM) and

energy dispersive X-ray (EDAX) analyses were done in a FEI QUANTA- 200 SEM. Photoluminescence measurements were carried out on a Jobin Yvon Nano Log instrument. The band-pass for excitation and emission was set at 3 nm. FT-RAMAN spectrum was carried out using a multi RAM, stand alone model (BRUKER RFS 27), with a spectral range of 4000–50 cm^{-1} and the laser source being Nd:YAG 1064 nm. Phase analysis was carried out by powder X-ray diffraction (XRD) technique (Rigaku diffractometer, CuK radiation, $\lambda = 1.5406\text{\AA}$). The Flowsorb II 2300 Micrometrics surface area analyzer was employed for measuring the surface area, pore volume and pore diameter of the sample. X-ray photoelectron spectroscopy (XPS) measurements were done using an Omicron ESCA Probe spectrometer with polychromatic Mg $K\alpha$ X-rays ($h\nu = 1253.6\text{ eV}$) with a constant analyzer energy of 20 eV. The samples were spotted as drop-cast films on a sample stub. High resolution transmission electron microscopy (TEM) of clusters was carried out with a JEOL 3010 instrument. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) studies were conducted using a Voyager-DE PRO Biospectrometry workstation from Applied Biosystems. Photovoltaic characterization was performed under 1 Sun simulated sunlight (Newport, Oriel class A) with AM1.5G conditions. I-V curves were recorded with a Keithley 2400 digital source meter under an applied external potential scan for an exposed area of 0.25 cm^2 (using masking). IPCE characterization was done using an Oriel Newport (tracq basic, model 77890) configured for the quantum cluster sensitized solar cell.

Supporting Information 2

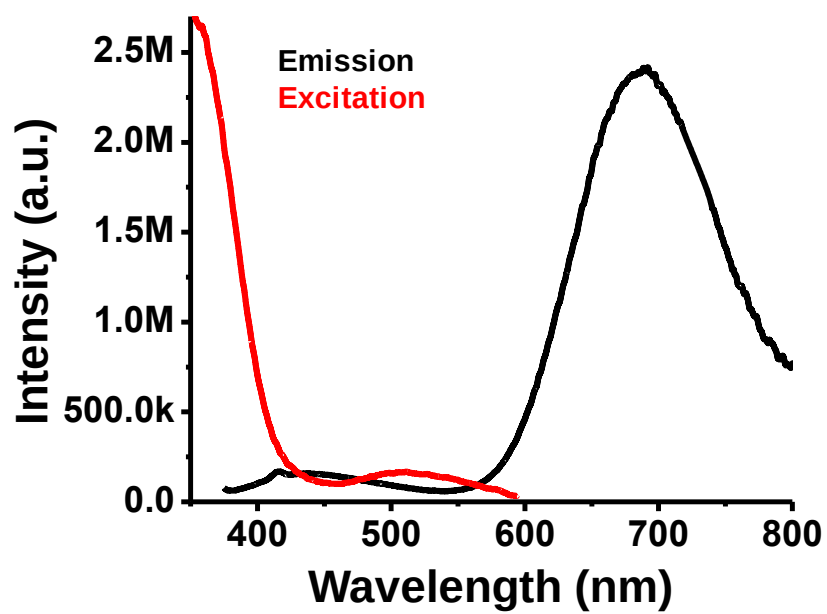


Fig. S1. Photoluminescence spectra of Au₃₀@BSA cluster.

