Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Outstanding visible light photocatalysis by nano-TiO_2 hybrids with nitrogen-doped carbon quantum dots and/or reduced graphene oxide

1. Figures:

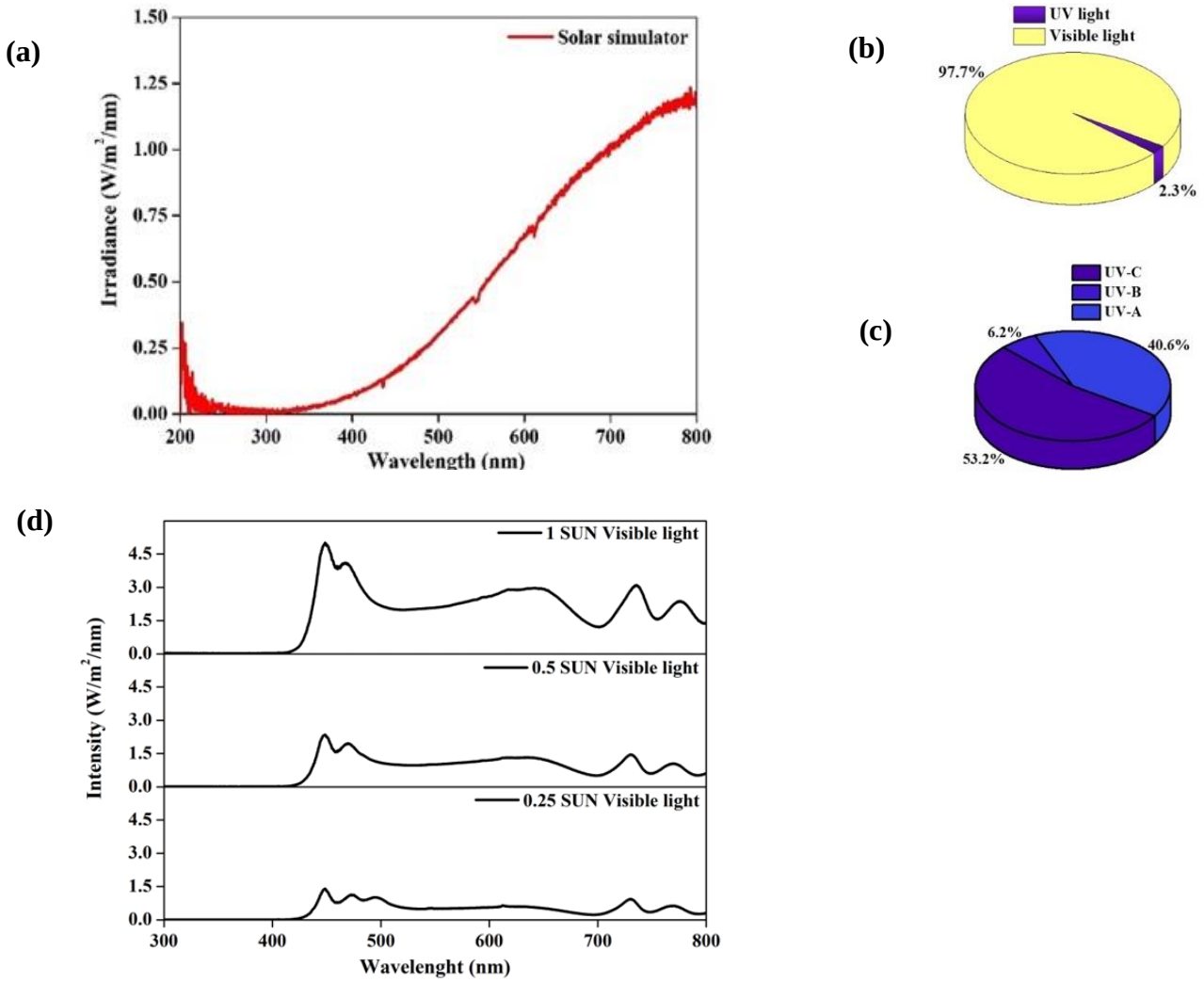

Figure S1. The optical properties of the solar simulator lights showing: (a) the irradiance spectrum of the quartz tungsten halogen lamp (Osram 1 kW R7s 22000 lm) (b) the light composition between 200-800 nm and (c) the ultraviolet radiation composition of the quartz