Electronic Supplementary Information (ESI)

Role of ZrO_2 in TiO_2 composites with rGO as an electron mediator for enhancing the photocatalytic activity for the photodegradation of methylene blue

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Characterization of GT composite using XPS

The survey spectrum and narrow scans of GT are shown in **Fig. S1**. The reduction of GO to rGO is confirmed by observing the decrease in C 1s and O 1s peaks intensity (**Fig. S1**b)[1]. The rGO–TiO_2 interactions in the composite were also investigated using XPS. The survey spectra (**Fig. S1**a) clearly indicate the presence of, C 1s, O 1*s*, and Ti 2p species on the surface of composite proving the successful composite of GT. The deconvoluted C1s XPS spectrum (**Fig. S1**b) of the sample clearly shows four types of carbon bonds, the C-C at 284.8 eV, C-O-C at 286.2 eV, Ti-O-C 288.4 at eV and π-π interactions at 289.6 eV.[2-5] The strong O 1s peak at 529.6 eV was related to Ti-C, as shown in **Fig. S1**c, the peak at 529.8 eV indicates the existence of the Ti–O-Ti bonds in GT.[6, 7] The presences of these peaks confirms the bond formation between TiO_2 and rGO.[8, 9] Overall, the XPS results suggest that the TiO_2 is chemically bound to rGO. The two strong characteristic peaks at 458.3 eV and 464.0 eV of Ti 2p as shown in **Fig. S1**d are attributed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ respectively which supports the binding energies of Ti^{4+} in the TiO_2 lattice.[6, 10]

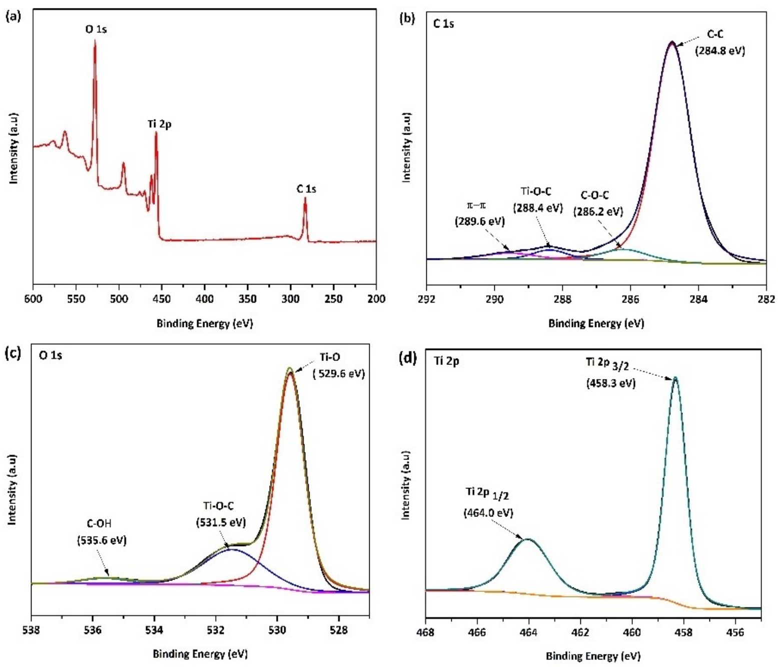

Fig. S1 - XPS survey spectrum (a) of GT composite and its corresponding high-resolution XPS spectra of C 1s (b), O 1s (c), and Ti 2p (d).