Supporting Information 3

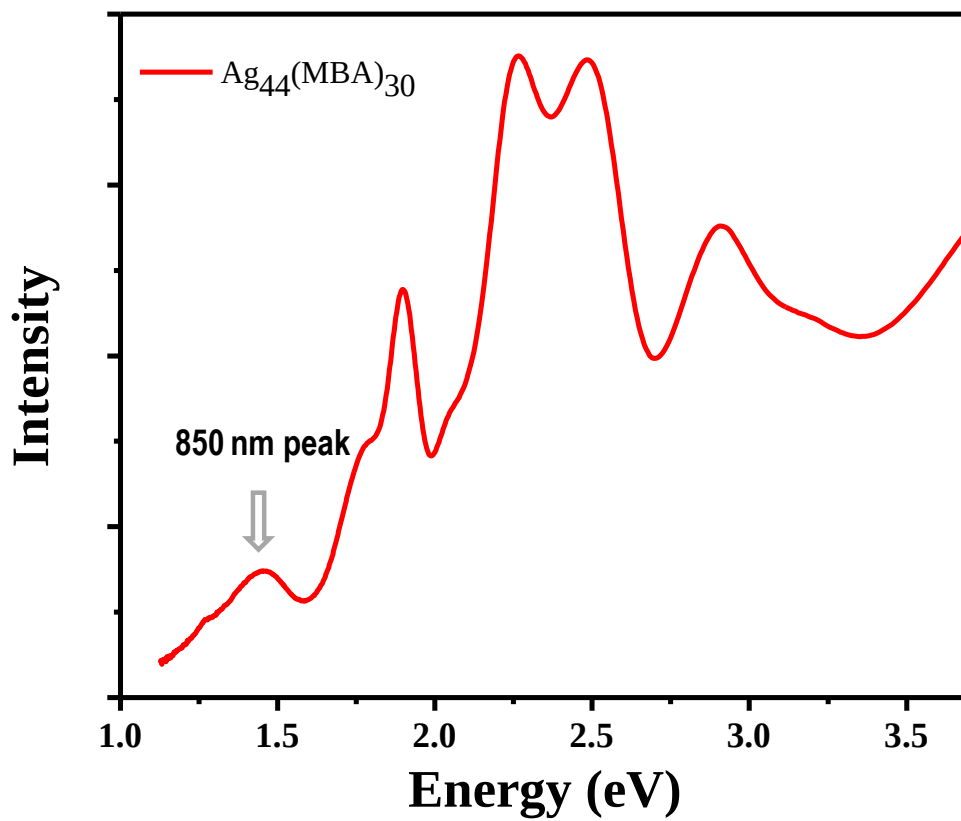


Fig. S2. UV/Vis spectra of $\text{Ag}_{44}\text{MBA}_{30}$ plotted in terms of energy.

Supporting Information 4

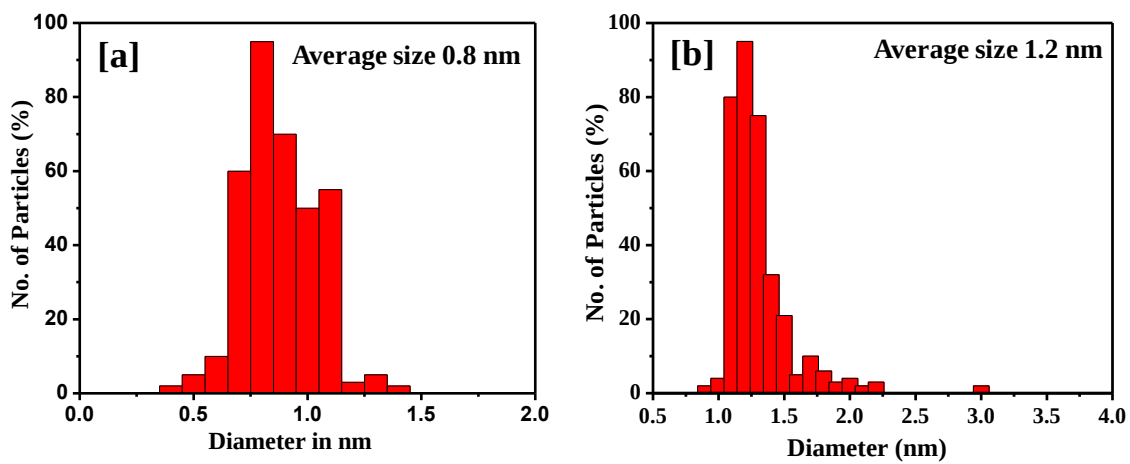


Fig S3. Particle size distribution of $\text{Au}_{30}\text{@BSA}$ and $\text{Ag}_{44}\text{MBA}_{30}$ clusters.

