Dye sensitized solar cells (DSSCs) have engendered great research interest with promising potentials in solar cell technology for their high power conversion efficiencies. In this study, we report a plasmon enhanced graphene oxide (GO)-based TiO2-GO-Au composite photo-anode toward the improved performance in our DSSCs. The structural and morphological properties of as synthesized GO and TiO2-GO-Au composites were investigated using Raman spectroscopy and ultra-high resolution transmission electron microscope (UHRTEM). Photovoltaic performances of DSSC containing TiO2-GO-Au composite photoanodes were studied on keeping the constant GO concentration (5 μL) and by varying the concentration of Au-nanoparticles (NP) [1, 3, 5 μL]. A systematic increment in the short circuit current density (JSc) was noticed while incorporating more Au NP to the photoanode probably due to the increased light absorption, higher optical path of absorbed light and faster electron transfer as a combined effect of GO and Au NP. Thus, a significant enhancement in the overall photovoltaic performance was observed in DSSCs with TiO2-GO-Au composite photoanode.

In this paper, we synthesized a novel TiO2-GO-Au composite photo-anode for enhanced photovoltaic performances of DSSCs by taking the advantages of both Au-nanoparticles (for plasmonic effect) and GO (for charge transfer and collection by quenching fast recombination). Structural, vibrational, and optical studies of TiO2-GO-Au composite were carried out. Photovoltaic measurements on our DSSCs containing TiO2-GO-Au composite photo-anode showed substantial improvement in power efficiency.

## Experimental

GO was prepared using modified Hummers method. The TiO2 nanopowder (∼ 10 nm, Sigma-Aldrich) slurry was prepared based on the reported method. GO (1 mg) were dispersed in distilled water (1 ml) and ultrasonicated for 1 hour. 5 μL GO mixture was added to TiO2 slurry followed by another ultrasonication for 1 hour. Gold nanoparticles (Au NP) [∼5 nm, Sigma-Aldrich, stabilized suspension in 0.1 mM PBS] were added to the resultant mixture in various concentrations (1, 3 and 5 μL). This paste was spin-coated on the ITO-glass substrate (active area of 0.16 cm2) and then sintered at 400°C for 30 min. TiO2, TiO2-GO and TiO2-GO-Au photo-anodes were imbeded into solution of commercial N719 dye for 4h. Counter electrode was prepared by coating platinum nanoparticle solution on ITO substrate and then it was annealed at 400°C for 15 min. Photo-anodes were taken out from the dye and sealed with counter electrodes using thermal sealant. Few drops of electrolyte were added to the assembled DSSC by capillary action.

The morphological characterization of pure and composite photo-anodes was carried out using ultra-high resolution transmission electron microscope (JHREM, JEOL JEM-2200FS). X-ray diffraction (XRD) measurements were done by Rigaku D/Max Ultima II X-ray diffractometer using a Cu-Kα source (wavelength: 1.5405 A°) operated at a scan rate of 0.5°/min over the 2 theta range of 20−80°. Optical absorbance characteristics were measured by UV-Vis spectrometer. Raman measurements were performed using Horiba-T64000 micro-Raman system with 514.5 nm argon ion laser as excitation source. Incident laser power on the samples was 0.4 mW and acquisition time for recording Raman spectra was kept 60 seconds (1 cycle). Photovoltaic measurements were done using Keithley-2401 electrometer under 1 sun AM 1.5 solar simulator.

