Atomically precise gold and silver clusters are a new class of sensitizers which can be used as substitutes for dyes in the classical dye-sensitized solar cells (DSCs). Here noble metal clusters protected by proteins and thiols (Au_{30}@BSA, Au_{25}SBB_{18}, and Ag_{44}MBA_{30}) have been used for photovoltaic studies. These metal clusters were used as sensitizers for the photoanodes fabricated using TiO\(_2\) nanoparticles. The TiO\(_2\) clusters and the solar cells were characterized by spectroscopy, microscopy, current-voltage (I-V) and incident photon-to-current conversion efficiency (IPCE) measurements. A systematic I-V study revealed a conversion efficiency of 0.35 % for the Au_{30}@BSA sensitized solar cell made from TiO\(_2\) NTs which showed an IPCE maximum of 3 % at ~ 400 nm.

### Introduction

Quantum clusters (QCs) are a new class of sub-nanometer sized materials, comprising of a few atoms protected by proteins or organic thiols and they are simply used using their metal cores, such as Au\(_{30}\), Au\(_{25}\), Au\(_{13}\), or Au\(_{23}\). These QCs have possible applications in single molecule spectroscopy, biological labeling, catalysis, and other fields. Amongst the various clusters synthesized so far at room temperature, some are extremely stable at room temperature. The high stability of bovine serum albumin (BSA) protected gold clusters (Au\(_{30}@\)BSA) is attributed to the complete protection of Au by proteins. In comparison, the stability of thiol-protected clusters is often associated to their closed shell electronic structure composed of \(n\) electrons (\(n = 2, 8, 18, 34, 58, 92, \ldots\)).

Quantum clusters have remarkable optical and electronic properties. They possess discrete energy states and exhibit characteristic luminescence. The luminescence of these atomically precise clusters has been found to be sensitive to many factors such as chemical contamination, pH, temperature, etc. Anchoring QCs on mesoscale particles leads to surface enhancement of their luminescence. The Au\(_{30}@\)BSA and Ag\(_{44}@\)BSA clusters display distinct features in their emission spectrum. The Au\(_{30}@\)BSA cluster has been demonstrated as a sensor for TNT (2,4,6-trinitrotoluene) and Hg\(^{2+}\) ions by quenching of cluster luminescence. These studies have been performed at a single particle level. Ultra-trace Hg\(^{2+}\) detection at 10\(^{-21}\) mole level using atomically precise Au@BSA clusters coated on single nanofibers was demonstrated. Quenching of the red emission upon exposure to mercury has been observed under a dark field fluorescence microscope. Many other researchers have also looked at the use of Au@BSA clusters in sensor applications.

In a dye/quantum dot (QD)-sensitized solar cell (DSC/QDSC), the dye or QD functions as a source of photoelectrons. The photoexcited electrons are injected into the conduction band of the semiconductor from the lowest unoccupied molecular orbital (LUMO) of the dye or the conduction band of the QD. The semiconductor employed is often nano titanium dioxide (TiO\(_2\)). The electrons are transported through TiO\(_2\) arrays in the photoelectrode to the back contact (usually a transparent conducting oxide such as fluorine-doped tin oxide (FTO) on glass). The oxidized dye/QD is regenerated using a redox electrolyte, which in turn is brought back to the original state by the electrons from the counter electrode. Several factors such as crystallinity, morphology, porosity of TiO\(_2\), absorption characteristics of the sensitizer, etc. play important roles in determining the overall efficiency of the solar cells.

