Efficiency of Solar-Light-Driven TiO2 Photocatalysis at Different Latitudes and Seasons. Where and When Does TiO2 Really Work?

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Guest Commentary

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Efficiency of Solar-Light-Driven TiO_2 Photocatalysis at Different Latitudes and Seasons. Where and When Does TiO_2 Really Work?

Although significant efforts are made worldwide toward developing increasingly better performing solar-light-responsive materials, one of the greatest remaining challenges for some solar technologies lies in the nature of the sunlight itself as it is received at the Earth's surface. This is particularly so in the area of photocatalysis, a technology with the potential to address growing energy and environmental concerns. Currently, commercial photocatalysts are based almost entirely on TiO_2 and depend on UV radiation with wavelengths in the range of 380−390 nm for activation. However, the UV contribution at the surface represents only a very small fraction of the available solar energy. Although new generations of visible-light-responsive systems have been prepared, and in a few cases produced at industrial scales, TiO_2 remains the dominant photocatalytic material in practical implementation today. With potential applications in pollution remediation (e.g., photocatalytic water and air purification) and clean energy production (e.g., artificial photosynthesis of short chain organics, hydrogen production through photocatalytic water splitting, etc.), it is surprising that there has not been more attention given to the availability of suitable solar UV irradiation intensities, which fundamentally affect the efficiencies and economics of placing photocatalysts in real world applications at various locations around the globe. Also, many references to irradiances relate to laboratory studies[1−4] (and references therein) with UV intensities very different from ambient outdoor conditions, which are dependent on geography, season, time of day, and prevailing weather conditions. In a recent review on photocatalysis, Ohtani[5] noted that UV irradiances at the Earth's surface were often quoted to be in the range of 3−5% of the total solar irradiance at the surface but found that this could not be properly referenced. In this Guest Commentary, we propose a simple but effective model (see the Supporting Information (SI) for a full derivation) to obtain UV contributions to solar radiation as a function of geography and season. This offers a means of assessing photocatalyst performances in the field as a function of geographical and seasonal variations in irradiation conditions where solar irradiance measurements are not routinely available. Our method adopts and further develops the air mass (AM) approach used by Ohtani[5] and others.[6] AM accounts for the path length of light transiting the atmosphere and is calculated as a function of latitude, season, and time of the day (see the SI). AM is correlated with experimental UV% data (measured by Riordan et al.,[7] SI) and the total solar irradiance according to Meinel and Meinel[8] (SI), enabling the calculation of UV irradiances and UV% at a given latitude, day of the year, and time of the day. When using the model to evaluate the irradiation conditions at solar noon (maximum intensity) for specific locations, it can be noted that the often-quoted 3−5% UV contribution is only achieved throughout the whole year at latitudes below 35° (Figure 1). This corresponds to the tropical and subtropical regions only! In the northern hemisphere, all of Europe, almost all of the U.S.A., and half of

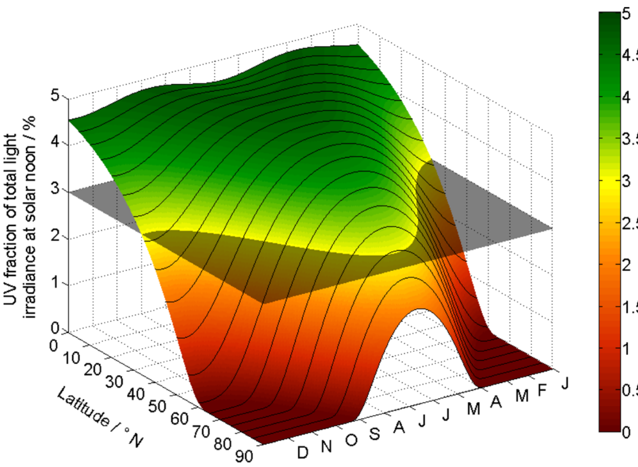

Figure 1. Modeled contribution of UV to total solar irradiance at solar noon as a function of latitude and time of year. The gray cross section marks the limit above which the commonly used 3−5% estimate is acceptable.

Asia are outside of this region. This indicates that, at least for a period of the year, which increases with increasing latitude, the UV intensity may be considerably lower than 3−5% and may challenge the economics of placing broad-band (UV-activated) semiconductor photocatalysts (such as TiO_2) at very high latitudes. It should be noted that an analogous approach can applied to the modeling for the southern hemisphere.