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Plasmon Enhanced Photovoltaic Performance in TiO2-Graphene Oxide Composite Based Dye-Sensitized Solar Cells

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Results and Discussion

Structural properties of pure TiO$_2$ and TiO$_2$-Au composite were confirmed by XRD, shown in Fig. 1. The Bragg peaks at 25.4 (101), 37.9 (004), 48.1 (200), 54 (105), 55.1 (211), 62.8 (204), 69 (116), 70.5 (220) and 75.1 (215) (PCPDFWIN #211272) clearly represent the anatase TiO$_2$ phase. The tiny peaks at 37.9 (111) (overlapping with the TiO$_2$ (004)), 44.1 (200), 64.1 (220), and 77.6 (311) are attributed to metallic gold (PCPDFWIN #040784) in the TiO$_2$-Au nanocomposite. The XRD pattern of GO has been shown in inset. The crystalline peak appears at 11.06$^\circ$ corresponding to $d_{002}$ spacing of 0.7790 nm, which is at the much lower side of the characteristic peak of hexagonal graphite at ~26.2$^\circ$ (corresponding to $d_{002}$ spacing of 0.335 nm). Diffraction peak of GO shifts to a lower angle and exhibits larger $d$-spacing compared to pristine graphite. It is due to the intercalation of water molecules and functionalization between graphite layers.

UHRTEM measurements are carried out to study the morphology of TiO$_2$-GO composites, where we confirmed the TiO$_2$ nanoparticles diameter to be $\sim$10$\pm$5 nm and presence of graphene sheet. We observed a homogeneous dispersion of TiO$_2$ particles in GO matrix confirming composite formation. Furthermore, we spotted multiple TiO$_2$ crystal interconnected with graphene sheet into TiO$_2$-GO composite. We also tried to capture the morphology of TiO$_2$-GO-Au system, but we were unable to monitor Au NP into the composite system. Further corroborating the presence of Au NP by Raman, photoluminescence and UV-Vis spectroscopic measurements were performed, which will be discussing in the following paragraphs.

Figure 3 shows the Raman spectra for pure TiO$_2$ and TiO$_2$-GO-Au composite photo-anode. The spectral analysis of TiO$_2$-GO-Au composite is shown in Fig. 3a depicting distinct phonon peaks at 143, 396, 517, 632 cm$^{-1}$ corresponding to anatase TiO$_2$. Inset of Fig. 3a shows the presence of two distinct Raman peaks in the higher frequency region of the spectra (1350, 1591 cm$^{-1}$) indicating characteristics phonon peaks related to carbon materials. Raman spectra for pure TiO$_2$ and TiO$_2$-Au composite have been plotted together in Fig. 3b. A slight red-shift in lowest $E_g$ mode of TiO$_2$ has been observed in case of TiO$_2$-GO-Au composite which can be attributed to induced stress due to Au NP loading.

The XRD pattern of GO has been shown in inset. The crystalline peak appears at 11.06$^\circ$ corresponding to $d_{002}$ spacing of 0.7790 nm, which is at the much lower side of the characteristic peak of hexagonal graphite at ~26.2$^\circ$ (corresponding to $d_{002}$ spacing of 0.335 nm). Diffraction peak of GO shifts to a lower angle and exhibits larger $d$-spacing compared to pristine graphite. It is due to the intercalation of water molecules and functionalization between graphite layers.
Photoluminescence (PL) spectrum of Au NP is recorded by using 514.5 nm argon ion laser as an excitation source represented in Fig. 4. We observed two distinct peaks at 557 nm and a broader peak at 590 nm. The presence of two peaks can be attributed to the different size distributions which can be explained by particle size and shape dependence of frequency associated with coherent oscillation of conduction band electrons with respect to the metallic nanoparticles induced by incident light.

Optical properties of Au NP, TiO2/Au and TiO2-GO-Au composite are shown in Fig. 5. Optical absorbance spectra have been depicted in Fig. 5a, where the surface plasmon resonance (SPR) band was observed at ~ 578 nm which again confirms the presence of Au NP in composite system. Further, the SPR was found to be clearly visible in the extinction spectra for TiO2-Au and TiO2-GO-Au composite, supporting multiple absorption edges present in the composite. It indicates the extended optical absorption of composite in visible range other than ultraviolet absorption edge of TiO2. To determine the optical bandgap, modified Kubelka-Munk function i.e., $(\alpha h \nu)^{1/2}$ versus the photon energy of the exciting light ($h \nu$) where, $\alpha$ is the absorption coefficient, $h$ is Planck’s constant, $\nu$ is the light frequency has been plotted in Fig. 5b. We observed double absorption edges at 2.51 and 1.52 eV in TiO2-GO-Au composite where first absorption edge belongs to GO and second one to Au, respectively. GO matrix along with Au NP could interact with TiO2 domains and this could give rise to an additional energy level between conduction band and valence band. Such modification in electronic band structure can also reduce the bandgap energy originating additional absorption edge at lower frequency.