TiO\(_2\) is the preferred metal oxide for DSCs due to its desired surface chemistry, abundance, low-cost, environment friendliness, and favorable alignment of its conduction band edge with the LUMO/CB of the dyes/QDs, etc. The conventional DSCs use Ru-based metal-organic dyes (N3, N719, and Black dye) for sensitization. Ru being a rare metal (rarer than gold), the Ru-based dyes are expensive. Therefore, search for non-Ru based dyes is essential for the success of DSCs. Amongst the...
non-Ru based dyes for DSCs,[31-36] the porphyrine-based ones were found to be ideal.[37-39] QCs can be utilized as substitutes for the dyes in DSCs as they also have the potential for absorbing light in the visible region and show high stability to visible and infrared light.[40-45] The plasmonic effect of noble metals can help in the enhancement in the performance of solar cells.[46,47]

In the present work, the usefulness of the BSA (bovine serum albumin), SBB (4-(t-butyl)benzylmercaptan) and MBA (4-mercaptobenzoic acid)-protected gold and silver QCs as sensitizers for solar cells has been compared. While there have been a few reports of cluster-based DSSCs, they have used only glutathione protected systems. A comparison of various QCs with varying ligands is essential as glutathione protected clusters are generally unstable especially in presence of electrolytes. Protecting ligands are important for proper linkages with TiO$_2$ as well as for imparting stability to the cluster systems. The TiO$_2$ nanotubes (NTs) employed as the photoanode were synthesized by the hydrothermal method. Amongst the low temperature methods, the hydrothermal/solvothermal method is a versatile route for the synthesis of nanomaterials.[50]

Experimental

Synthesis and characterization of the Au$_{30}$@BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ quantum clusters, TiO$_2$ nanotubes and the solar cell fabrication methodology are discussed in detail in the Supporting Information 1 (SI-1).

Results and Discussion

The characteristic properties of the synthesized Au$_{30}$@BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ clusters are shown in Figure 1. In view of their reported properties, we present only the essential aspects here. The synthesized Au$_{30}$@BSA clusters did not show any distinct absorption feature in the visible region, though a characteristic onset of absorption was observable at 520 nm (Figure 1a). Au$_{30}$@BSA is a water soluble luminescent cluster.
exhibiting bright red emission at 680 nm when excited at 365 nm at room temperature (Figure S1 in supporting information (SI)). Photographs of the brown-colored cluster solution under visible light and UV light are shown as insets (i) and (ii) in Figure 1a. Mass spectra of the protein and the cluster were measured by MALDI-TOF-MS using sinapinic acid as the matrix. The spectra were collected in the positive ion mode. BSA shows a distinct peak at 67 kDa in agreement with the literature (Figure 1a). For Au30@BSA, the major peak is positioned at m/z 74 kDa. The difference between the above two peaks corresponds to Au30 which suggests that the cluster is fully encapsulated by a single protein molecule. HRTEM images also show the presence of sub-nanometer sized clusters of Au30@BSA (Figure 1a (iv)) as dark spots highlighted as broken circles in yellow color. HR-TEM image of a single cluster is not possible in an isolated state because the sub-nano clusters (~0.8 nm) are prone to electron beam-induced aggregation. A graphical representation of Au30@BSA is shown in Figure 1a (v). In contrast to Au30@BSA, the thiolate-protected gold cluster (Au25SBB18) has a well-defined optical absorption spectrum as shown in Figure 1b, revealing discrete molecule-like features which are characteristic of Au25 QCs. Absorption spectra of the quantum clusters of Au25SBB18 show peaks at 448 nm and 683 nm, respectively. The peak at 448 nm has ligand-metal (SBB-Au25) character. The absorption at 683 nm is due to the inband transition derived from sp orbitals of Au. This peak is characteristic of the Au25 clusters and occurs in all spectra of Au25 clusters reported in the literature. The structure of Au25SBB18 is shown in Figure 1b (i). DCTB (trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as the matrix for MALDI MS measurements of Au25SBB18. An intact molecular ion peak observed at m/z 8151 in Figure 1b (ii) confirms that the cluster is Au25SBB18 and its high intensity is indicative of the purity of the prepared cluster.