Supporting Information 5

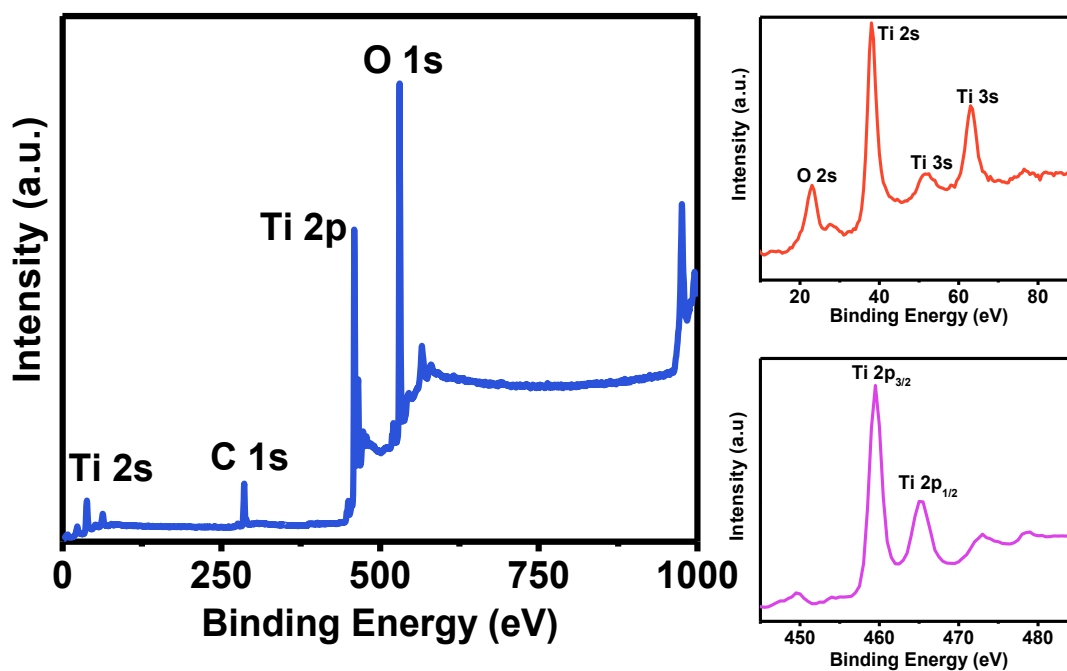


Fig. S4. XPS survey spectrum of the prepared TiO₂ NTs. Expanded views of some of the individual regions are also shown.

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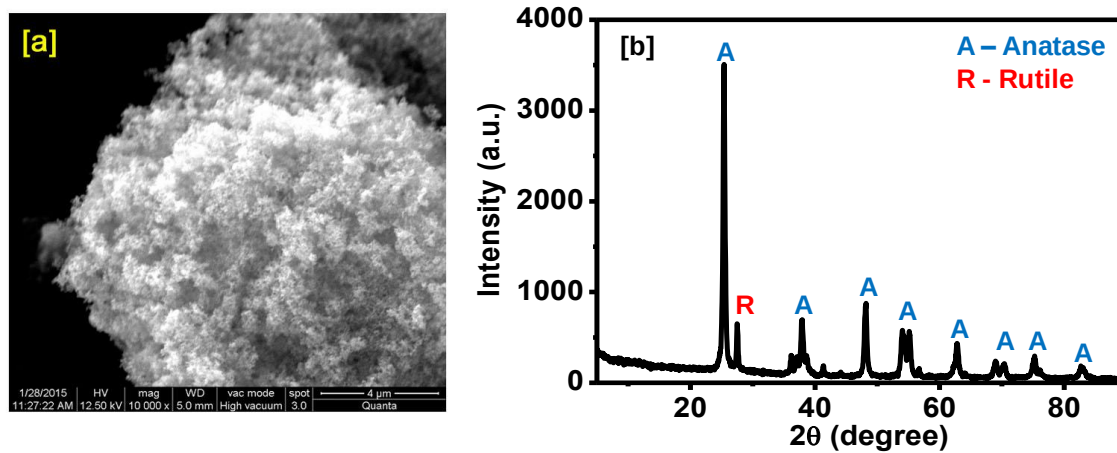


Fig. S5. SEM image [a] and XRD pattern [b] of P25 TiO₂.

