Electronic Supplementary Information

Processable Dispersions of Photocatalytically Active Nanosheets derived from Titanium diboride: Self Assembly into Hydrogels and Paper-like Macrostructures

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Section 1: Physico-chemical Characterization

1.1 Microscopic Characterization of Standard TiB$_2$

**Figure S1:** FESEM images of the standard TiB$_2$ particles, as obtained from the chemical vendor (designated as particles size $<$10 µm). The particles were dusted on conducting carbon tape prior to analysis under the FESEM.

**Figure S2:** TEM images of the as obtained TiB$_2$ particles, dispersed in ethanol and dropcasted on carbon coated Cu grids.
1.2 Characterization of Nanosheets derived from TiB₂

**Figure S3:** FESEM of the lyophilized powder-form of the nanosheets, showing the presence of fiber-like structures.

**Figure S4:** FESEM of the lyophilized powder-form of the nanosheets, showing the presence of fiber-like structures.
**Figure S5**: FESEM of the lyophilized powder-form of the nanosheets obtained after dialysis.

**Figure S6**: HRTEM studies of the powder form of the nanosheets re-dispersed in water and deposited onto the Cu grids.
**Figure S7:** AFM image showing the edge of an ultra-large sheet and the height profile corresponding to the line marked on the sheet, indicating a thickness < 10 nm.
Figure S8: Optical micrographs of the nanosheets deposited on Si/SiO$_2$ wafer. Nanosheet marked as (i) is subsequently zoomed in images b and c; nanosheet marked as (ii) is zoomed and shown in d, the top part and bottom part of this sheet are further zoomed in e and f respectively.
Figure S9: TEM (a-c) and HRTEM (d-f) images of the samples drawn at the beginning of reaction.

Figure S10: TEM (a-d) and HRTEM (e-f) images of sample drawn after completion of reaction.
Figure S11: TEM and HRTEM studies of the sample drawn after 4 hours of reaction. Upon zooming in on the low magnification image in a), fibrous structures are seen as shown in b). The high resolution image of a region in b) is depicted in c). The further zoomed in image in d) shows presence of particulate species which are prenucleation clusters.
Figure S12: XRD patterns of standard TiB$_2$ powder and the sample after 1 hour and 24 hours of reaction affirm the oxidative attack of H$_2$O$_2$. The ◊ symbol indicates H$_3$BO$_3$ and ● indicates titanium dioxide (rutile) compounds (JCPDS card no. 73-2158 and JCPDS card no. 21-1276 respectively).

X-ray diffraction studies of the TiB$_2$ nanosheets helped us obtain more insights into the interaction of TiB$_2$ with aqueous H$_2$O$_2$. Liu et al. in their study of acidic hydrolysis of TiB$_2$ in water, have reported that the TiB$_2$ undergoes a layer-by-layer dissolution. The surface Ti is prone to readily adsorb OH from water and owing to surface hydrolysis, water soluble Ti complexes form spontaneously. Such a dissolution of TiB$_2$ is followed by the nucleation and subsequent growth of TiO$_2$ species. They also comment on the fate of the 2D boron networks in the TiB$_2$ undergoing dissolution as follows. Ti complex formation alters the coordination state of boron, which favors the adsorption of OH group onto the boron atoms. In acidic media, the hydroxylated boron species eventually forms stable H$_3$BO$_3$, the evidence for which was observed from XRD analysis of the byproduct after the hydrothermal hydrolysis of TiB$_2$, as explained ahead. The XRD patterns of the lyophilized powder form of the reaction mixture recovered after 1 hour and 24 hours of reaction are compared with that of standard TiB$_2$ in Fig. S9 in the ESI. The peak corresponding to the (001) plane in TiB$_2$ ($2\theta = 27.5^0$) is gradually falling in intensity, with a concomitant increase in a new peak around $2\theta = 12.4^0$ which
corresponds to H$_3$BO$_3$. It may be noted that the diffraction pattern of the samples could not be completely matched with any compound in the database. The peak corresponding to ~27° in the samples withdrawn after reaction, could also be indexed to (110) plane of rutile TiO$_2$, in line with the hydrolysis of TiB$_2$ as outlined earlier in this paragraph. The major peaks may be hence assigned to TiB$_2$, TiO$_2$ and H$_3$BO$_3$. The contributions from the latter become more prominent after the reaction with H$_2$O$_2$ happens. It may also be noted that literature pertaining to the interaction of TiB$_2$ with H$_2$O$_2$ or the hydrolysis of TiB$_2$, often comment that the oxides of boron are present separately in the aqueous phase. But it may be noted that, even after 24 hours of dialysis the oxy-boron species have not been removed from the sample indicating they are a structural part of the nanosheets.