The average size of the cluster was determined to be less than 2 nm from TEM (Figure 1b (iii)). Interestingly, the clusters did not show any significant electron-beam-induced aggregation, a common phenomenon observed in other Ag and Au clusters. This may be due to the enhanced stability provided by the bulky ligand shell around the cluster. The Au30@BSA clusters appeared monodisperse and the average size of the clusters was 0.8 nm. The inset of Figure 1c (ii) shows the HRTEM image of Ag44MBA30 whose core size was found to be 1.2 nm. A histogram showing size distribution of Ag44MBA30 is shown in the SI (Figure S3). For Au30SBB18 clusters, the average size was >2 nm as confirmed by TEM and it did not show any electron beam-induced aggregation. The optical absorption spectrum of Ag44MBA30 shows several peaks in the 300-1000 nm region (Figure 1c). Five intense bands at 850, 651, 545, 496 and 423 nm, respectively, have been observed along with three broad bands centered at around 703, 608 and 386 nm. These characteristics bands confirm the purity of the clusters. The prominent peak at 850 nm is plotted in energy scale and shown in Figure S2. The structure of Ag44MBA30 is shown in Figure 1c (i). All the characterization data show that a highly homogenous cluster has been used for the preparation solar cells.

The X-ray diffraction (XRD) pattern of the TiO2 NTs is shown in Figure 2a. The peaks in the XRD were indexed corresponding to the standard database, JCPDS No. 21-1272. The most intense diffraction peak observed at 20 of 25.43° corresponds to the (101) plane of anatase TiO2. The average crystallite size of the TiO2 NTs calculated from the Debye-Scherer formula:

\[
L = \frac{0.9\lambda}{\beta \cos \theta}
\]

[where L is the average particle size, \(\lambda\) is the X-ray wavelength, \(\beta\) is the full width at half maximum (FWHM) and \(\theta\) is the Bragg’s angle] was 11.71 nm, which is in close agreement with the TEM results. The synthesized TiO2 was characterized by spectroscopy and microscopy. The surface morphology of the hydrothermally prepared TiO2 NTs was examined by SEM analysis. It can be seen in Figure 2a (i) that the TiO2 NTs are uniformly distributed. The TEM images (Figure 2a (ii)) illustrate the TiO2 NTs produced were well shaped and randomly oriented. TEM analysis also...
yielded the diameter and length of the TiO$_2$ NTs with an internal cavity of 10 - 12 nm and 200 - 250 nm, respectively. In the Raman spectrum (Figure 2b) of TiO$_2$, the peaks centered at 144, 196 and 638 cm$^{-1}$ denote the E$_g$ Raman modes and that at 397 and 514 cm$^{-1}$ represent B$_1g$ and A$_1g$ Raman modes, respectively, of anatase TiO$_2$.[63,64]

No other peaks characteristic of any other form of TiO$_2$ (say rutile for example) were observed either in the XRD or in the Raman spectrum, indicating the phase purity of the prepared TiO$_2$ NTs. The nitrogen adsorption-desorption isotherms of the TiO$_2$ NTs are depicted in the inset Figure 2b (i). The Brunauer-Emmett-Teller (BET) surface area of the TiO$_2$ NTs was estimated to be 469 m$^2$/g, which is higher than that of the commercially available P25 TiO$_2$ (~40 m$^2$/g).[65] The Barrett-Joyner-Halenda (BJH) pore volume and pore size of the TiO$_2$ NTs were found to be 0.896 cm$^3$/g and 9 nm, respectively indicating the mesoporosity of the TiO$_2$. X-ray photoelectron spectroscopy (XPS) was carried out to examine the phase purity and oxidation state of Ti in TiO$_2$ (see SI, Figure S4). The XPS spectra confirm the existence of Ti in its Ti$^{4+}$ state based on the presence of the two peaks located at 458.8 eV and 465.3 eV, corresponding to 2p$_{3/2}$ and 2p$_{1/2}$ of Ti$^{4+}$, respectively. The O1s peak at a binding energy of 530.7 eV is attributed to O$^2_\text{--}$O. The XPS analysis also confirmed the absence of impurities in the synthesized TiO$_2$ NTs.[66] SEM and XRD were also used to characterize commercial P25 (see SI, Figure S5). XRD showcased the co-existence of rutile and anatase phases in P25 versus pure anatase phase in the TiO$_2$ NTs.