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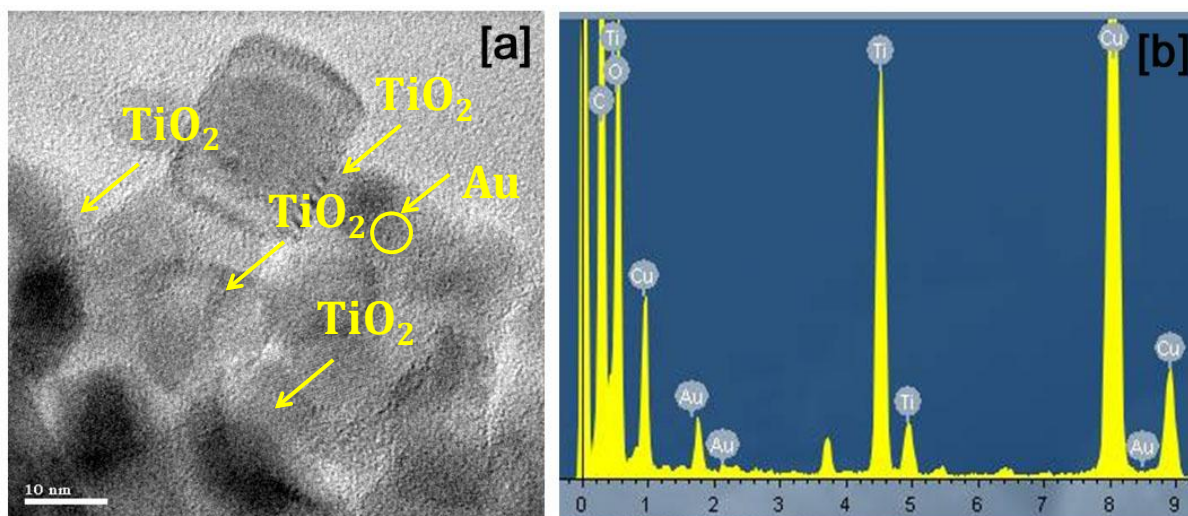


Fig. S6. TEM image [a] and corresponding EDAX spectrum [b] of $\text{Au}_{30}@\text{BSA}$ modified TiO_2 .

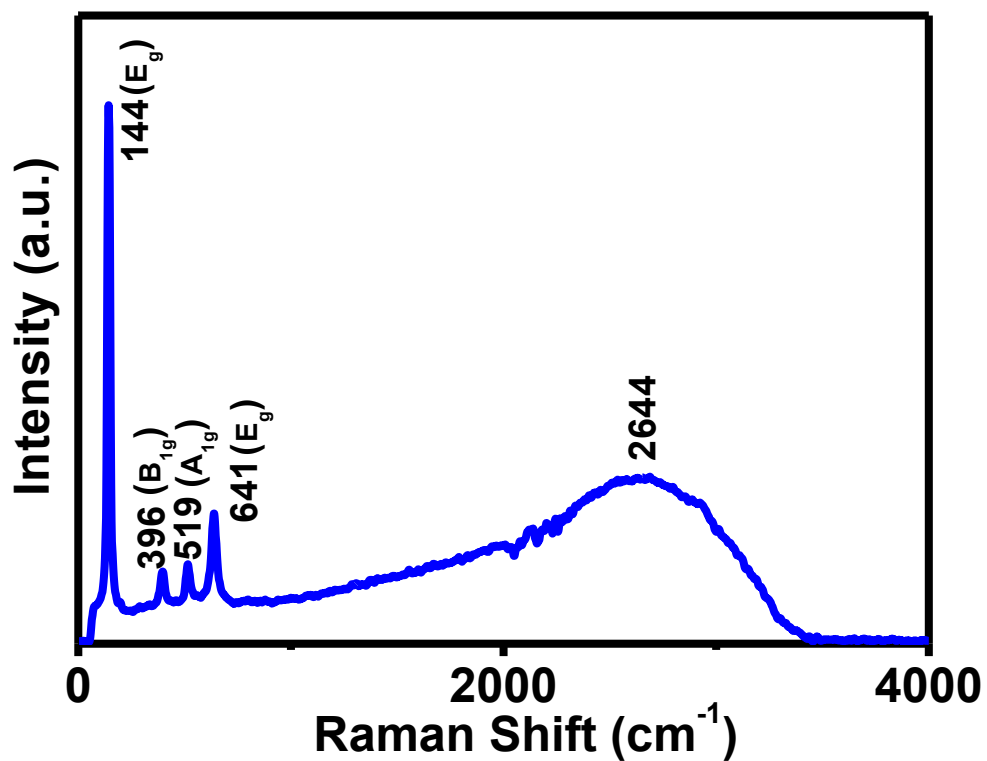


Fig. S7. Raman spectrum of the Au₃₀@BSA modified TiO₂. The Raman shift of 2644 cm⁻¹ is close to the luminescence maximum of the cluster at 619 nm. Assignments of the Raman lines are indicated.