tungsten halogen lamp (Osram 1 kW R7s 22000 lm linear halogen lamp); (d) The optical properties of the Minisol^{TM} LED solar simulator with wavelength in the range of 400-800 nm. The light intensity was varied from 1-0.25 sun setting and irradiance was recorded using Ocean Optics spectrophotometer. The distance of the lamp from the photocatalytic reactor was kept constant (27 cm).

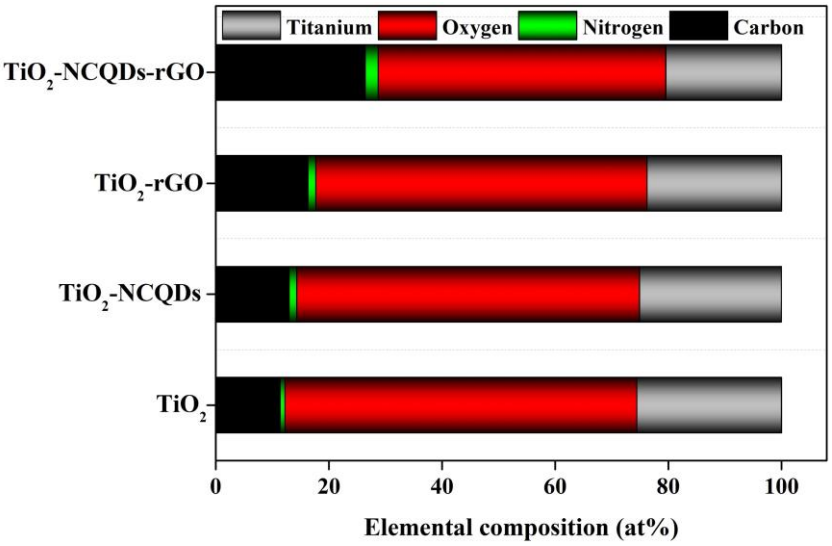

Figure S2: The XPS elemental composition of TiO_2 and its carbonaceous nanocomposites.