One of the primary applications of photocatalysis is the mitigation of air pollution, specifically the control of NO_x concentrations in areas of high traffic congestion. The model described here has been applied to the site of a photocatalytic pavers trial in Copenhagen (latitude 55.68° N). The modeled variation in UV irradiation conditions is shown in Figure 2. The

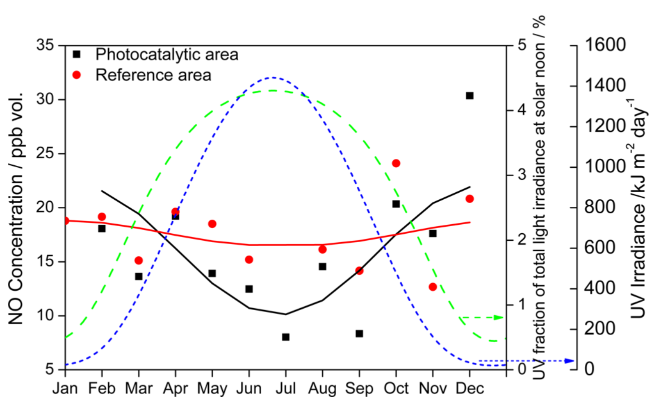

Figure 2. Measured NO concentration profiles at Gasværksvej, City of Copenhagen, Denmark (latitude 55.68° N) together with modeled irradiance characteristics for the site.

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measured NO concentrations recorded during the period 2012−2013 are also shown in the figure, which highlights a significant difference between the seasonal NO concentration profile measured in the photocatalytic test area when compared with the reference area (which may also be expected to accommodate seasonal variations in traffic volume). It is interesting to note the synergy with the modeled UV irradiance characteristics; maximum NO removal (minimum concentration) is correlated with maximum UV irradiance (see Figure 2). It may also be noted that by comparing trendlines for reference and photocatalytic areas (Figure 3), significant NO

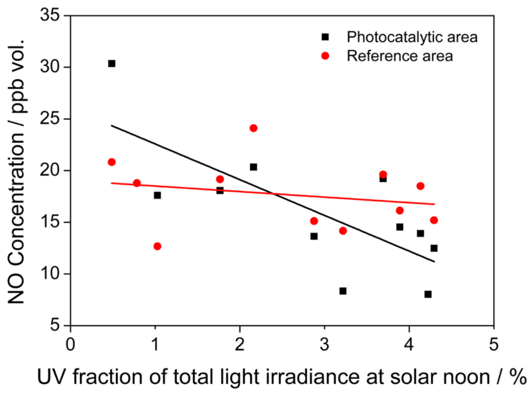

Figure 3. Measured NO concentrations at Gasværksvej, City of Copenhagen, Denmark, versus the calculated UV fraction of total light irradiance at solar noon received at the same location.

reduction is only achieved when the UV% exceeds 2.5%. This condition persists for only 6 months of the year at this site, during which there is a correlation between NO concentration and UV irradiance.

In the example shown, a reasonable correlation has been achieved between the modeled variation in UV% at solar noon (maximum intensity) and photocatalytic performance in the field. However, a further factor to consider is the length of day, which is also a function of the latitude and the time of year. A more accurate analysis can be obtained by integrating UV irradiances over a 24 h period for each condition of latitude and day of the year (see the SI) to provide the total UV energy reaching the Earth's surface in a solar day as a function of latitude and time of year, illustrated in Figure 4. It can be seen

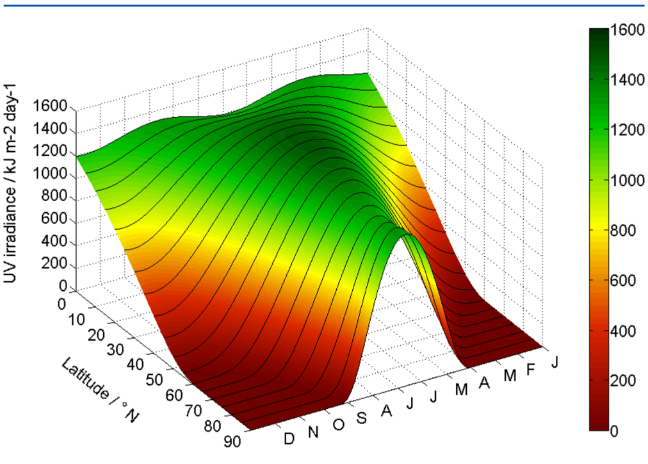

Figure 4. Total UV irradiances as a function of latitude and day of the year.

that even at high latitudes, high UV exposures can be experienced by virtue of the long summer days; lower UV% are compensated for by increased daylight hours. A consequence of this is that the effective variation of the total available UV energy between summer and winter (particularly so for very high latitudes) is much greater than that predicted from the solar noon data only (UV% trend in Figure 1). The comparison of approaches can be seen in Figure 2, which shows the respective irradiance profiles, expressed as UV% at solar noon (green) and as UV irradiance in kJ m^{-2} day^{-1} (blue), relevant to the field test in Copenhagen. A recalculation using the integrated UV irradiances approach indicates that adequate NO reduction is achieved for total UV irradiance exceeding 600 kJ m^{-2} day^{-1} for this location.

This Guest Commentary offers a means of calculating UV irradiances and predicting the field performance of photocatalysts while taking account of seasonal variation and geographical location. It highlights the limitation of photocatalysts dependent on UV irradiance and offers a method to model the suitability and therefore the economic viability of TiO_2 in particular locations.

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ASSOCIATED CONTENT

Supporting Information

Equations used for the proposed model, ratio of integrated UV direct-normal solar radiation to the total direct-normal solar radiation, and Riordan data fitting parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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