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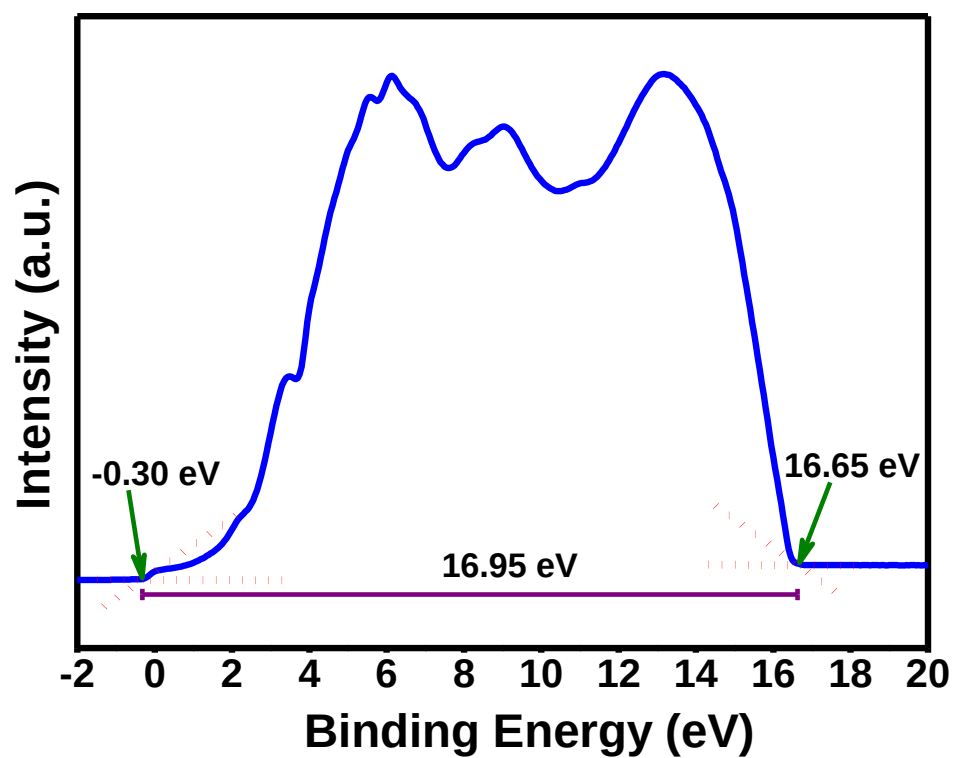


Fig. S8. UPS spectrum of standard polycrystalline Ag.