Pore analysis of TiO_2, GT and GTZ-20 composites

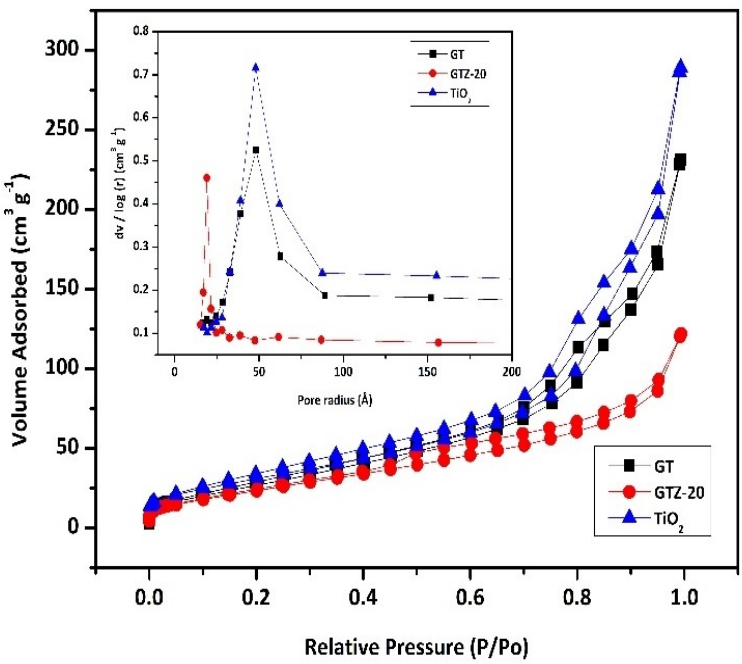

Fig. S2 - Nitrogen adsorption/desorption isotherms of TiO_2, GT and GTZ-20. The inset shows their pore size distribution.

Band gap estimation of TiO_2 and ZrO_2 metal oxides

The reflectance spectra were transformed to Kubelka–Munk coordinates (KM, α) and then Tauc's plot was constructed to estimate the band gaps of the commercially obtained titanium dioxide and zirconium (IV) oxide. [11, 12] The band gap values of TiO_2 and ZrO_2 were found to be 3.53 eV and 4.40 eV respectively, this further confirms the successful synthesis of GT and GTZ-X composites, as the band gap values of the synthesized composites are lower than their respective metal oxides.

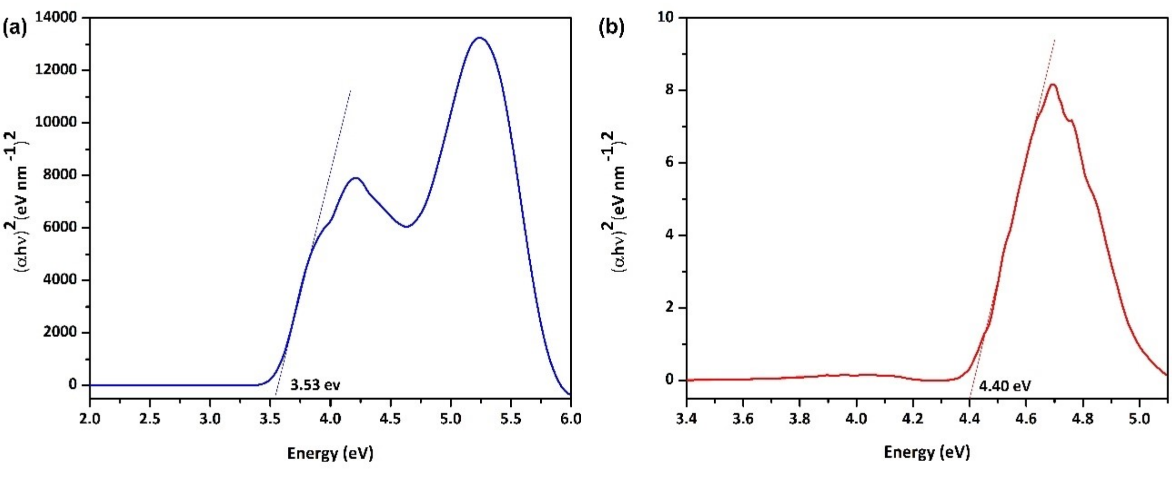

Fig. S3 - Band gap estimation using a Tauc plot of TiO_2 (a), and ZrO_2 (b).

LC-MS Analysis of GT and GTZ-20

Methylene Blue and its products that were present in the solutions degraded by the samples, were separated and analyzed using LC–MS, and MS chromatograms were obtained as shown in **Fig. S4**.