The TiO$_2$ NTs and P25 electrodes prepared by doctor-blading (and subsequent sintering at 450°C) were immersed into the cluster solutions. For comparative studies, two different thicknesses of TiO$_2$ NT and P25 TiO$_2$ (12 and 18 µm, respectively) were used. In this study, we fabricated the quantum cluster-sensitized solar cell (QCSSC) by applying the same processing conditions as for DSSCs; in the former, quantum cluster substitutes the dye. The experimental details can be found in SI.

The Au$_{30}$@BSA modified TiO$_2$ NT was further characterized via TEM, XPS and Raman spectroscopy to confirm the presence of Au QCs on the TiO$_2$ NT surface. The increase in weight was observed after immersion of the TiO$_2$ electrode into the Au$_{30}$@BSA cluster solution. TEM analysis showed that the clusters were coated onto the surface of the TiO$_2$ electrode (see SI, Figure S6). This was confirmed from the EDS data shown in Figure S6 (clusters and TiO$_2$ are labeled). XPS analysis was carried out to examine the elemental composition of Au$_{30}$@BSA-modified TiO$_2$ photoanode and to identify the oxidation state of Au in TiO$_2$ doped Au cluster shown in Figure 3(a-d). The fully scanned survey spectrum of Au modified TiO$_2$ is shown in Figure 3a which shows Au, Ti, O, N and C. The XPS spectrum displayed the characteristic peak of Au showing nearly zero oxidation state. The 4f core-level photoemission spectrum of Au$_{30}$@BSA is expanded in Figure 3b. The BE of Au$^{2+}$/Au$^{3+}$ of the gold QCs comes in between 84 and 86 eV.[67] Two components due to Au$^{2+}$ (84.5 eV for 4f$_{7/2}$ and 88.2 eV for 4f$_{5/2}$) and Au$^{3+}$ (86.1 and 89.7 eV) are used to fit the spectrum. Most of the intensity is due to Au$^{2+}$ and the Au$^{3+}$ components are assumed to be due to the protein bound surface atoms of the cluster.

From Figure 3c, the spin-orbit split components ($2p_{1/2}$ and $2p_{3/2}$) of the Ti 2p peak were de-convoluted into two components centered at 458.5 and 464.1 eV. The measured separation between the Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peaks was 5.6 eV, which is consistent with the binding energy separation observed for stoichiometric TiO$_2$. The O1s peak of Au modified TiO$_2$ on the surface could be fitted to three Gaussian curves centered at ~530.8, ~532.6, and ~533.9 eV, respectively shown in Figure 3d. The O1 species at the low binding energy of 530.8 eV belongs to O$^2_\text{--}$ions in the anatase TiO$_2$ structure.[67-69] The O1 species with a medium binding energy centered around 532.6 eV is attributed to O and O$^2_\text{--}$ ions in the oxygen deficient region mainly caused by oxygen vacancies.[70] The high binding energy species, OIII centered at ~533.9 eV belong to the absorbed or dissociated oxygen or OH species on the surface of TiO$_2$.[71] The sample was finally analyzed by Raman spectroscopy (Figure S7). The anatase phase of the TiO$_2$ matrix was observed along with the luminescent feature of the cluster, around 2644.3 cm$^{-1}$ (619 nm); note that the sample was excited using 532 nm laser.