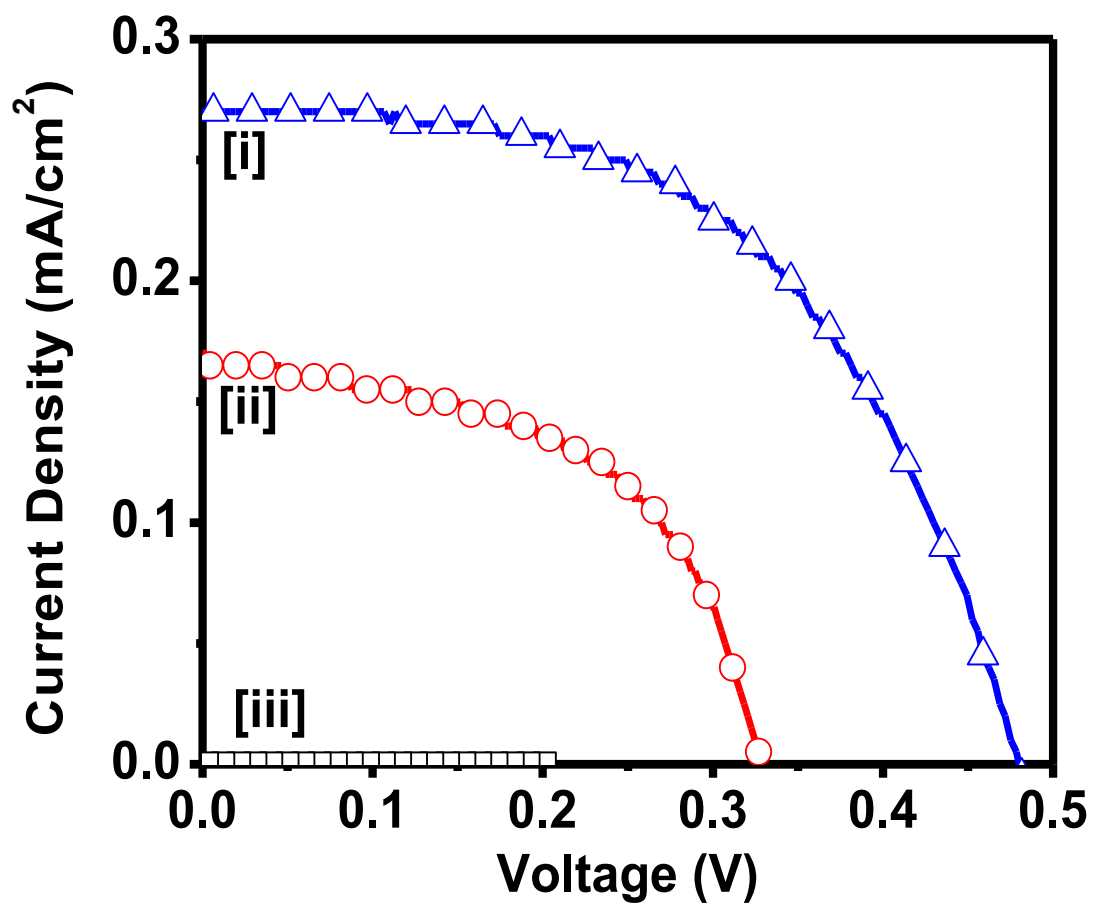


Fig. S9. *I*-*V* characteristics of the QCSSC with 18 μm thick TiO_2NTs photoanode sensitized with BSA [i], absence of sensitizer [ii] and dark current [iii].

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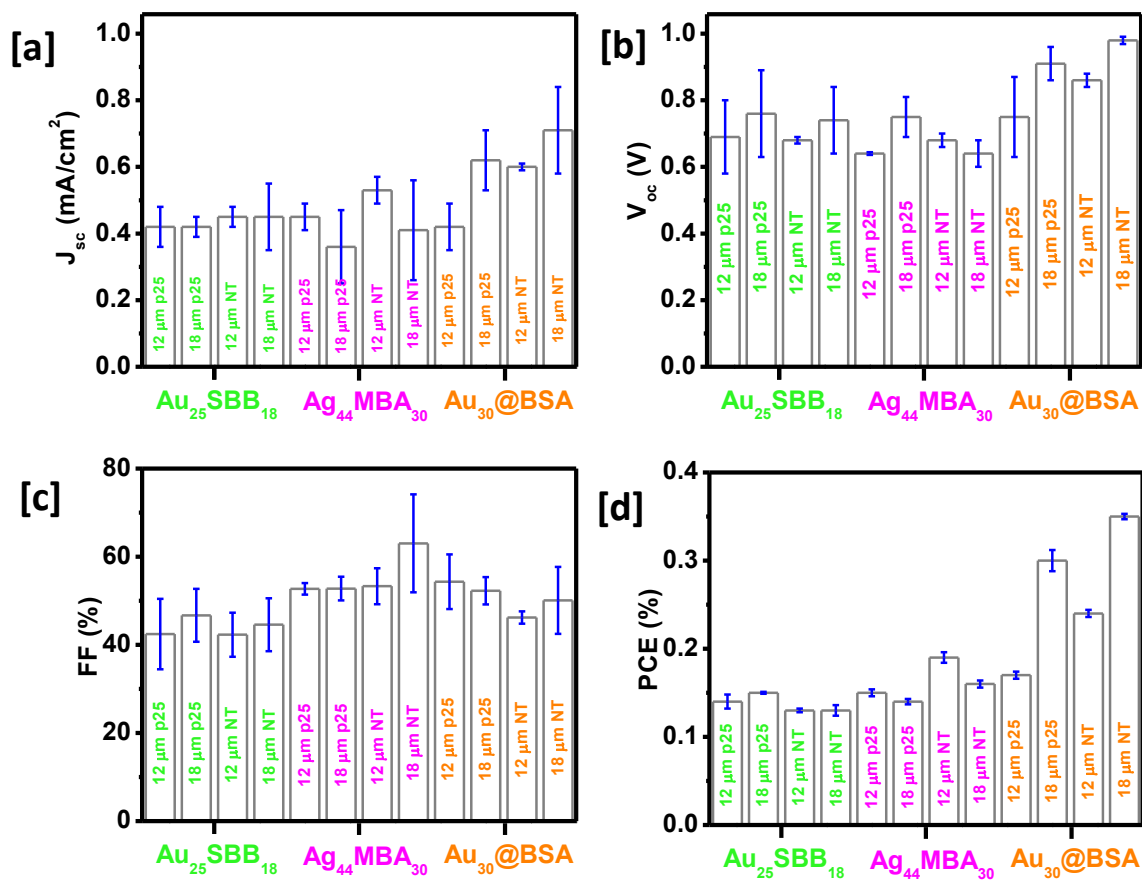