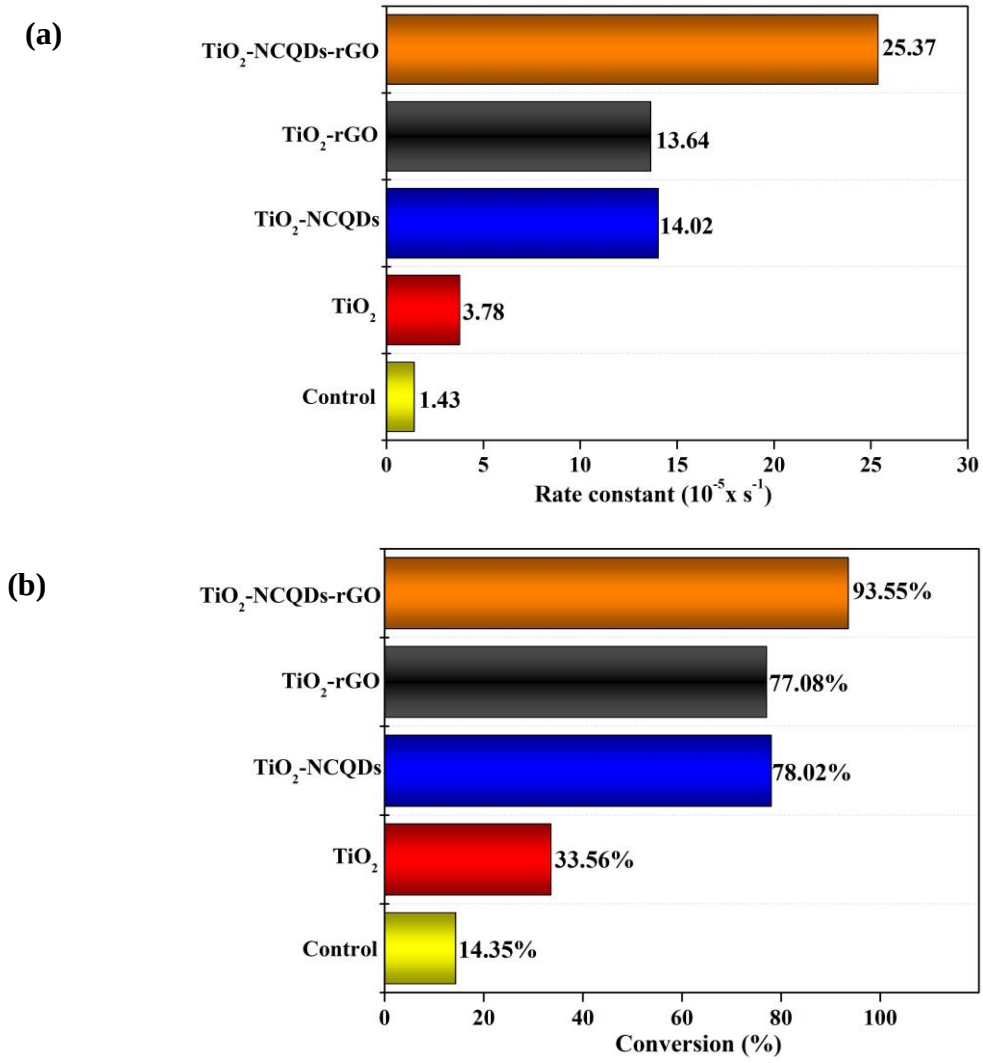

Figure S3: Photo-response activities of the catalyst, showing photodecomposition of methylene blue under visible light ($\lambda_{irradiation} \geq 400$ nm (0.5 sun); (a) first order rate constants and (b) the final % conversation (C= final concentration to C_0 = initial concentration, C/C_0 x100) for each photocatalyst during the total solar light exposure period. In both graphs, control = methylene blue.