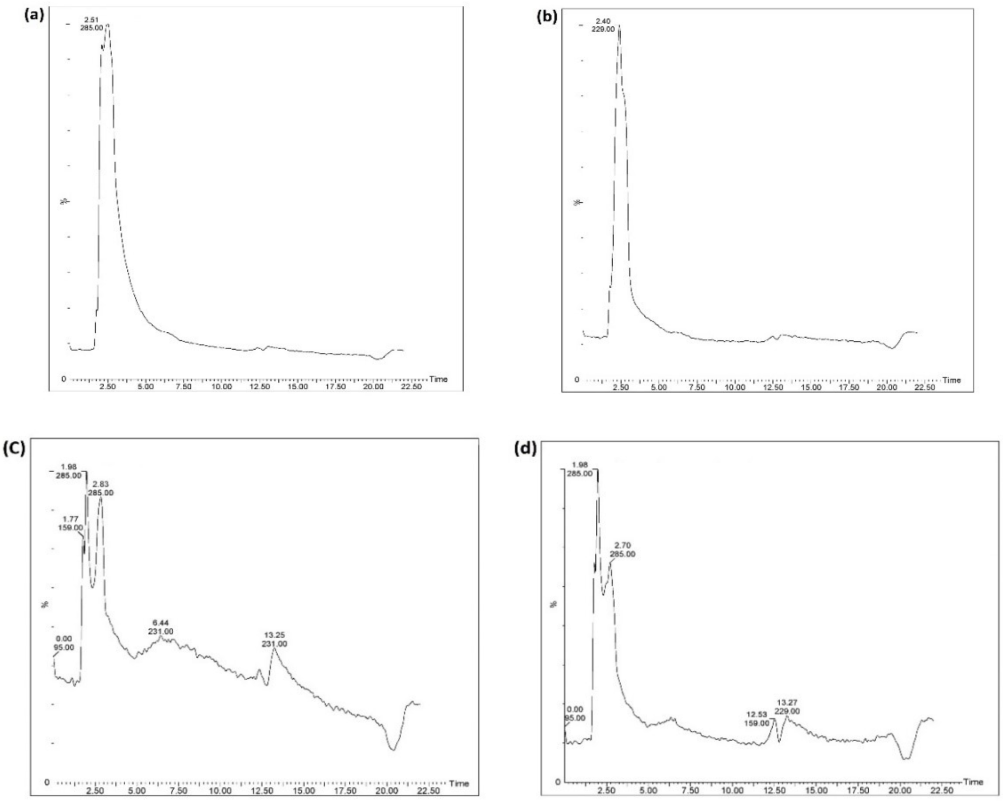

Fig. S4 - LC-MS chromatogram; of GT at 30 min (a), 100 min (b), GTZ-20 at 30 mins (c), and 100 min (d).

First derivative analysis of photocatalytic data

It was shown that the adsorption-desorption equilibrium time was reached within the first 10 mins as shown in **Fig. S5**. However, in order to confirm the adsorption equilibrium a prolonged time of 30 min was determined as the optimum equilibrium time.

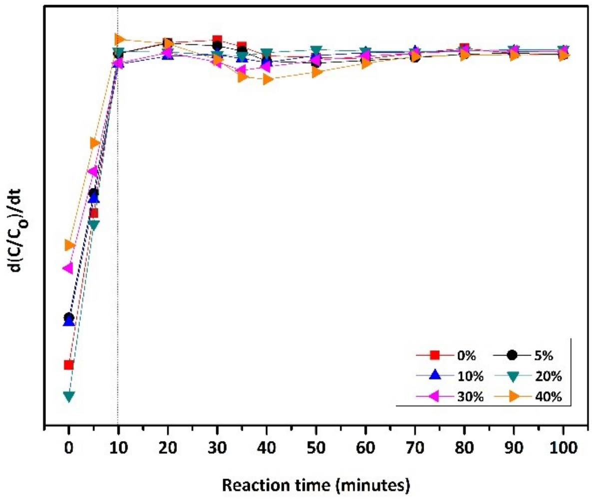

Fig. S5 - First derivative analysis of photocatalytic data to determine adsorption equilibrium.

References

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