Fig. S10. Error bar graphs of short-circuit current density, J_{sc} [a], open-circuit voltage, V_{oc} [b], fill factor (FF) [c] and power conversion efficiency (PCE) (d) of Au₂₅SBB₁₈, Ag₄₄MBA₃₀ and Au₃₀@BSA clusters on p25 and NT TiO₂ with two different thicknesses (12 and 18 μm). Error bars represents minimum and maximum values.

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Table 1. Dark current details of Au₂₅SBB₁₈, Ag₄₄MBA₃₀ and Au₃₀@BSA QCSSCs.

Photoanode	Thickness (μm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	η (%)
Au ₂₅ SBB ₁₈					
P25	12	0.14	0.0011	43.97	0.00006
P25	18	0.24	0.0023	32.96	0.00019
NT	12	0.24	0.0022	36.46	0.00019
NT	18	0.33	0.0032	33.39	0.00035
Ag ₄₄ MBA ₃₀					
P25	12	0.16	0.0052	26.91	0.00020
P25	18	0.08	0.0036	40.49	0.00012
NT	12	0.24	0.0051	19.57	0.00023
NT	18	0.19	0.0068	26.23	0.00035
Au ₃₀ @BSA					
P25	12	0.10	0.0011	46.00	0.00005
P25	18	0.19	0.0022	44.80	0.00019
NT	12	0.14	0.0015	43.30	0.00009
NT	18	0.20	0.0012	42.13	0.00011

References:

- [1] A. Desireddy, B.E. Conn, B. E. J. Guo, B. Yoon, R.N. Barnett, B.M. Monahan, K. Kirschbaum, W.P. Griffith, R.L. Whetten, U. Landman, T.P. Bigioni, *Nature* **2013**, *501*, 399–402.
- [2] Z. Wu, J. Suhan, R. Jin, *J. Mater. Chem.* **2009**, *19*, 622–626.
- [3] J. Xie, Y. Zheng, J.Y. Ying, *J. Am. Chem. Soc.* **2009**, *131*, 888–889.
- [4] A. Mathew, G. Natarajan, L. Lehtovaara, H. Hakkinen, R.M. Kumar, V. Subramanian, A. Jaleel, T. Pradeep, *ACS Nano* **2014**, *8*, 139–152.
- [5] N. Sasirekha, B. Rajesh, Y.W. Chen, *Thin Solid Films* **2009**, *518*, 43–48.
- [6] S.H. Lim, J. Luo, Z. Zhong, W. Ji, J. Lin, *Inorg. Chem.* **2005**, *44*, 4124–4126.
- [7] A.S. Nair, R. Josse, Y. Shengyuan, S. Ramakrishna, *J. Colloid Interface Sci.* **2011**, *353*, 39–45.
- [8] G.S. Anjusree, A. Bhupathi, A. Balakrishnan, S. Vadukumpully, K.R.V. Subramanian, N. Sivakumar, S. Ramakrishna, S.V. Nair, A.S. Nair, *RSC Adv.* **2013**, *3*, 16720–16727.