DSSCs were fabricated using the different photo-anodes mentioned in Table 1. Figure 6a depicts the photocurrent densities (J) versus voltage (V) characteristics for these cells. The various important parameters, such as open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor (FF), and efficiency ($\eta$) were calculated for each cell to compare the photovoltaic responses, as tabulated in Table 1. The values of $J_{SC}$, $V_{OC}$, FF, and $\eta$ was found to increase in case of TiO2-GO composite photo-anode (cell B) as compared to pure TiO2 (cell A). This enhanced overall photoresponse clearly suggests the improved charge injection and charge transfer by means of reducing recombination rates and possibly due to tiny bandgap narrowing into DSSC operation. It has also been reported that modifying photo-anode with graphene oxide increases dye adsorption into it. So the higher surface area could also advance a rise in $J_{SC}$. Furthermore, we observed the higher $J_{SC}$ values on Au NP loading into TiO2-GO composite photo-anode (cell C-E). This enhancement in $J_{SC}$ could be a consequence of plasmon induced improved charge generation and transfer. Enhanced light absorption and light scattering capabilities due to surface plasmons associated with Au nanoparticles advance to higher optical path length and thus enhance the charge generation efficiency. We observed a significant rise in $V_{OC}$, FF, and $\eta$ for TiO2-GO-Au composite photo-anode containing 1 μL Au NP (cell C), as described in Table 1. A slight decrease in FF and efficiency was observed on higher loading of Au NP. It could be due to the increase in resistance in terms of increased electron scattering rate and thus hindering charge transport in DSSC operation. Although, increment in $J_{SC}$ was consistent on increasing concentration of Au NP possibly due to increased light absorption and charge trapping by Au NP. Furthermore, transient photocurrent characteristics for all the cells (A-E) were also measured by several on-off cycles for every 15 seconds of incident light from solar simulator at zero-biasing, as represented in Figs. 6b–6f. A rapid rise and decay in photocurrent value was found to be consistent over several cycles. A higher value of $J_{SC}$ has been observed for the DSSC containing composite photoanode as compared to DSSC with photoanode of pure TiO2 in correlation with the J-V data. Also, an exponential decay in photocurrent was observed in cell A while ON state. Such type of exponential decay in short circuit photocurrent transient characteristics could be due to increased surface recombination velocity of photogenerated charge carrier. Which is different from other cells containing graphene oxide.

**Conclusions**

We have fabricated TiO2-GO-Au composite photo-anode for dye sensitized solar cell that showed significant rise in overall photoconversion efficiency. We have tried to develop an approach to quench
Figure 6. (a) J-V characteristics and (b)-(f) transient photocurrent characteristics of DSSCs based on pure TiO\textsubscript{2} and TiO\textsubscript{2}-GO-Au composite photoanodes with concentration of GO (5 μL) and increased concentration of Au NP (1, 3, 5 μL).

the larger recombination rate and back reaction due to higher loading of metal nanoparticles by further modifying plasmon enhanced photo-anode with graphene oxide. A systematic increment in the short circuit current density of DSSC was observed containing TiO\textsubscript{2}-GO-Au composite photoanode with a variable concentration of Au NP. Improved charge generation, charge transfer, and charge collection was achieved by a combining effect of increased light absorption, higher optical path of absorbed light, and faster electron transfer in TiO\textsubscript{2}-GO-Au composite photo-anode for DSSC operation.

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