Figure 4a shows a schematic representation of occupied and unoccupied electronic energy levels near the Fermi level, $E_F$. $E_{\text{vac}}$ is the vacuum level at which the energy of the electron is zero. $E_{\text{CBM}}$ and $E_{\text{VBM}}$ are the conduction-band minimum and the valance band maximum, respectively. Other abbreviations are: $E_j$ - energy gap, IP - ionization potential and EA - electron affinity. Figure 4(b-d) show the typical HeI UPS spectra of standard Au$_{30}$BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ respectively. The location of the Fermi level relative to the vacuum level, $E_{\text{vac}} - E_F$ can be determined using the following relation:[71,72]

$$\nu = |E_{\text{cutoff}}| + E_{\text{vac}} - E_F$$

where $|E_{\text{cutoff}}|$ is the location of the inelastic cutoff and $\nu$ is the incident photon energy of 21.21 eV. The work function of Ag is 4.26 eV. From the UPS spectrum, $E_{\text{cutoff}}$ of standard Ag is 16.95 eV (Figure S8). The $|E_{\text{cutoff}}|$ of Au$_{30}$BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ are 16.27, 16.45 and 16.18 eV, respectively as indicated in Figure 4(b-d). From this $E_{\text{vac}} - E_F$ was calculated and the values for Au$_{30}$BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ are 4.94, 4.76 and 5.03 eV, respectively. The ionization potential (IP) is the location of the valence-band maximum (VBM), $E_{\text{VBM}}$ relative to $E_{\text{vac}}$. $E_{\text{VBM}}$ can be determined by choosing the point of maximum inflection near $E_j$ as indicated in Figure 4(b-d), and the $E_j - E_{\text{VBM}}$ were 1.52, 1.67 and 1.45 eV and IP values (equivalent to the HOMO level of the clusters) were calculated to be 6.46, 6.43 and 6.64 eV for Au$_{30}$BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ respectively. The inset of Figure 4c showed the point of inflection of Au$_{30}$ SBB$_{18}$, Since UPS only probes occupied states, conduction band minimum (CBM) cannot be determined from the UPS measurements.

However, the $E_{\text{CBM}}$ values were estimated knowing the IP values (described above) and the optical band-gap, $E_g$ determined from UV-Vis measurements. These were 1.65, 1.33 and 1.18 eV for Au$_{30}$BSA, Au$_{25}$SBB$_{18}$ and Ag$_{44}$MBA$_{30}$ respectively.
Thus calculated EA values were found to be 4.81, 5.10 and 5.30 eV, respectively, with respect to the vacuum level. Thus it can be summarized that the values of $E_{\text{HOMO}}$ of the clusters are -6.46, -6.43 and -6.48 eV and that of $E_{\text{LUMO}}$ are -4.81, -5.10 and -5.30 eV, respectively. A schematic and the energy level diagram of the quantum cluster-sensitized solar cell can be depicted as in Figure 5a and 5b, respectively. A schematic and the energy level diagram of the quantum cluster-sensitized solar cell can be depicted as in Figure 5a and 5b, respectively.

The redox potential of the cobalt electrolyte, $[\text{Co(bpy)}_3]^{2+}$ $\rightarrow [\text{Co(bpy)}_3]^{3+}$ and the band-gap of anatase TiO$_2$ were taken from literature.$^{[73,74]}$ The positions of the valence and conduction bands of TiO$_2$ were determined using ultraviolet photo-emission spectroscopy and the band-gap was taken as 3.2 eV.$^{[70]}$ The current density-voltage ($J$-$V$) curves for Au$_{25}$SBB$_{18}$, Au$_{30}$@BSA and Ag$_{44}$MBA$_{30}$ QCSSCs fabricated with 12 and 18 nm thick TiO$_2$ NTs and P25 TiO$_2$, respectively, are shown in Figure 6(a-c). Note that in all systems, saturation coverage of the cluster was used. The energy conversion efficiency ($\eta$) was calculated from the short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill-factor (FF) (obtained from the $I$-$V$ measurements) and intensity of the incident light ($P_{in}$) according to the formula:

$$\eta = \frac{[J_{sc}(\text{mA.cm}^{-2})][V_{oc}(\text{V})][FF]}{P_{in}(\text{mW.cm}^{-2})} \quad (3)$$