Light intensity studies

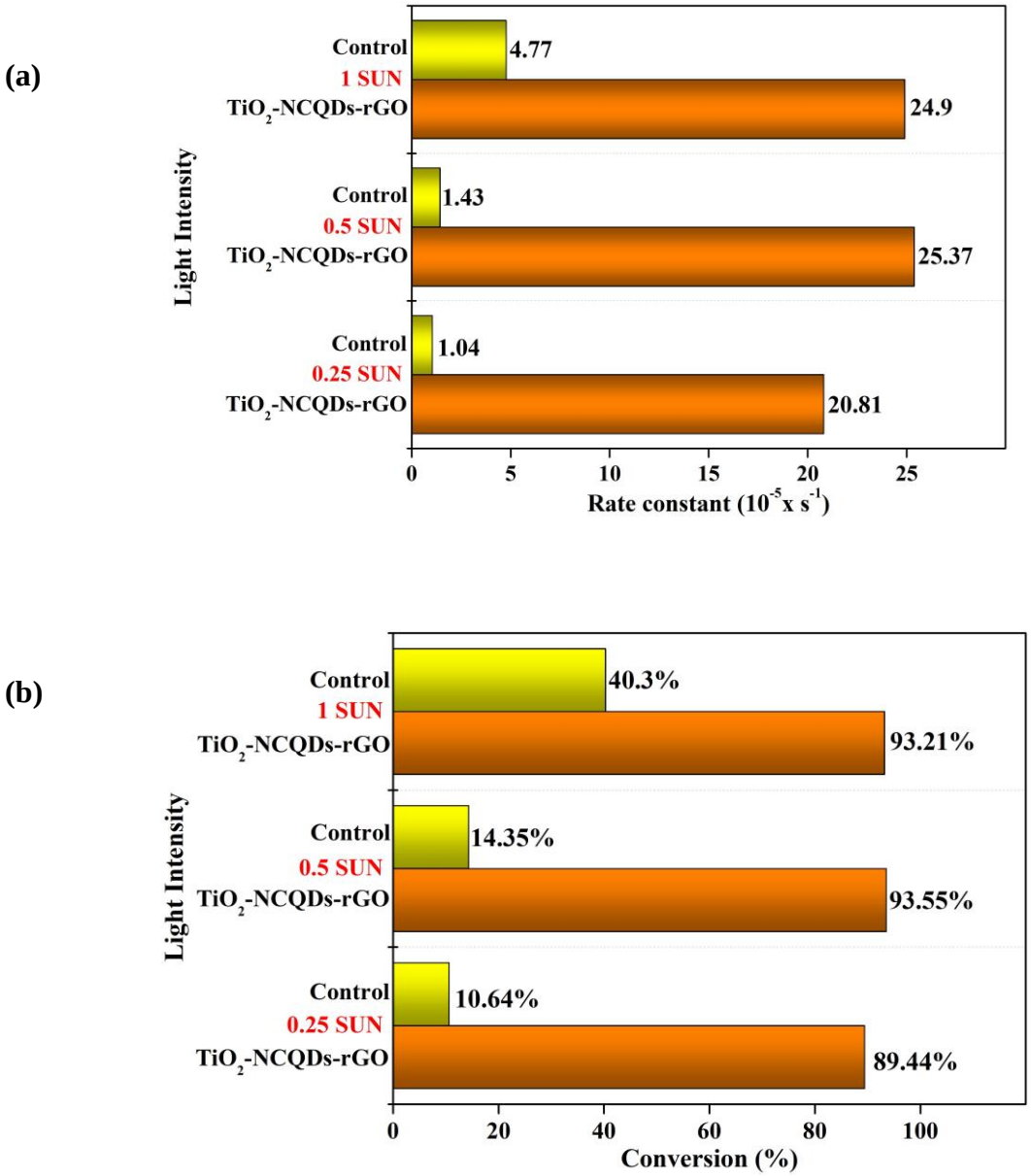

Figure S4: Photo-response activities of the best performing catalyst, TiO_2-NCQDs-rGO, showing photodecomposition of methylene blue under different light intensities (1-0.25 sun) in visible light region only ($\lambda_{irradiation} \geq 400$ nm); (a) first order rate constants and (b) the final % conversation (C= final concentration to $C_{0\,=}$ initial concentration, C/C_0 x100) for each photocatalyst during the total solar light exposure period. In both graphs, control = methylene blue.

2. Tables:

Table S1: Adsorption coefficients (q_t), TEM particle size and size distribution (nm), and SA_{BET} values ($m^2 g^{-1}$) for each corresponding photocatalysts.

Sample name	q_t	TEM (nm)		SA_{BET} ($m^2 g^{-1}$)
		mean particle size	particle size distribution	
TiO_2	4.4	5.4 ± 1.2	3.22 - 8.22	232
TiO_2-rGO	14.2	5.3 ± 1.7	2.13 - 11.56	254
TiO_2-NCQDs	5.5	4.5 ± 0.9	2.92 - 6.34	238
TiO_2 –NCQDs-rGO	11.2	4.5 ± 1.0	2.74 - 7.1	253

Table S2: Calculated Apparent Quantum Efficiency (AQE) values using different light sources.

Sample name	UV-Vis solar simulator Quartz tungsten halogen lamp (Osram 1 kW R7s 22000, $\lambda_{irradiation}$ = 200-1000 nm)	Visible solar simulator Minisol ™ LED solar simulator (LSH-7320, MKS Newport) $\lambda_{irradiation}$ = 400-1000 nm)
TiO_2	0.9	0.6
TiO_2-NCQDs	1.3	1.0
TiO_2-rGO	2.1	1.0
TiO_2-NCQDs-rGO	2.1	1.6

Table S3: Light intensity variations for the best performing catalyst, TiO_2-NCQDs-rGO, and the calculated AQE values.

Minisol ™ LED solar simulator (LSH-7320, MKS Newport)	Light intensity		
	1 sun	0.5 sun	0.25 sun
AQE	0.9%	1.6%	4.6%

3. Equations:

1. Adsorption coefficients were also determined using Langmuir-Hinshelwood model (**Table S1**).[1]

$$q_t = \frac{\Delta C \bullet 1000 \bullet M \bullet V}{m} \qquad \textbf{(Eq. S1)}$$

Where:

- $\Delta C = C_0 - C_t$ (C_0: initial concentration and C_t: equilibrium concentration) [mol/L]
- M is the molecular mass of methylene blue [g/mol]
- V is the reaction mixture volume [L]
- m is the mass of the photocatalyst [g]

2. Apparent Quantum Efficiency[2]

$$N_P = \frac{I}{E_P} = \frac{\int_{200}^{1000} I\, d\lambda \times 10^{-9}}{h \times c} \qquad \textbf{(Eq. S2)}$$

$$N_P = \frac{I}{E_P} = \frac{\int_{400}^{1000} I\, d\lambda \times 10^{-9}}{h \times c} \qquad \textbf{(Eq. S3)}$$

Where:
N_P =number of photons
I = power density
E_P = energy of photon
h= Plank constant
c= speed of light

$$N_{P\,Total} = N_P \times t_{irradiation} \times S_{reactor} \qquad \textbf{(Eq. S4)}$$

Where:
$N_{P\,Total}$= total number of photons generated by the simulator during the photocatalytic process
N_P = number of photons
$t_{irradiation}$= the irradiation time of the photocatalytic process [s]
$S_{reactor}$= reactor irradiation surface [m^2]

$$AQE(\%) = \frac{NPM_{MB}}{N_{P\,Total}} \times 100 \qquad \textbf{(Eq. S5)}$$

Where:
AQE= Apparent Quantum Efficiency [%]
NPM_{MB}= number of photodegraded molecules of methylene blue
$N_{P\,Total}$= total number of photons generated by the simulator during the photocatalytic process

[1] Nguyen-Phan, T. D. *et al.* The role of graphene oxide content on the adsorption-enhanced photocatalysis of titanium dioxide/graphene oxide composites. *Chem. Eng. J.* 170, 226–232, (2011).
[2] Braslavsky, S. *et al.* Glossary of terms used in photocatalysis and radiation catalysis (IUPAC Recommendations 2011). *Pure Appl. Chem*. 83(4), 931–1014, (2011).

4. Additional References

XPS analysis: As stated in the main text: “It is prudent at this point to state that all calibration of the spectra have been made to the Ti($2p_{3/2}$) peak taken to be 459.3 eV in line with that of Diebold and Madey [1]. Whilst, for example, the NIST database [2] has a mean value of ca. 458.5 eV, there is significant deviation (approx. 1.5 eV)[3].”

[1] U. Diebold, T.E. Madey, TiO_2 by XPS , Surf. Sci. Spectra. 4 (1996) 227–231. https://doi.org/10.1116/1.1247794.
[2] C.P. Alexander Naumkin, Anna Kraut-Vass, Stephen Gaarenstroom, NIST X-ray photoelectron spectroscopy database, NIST Stand. Ref. Database 20, Version 4.1. (2012).
[3] J.T. Mayer, U. Diebold, T.E. Madey, E. Garfunkel, Titanium and reduced titania overlayers on titanium dioxide(110), J. Electron Spectros. Relat. Phenomena. 73 (1995) 1–11. https://doi.org/10.1016/0368-2048(94)02258-5.

Theoretical calculations : Plane-wave DFT as implemented in the VASP code was used [1,2].

[1] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50. https://doi.org/10.1016/0927-0256(96)00008-0.
[2] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium, Phys. Rev. B. 49 (1994) 14251–14269. https://doi.org/10.1103/PhysRevB.49.14251.