**Figure S13:** XPS spectra of samples after 4 hours of reaction

**Figure S14:** XPS spectra of samples after 24 hours of reaction
**Figure S15:** FESEM/EDX of standard TiB$_2$ and the lyophilized powder-form of the nanosheets.
Figure S16: Comparison of Raman spectra of standard TiB$_2$ and nanosheets derived from TiB$_2$. 
Section 2: Hydrogels formed from aqueous dispersions of nanosheets derived from TiB₂

Figure S17: Addition of a reducing agent, ascorbic acid, results in a chemical action on the gel sample, transforming it into a liquid-like state, with an associated color change from yellow to bright orange.

Figure S18: FTIR spectra of the gel and reduced sample are compared; the intensity of the boron-oxy functional groups have decreased indicating that the loss of gel-like properties could be due to the disappearance of the borate based cross linking upon chemical reduction.
Figure S19: FESEM of the reduced samples; (a) morphology of the reduced sample, (b) morphology of the reduced sample after dialysis.
**Figure S20:** XRD patterns of samples withdrawn after 4 hour and 24 hour reaction corresponding to different TiB$_2$:H$_2$O$_2$ ratios. (Kindly note that the patterns are normalized and hence do not feature the Y-axis values.)

**Figure S21:** FTIR spectra of samples after 4 hour and 24 hour reaction corresponding to different TiB$_2$:H$_2$O$_2$ ratios
Section 3: Assembling Paper-like Macrostructures

3.1 Free-standing paper like films from nanosheets derived from TiB₂

Figure S22: FESEM imaging of a fractured piece of the free-standing paper show the hierarchical assembly of the nanosheets in a layer-by-layer arrangement. The figures b and c are zoomed in versions of the structure depicted in Figure S22a.

Figure S23: XRD analysis of TiB₂ powder, TiB₂ based nanosheets and free-standing paper-like film of TiB₂ based nanosheets.
Section 3.2 Hybrid paper-like structures composed of graphene oxide and TiB$_2$ derived nanosheets

**Figure S24**: Mixed dispersions of nanosheets derived from TiB$_2$ and GO nanosheets upon vacuum filtration also form free standing hybrid films.

**Figure S25**: FESEM imaging of the hybrid films reveal the layer-by-layer assembly
Figure S26: FESEM imaging of the GO nanosheet-TiB$_2$ derived nanosheet hybrid films: (a) a piece of the film on conducting carbon film; (b) view of the edge of the film; (c-d) closer view of the edge showing layer by layer arrangement of sheet like structures
Figure S27: FESEM-EDX elemental mapping of the hybrid film of graphene oxide/TiB$_2$ derived nanosheets which shows the distribution of elements carbon (C), oxygen (O), titanium (Ti), Boron (B) and Platinum (Pt - due to platinum sputtering) in the hybrid film.
Figure S28: EDX spectrum of the hybrid film of graphene oxide nanosheets with TiB$_2$ based nanosheets depicts the presence of carbon, boron, oxygen, aluminum (due to Anodisc membrane used for filtration), titanium, sulfur (from modified Hummer’s method used in GO synthesis), and platinum (Pt sputtering).
**Figure S29**: XRD patterns of GO paper and hybrid paper.
Figure S30: FTIR spectra comparison of the film of GO nanosheets and hybrid film prepared from the mixture of TiB$_2$ based nanosheets and GO nanosheets. FTIR spectra of both the films show almost the same peaks because most of the chemical functionalization of boron and carbon lies in the same region. However, B-O stretching peak is present only in the hybrid paper as shown in b), indicating presence of TiB$_2$ derived nanosheets in the hybrid.
Section 4: Photocatalytic action of the TiB$_2$ derived nanosheets

Figure S31: Dark adsorption on TiB$_2$ derived nanosheets of different RhB concentrations (a) 5 μM, (b) 10 μM, (c) 20 μM, (d) 30 μM, (e) 40 μM and (f) 50 μM.
Figure S32: (a) Langmuir adsorption isotherm, (b) Freundlich adsorption isotherm and (c) adsorption capacity for RhB adsorption.
Table S1. Adsorption parameters for RhB on TiB$_2$ nanosheets.