The values of the $V_{oc}$, $J_{sc}$, FF and $\eta$ are summarized in Table 1. The redox electrolyte employed was Co$^{3+}$/Co$^{2+}$ redox couple. The traditional I$^-$/I$^-$ redox electrolyte was not used because the cluster cores were prone to oxidation by I$^-$. A comparison of the photovoltaic parameters implies that solar cells with Au$_{30}$@BSA as the sensitizer showed the highest energy conversion efficiencies (0.17-0.35%) amongst the three. The Au$_{30}$@BSA on 18 μm thick P25 TiO$_2$ and 18 μm thick TiO$_2$NT electrodes showed an efficiency of 0.30% and 0.35%, respectively. This enhancement is due to an increase in the photovoltaic parameters namely: $V_{oc}$ and $J_{sc}$ compared to the other systems. The Au$_{30}$@BSA-modified 18 μm thick TiO$_2$ NT solar cell exhibited a photocurrent of 0.98 mA/cm$^2$ and an open-circuit voltage of 0.71 V, as opposed to a low photo response obtained (0.17 mA/cm$^2$ of photocurrent and 0.33 V of open-circuit voltage) in the absence of the Au$_{30}$@BSA sensitizer (SI, Figure S9). This implies that the enhanced photocurrent observed in the case is due to the sensitizing property of the Au$_{30}$@BSA clusters. Simple dark current-voltage traces of the solar cells are shown in Figure 6 itself which correspond to the
The characteristics of diode. The corresponding $J_{sc}$ and $V_{oc}$ values of dark current values are tabulated in SI Table 1. 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 $\text{Au}_{25}\text{SBB}_{18}$, $\text{Ag}_{44}\text{MBA}_{30}$ and $\text{Au}_{30}\text{@BSA}$ clusters on P25 and TiO$_2$ NT with two different thicknesses (12 and 18 $\mu$m, respectively) are shown in Figure S10. Error bars (Figure S10) represents minimum and maximum values. It would be interesting to know why the $\text{Au}_{30}\text{@BSA}$ system showed better photovoltaic parameters in comparison to the other two clusters despite its larger band-gap.

A possible explanation could be given based on the energy level diagram shown in Figure 5b. It is evident from Figure 5b that the LUMO level of the $\text{Au}_{30}\text{BSA}$ cluster is positioned above the CB maximum of the TiO$_2$ whereas it is at the same and below, respectively, than that of TiO$_2$ for $\text{Au}_{25}\text{SBB}_{18}$ and $\text{Ag}_{44}\text{MBA}_{30}$. This implies that the injection of the photoexcited electrons from the LUMO of the quantum cluster to the CB of the TiO$_2$ is energetically favorable only in the case of $\text{Au}_{30}\text{BSA}$ though its band-gap (1.65 eV) is larger than that of the TiO$_2$ (3.4 eV).
(1.33 eV and 1.18 eV, respectively). The LUMO of the Au\textsubscript{25}SBB\textsubscript{18} (-5.10 eV) is positioned almost at the same level as the CB of TiO\textsubscript{2} (-5.11 eV) and the electron transfer is less energetically favorable. The energy level alignments further imply that the photoinjected electrons are also vulnerable to back-electron transfer. These account for the lower efficiency of Au\textsubscript{25}SBB\textsubscript{18}. In the case of Ag\textsubscript{44}MBA\textsubscript{30}, the LUMO level (-5.30 eV) is positioned below the CB of the TiO\textsubscript{2} (-5.11 eV) thus making injection of the photoexcited electrons to the TiO\textsubscript{2} totally unfavorable. It must also be noted that BSA ligands have functional groups such as –COOH and -NH\textsubscript{2} which are desired for anchoring onto the TiO\textsubscript{2} surfaces (with the surface –OH groups) chemically which ensures a good electronic coupling between Au\textsubscript{30}@BSA and TiO\textsubscript{2} for efficient electron transfer. The photostability of atomically precise clusters in cluster-loaded TiO\textsubscript{2} is of vital importance for their end use as sensitizers in solar cells. Metal clusters of different core sizes and surface passivation ligands have unique structures and distinct photostability parameters. It is generally observed that thiol-protected quantum clusters have reasonably good stability under long excitation times.\textsuperscript{[76-78]} However, a recent study by Liu and Xu throws light on the instability of the quantum clusters, loaded on TiO\textsubscript{2} electrodes.\textsuperscript{[79]} It was observed that glutathione (SG)-protected Au\textsubscript{25} clusters (Au\textsubscript{25}(SG)\textsubscript{18})-loaded TiO\textsubscript{2} electrodes upon irradiation with simulated solar light/visible light, undergo partial oxidative transformation to a mixture of large plasmonic nanoparticles (~15 nm) and quantum clusters. However, the precise factors controlling the structures and photostability of such complex material systems are still not known and hence a combined theoretical and experimental approach connecting the role of vital parameters such as geometric shell closing, electronic shell closing and surface passivation of ligands need to be considered to answer this fundamentally important question.\textsuperscript{[80]}

In 2013, Nakata et al.\textsuperscript{[49]} have obtained a conversion efficiency of 0.034% for the TiO\textsubscript{2} photoanode sensitized with both glutathione-protected Au\textsubscript{25}Cluster and N719 using hydroquinone electrolyte. TiO\textsubscript{2} electrodes sensitized with glutathione protected Au\textsubscript{25} and N719 showed the conversion efficiencies of...
0.005% and 0.007%, respectively. When these reports are compared with the present work, the Au$_{30}@$BSA-sensitized TiO$_2$ NT and P25 cell show better efficiencies of 0.35% and 0.30%, respectively. This highlights the fact that similar systems have to be compared to get better results.

**Conclusions**

The utility of several quantum clusters of different types as sensitizers for TiO$_2$ is reported. A systematic study with various quantum clusters (Au$_{25}$SBB$_{18}$, Ag$_{44}$MBA$_{30}$ and Au$_{30}@$BSA) on two different TiO$_2$ materials showed that the protein-protected gold cluster (Au$_{30}@$BSA) in the QCSSC has shown promising efficiency as a light harvesting system. The Au$_{30}@$BSA modified TiO$_2$ NTs showed energy conversion efficiency of 0.35% which is higher compared to the other clusters used for analysis. It is evident from various analyses that the Au$_{30}@$BSA modified TiO$_2$ NTs system showed better absorption of light in the visible region and has increased light scattering due to the dimensions of the NTs. Factors such as the favorable alignment of the LUMO of the cluster to the CB of TiO$_2$, and the presence of –COOH groups in the ligands (which causes better electronic coupling between the orbitals of the cluster and the CB of TiO$_2$) were responsible for the high efficiency of the Au$_{30}@$BSA modified TiO$_2$ NTs system. This study suggests further exploration of other protein-protected clusters for solar cell applications.

**Supporting Information (SI) Summary**

Details on materials and methods and characterization including photoluminescence spectra of Au$_{30}@$BSA cluster, UV-Vis spectra of Ag$_{44}$MBA$_{30}$ histograms showing size distribution of the clusters, XPS spectrum of TiO$_2$ NTs, SEM image and XRD, respectively, of P25 TiO$_2$, TEM/EDS and Raman spectra of Au$_{30}@$BSA modified TiO$_2$, and UPS spectrum of standard polycrystalline Ag. Fabrication of solar cells with the clusters and a table showing their dark current characteristics.
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Conflict of Interest

The authors declare no conflict of interest.

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