<table>
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<tr>
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<th>Langmuir model</th>
<th>Freundlich model</th>
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<tr>
<td></td>
<td>$q_m$</td>
<td>$K_L$</td>
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<td></td>
<td>125.0</td>
<td>0.0001</td>
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Table S2. Comparison of the adsorption capacity and photocatalytic activity of the TiB₂ derived nanosheets with some adsorptive photocatalysts reported in the recent literature.

<table>
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<tr>
<th>Sl. No.</th>
<th>Adsorptive Photocatalyst</th>
<th>Adsorption capacity</th>
<th>Light source</th>
<th>Pollutant (Concentration)</th>
<th>Degradation (Reaction time)</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>InVO₄/ZnFe₂O₄</td>
<td>97.1 mg g⁻¹</td>
<td>Vis</td>
<td>MB (25 mg L⁻¹)</td>
<td>84.7% (240 min)</td>
<td>²</td>
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<tr>
<td>2.</td>
<td>NaYF₄:Yb/Er@CdS-Au-RGO</td>
<td>9.8 mg g⁻¹</td>
<td>Vis</td>
<td>CFX (5 X 10⁻⁵ M)</td>
<td>90.0% (180 min)</td>
<td>³</td>
</tr>
<tr>
<td>3.</td>
<td>g-C₃N₄-ZnO/graphene</td>
<td>65.8%</td>
<td>Vis</td>
<td>RhB (20 mg L⁻¹)</td>
<td>81.0% (120 min)</td>
<td>⁴</td>
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<tr>
<td>4.</td>
<td>TiO₂/SiO₂/Ag</td>
<td>9.2 mg g⁻¹</td>
<td>Vis</td>
<td>OTC (50 ppm)</td>
<td>62.0% (120 min)</td>
<td>⁵</td>
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<td>5.</td>
<td>BiOBr/RGO</td>
<td>24.0%</td>
<td>Vis</td>
<td>RhB (20 mg L⁻¹)</td>
<td>TOC = 3.7 mg L⁻¹ (300 min)</td>
<td>⁶</td>
</tr>
<tr>
<td>6.</td>
<td>N-CaTiO₃-RGO</td>
<td>16.0 mg g⁻¹</td>
<td>Vis</td>
<td>MB (4 X 10⁻⁵ M)</td>
<td>95.0% (180 min)</td>
<td>⁷</td>
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<tr>
<td>7.</td>
<td>Porous g-C₃N₄</td>
<td>41.0%</td>
<td>Vis</td>
<td>SDZ (10 mg L⁻¹)</td>
<td>83.2% (90 min)</td>
<td>⁸</td>
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<tr>
<td>8.</td>
<td>ZnO/rGO–rGH</td>
<td>65.0%</td>
<td>UV</td>
<td>BPA (10 mg L⁻¹)</td>
<td>100% (20 min)</td>
<td>⁹</td>
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<tr>
<td>9.</td>
<td>TiO₂-Graphene</td>
<td>120.0 mg g⁻¹</td>
<td>UV</td>
<td>MB (10 ppm)</td>
<td>100% (30 min)</td>
<td>¹⁰</td>
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<tr>
<td>10.</td>
<td>TiB₂ derived nanosheets</td>
<td>125.0 mg g⁻¹</td>
<td>Natural sunlight</td>
<td>RhB (2 X 10⁻⁵ M)</td>
<td>92.0% (90 min)</td>
<td>This work</td>
</tr>
</tbody>
</table>

Ciprofloxacin (CFX), Methylene blue (MB), Oxytetracycline (OTC), Sulfadiazine (SDZ), Bisphenol A (BPA)
References: