

# Greener Production of Vanillin

## MARIO PAGLIARO

Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo, Italy

**Mario Pagliaro** is a chemistry and energy scholar based at Italy's Research Council in Palermo, Italy, where he leads a research group focusing on nanochemistry, sustainability and the bioeconomy. Rapidly approaching 10,000 citations as of early 2019, he ranks amongst Italy's most cited scientists in nanotechnology and materials science. In recognition of his "significant contributions to the chemical sciences" in 2014 he was designated Fellow of the Royal Society of Chemistry.

His team's work has been widely highlighted by national and international press, including by MIT Technology Review, Advanced Science News, Italy's national television, newspapers and magazines. He also serves on the advisory and editorial boards of several internationally recognized journals.



Almost the entire fraction of the global and increasing vanillin demand (~20,000 tonnes in 2018) is met by synthetic vanillin produced at five plants (three in China, one in France and one in the U.S.) from petroleum-derived phenol (converted into guaiacol) and glyoxylic acid. The latter acid and guaiacol react in a two-step process starting with condensation promoted by base, followed by oxidative decarboxylation of vanillylmandelic acid to vanillin

catalyzed by copper(II) in an aqueous alkaline medium at a temperature of 80-130 °C. Crude vanillin is then purified via vacuum distillation and recrystallization to obtain vanillin of commercial grade (1).

The resulting synthetic vanillin is sold at about 10\$/kg to food (especially chocolate), flavor and fragrance, and pharmaceutical companies.

### Sunlight and air driving vanillic acid synthesis

In 2016 a joint Italy-China team reported that ferulic acid dissolved in water is selectively oxidized to vanillic acid in high yield (~60%) under remarkably mild and green conditions, namely at room temperature with air as primary oxidant, over a catalytic amount of nanostructured  $\text{Bi}_2\text{WO}_6$  (6).

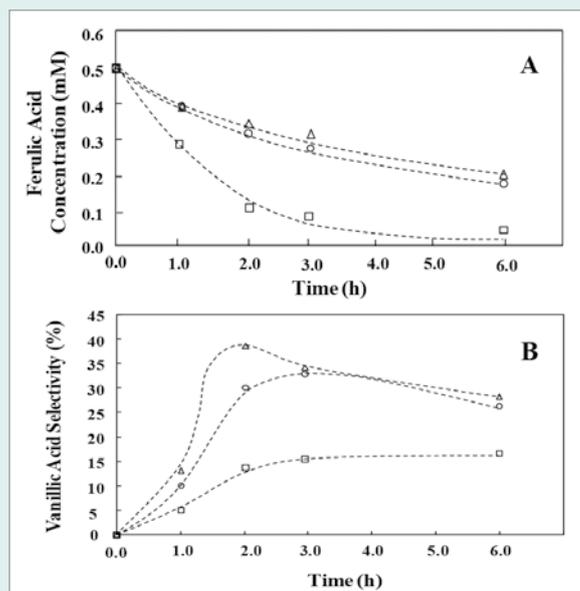
The reaction is both simple (carried out in a closed tube, under stirring a 0.6 mM ferulic acid solution in water containing a 1.5 g  $\text{L}^{-1}$  catalyst suspension in the dark), and selective affording the formation of vanillic acid only. Vanillic acid is a valued fragrance and flavoring agent, endowed with several further beneficial health effects due to its chemopreventive, hepatoprotective and cardioprotective activity.

As it happens in the case of glycerol dissolved in water selectively photooxidized to dihydroxyacetone (7), the sol-gel entrapment of nanostructured  $\text{Bi}_2\text{WO}_6$  in silica and organosilica matrices enhances the activity and the selectivity of the short-gap semiconductor in the sunlight-driven photo-oxidation of ferulic acid dissolved in water with air as the primary oxidant (8).

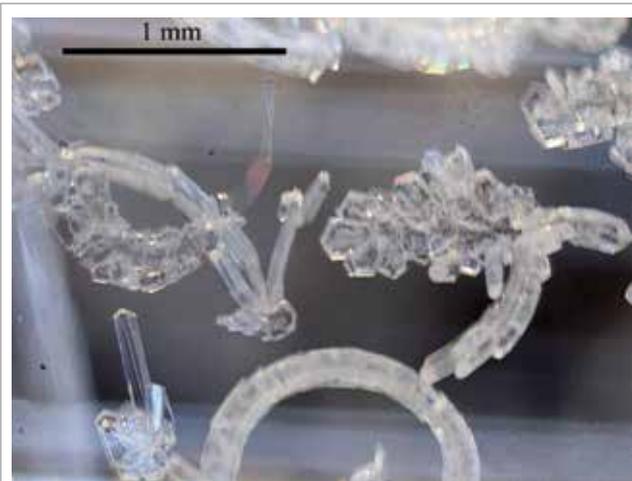
In brief, the catalytic activity of  $\text{Bi}_2\text{WO}_6$  catalytic centers in the SiliaSun catalyst where it constitutes only 10 wt% of the material is higher than in the bare photocatalyst (Figure 2).

Vanillic acid and vanillin are the only photooxidation products obtained. The total organic carbon (TOC) analysis performed before and after reaction shows a difference between the two TOC values of 26.94 ppm, practically corresponding to the loss of  $\text{CO}_2$  from the ferulic acid side chain.

For comparison, the oxidation of ferulic acid was performed under the same experimental conditions in the presence of commercial photocatalytic  $\text{TiO}_2$  (P25, Evonik) results in almost complete substrate mineralization after 1 h irradiation. Indeed, differently from  $\text{TiO}_2$  mediated photooxidations,  $\text{Bi}_2\text{WO}_6$  induced photocatalytic oxidation processes do not proceed through  $\cdot\text{OH}$  radicals but via direct holes and via more selective peroxidic species including the superoxide anion (9).



**Figure 2.** Concentration of ferulic acid during irradiation time (A) and correspondent selectivity values towards vanillic acid (B) for  $\text{Bi}_2\text{WO}_6$  ( $\square$ ), SiliaSunMe0% ( $\square$ ), and SiliaSunMe10% ( $\Delta$ ) photocatalysts. [Reproduced from Ref.8, with kind permission].



**Figure 1.** Vanillin crystals obtained by photocatalytic oxidation of ferulic acid in water by  $\text{TiO}_2$  photocatalysis under UV irradiation according to the process in Ref.5. [Image courtesy of Prof. L. Palmisano, University of Palermo].

Contrary to what happened with citric acid originally sourced from lemon juice, (2) however, the industrial synthesis did not entirely displace the natural extraction route, with *Vanilla planifolia* being increasingly harvested in several warm countries, including Madagascar, Indonesia, Mexico, Uganda, Belize, Tahiti, India and Australia.

By early 2015, indeed, one of the world's largest food and chocolate manufacturers, and the single user of synthetic vanillin, announced forthcoming plans to eliminate artificial additives including synthetic vanillin from chocolate sold in the U.S. (3).

The latter and related similar decisions led to a 20-fold price increase between 2012 and 2018. This powerful economic trend creates room for rapid expansion of alternative routes to vanillin, especially to biobased production methods starting from ferulic acid which had remained a niche of the vanillin market (4); but also to completely new chemical routes alternative to the guaiacol-based chemical route.

In 2012, Palmisano and co-workers reported the first photocatalytic synthesis of vanillin from ferulic acid mediated by nanostructured  $\text{TiO}_2$  (100% anatase) carried out in water with oxygen as the only oxidant and UV light driving the photocatalytic reaction (5).

The reaction is not selective and the vanillin yield (12% selectivity with 14% substrate conversion after 90 min irradiation) was low. Yet, the highly pure (>99.8%) nature of the vanillin crystals obtained after deposition of the permeate vanillin vapors at ambient temperature (Figure 1) is so high to make this organic solvent- and metal-free vanillin form of practical interest.

The case for photocatalysis in water had been established.

## REFERENCES

1. D. Havkin-Frenkel, Vanillin, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York: 2018; pp.1-12.
2. R. Ciriminna, F. Meneguzzo, R. Delisi, M. Pagliaro, Citric acid: Emerging Applications of a Key Biotechnology Industrial Product, *Chem. Centr. J.* 2017, 11:220.
3. M. M. Bomgardner, The problem with vanilla, *Chem. Eng. News* 2016, 94 (36), 38-42.
4. G. Banerjee, P. Chattopadhyay, Vanillin biotechnology: the perspectives and future, *J. Sci. Food Agric.* 2019, 99, 499-506.
5. V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, F. Parrino, M. A. Puma, Synthesis of vanillin in water by  $\text{TiO}_2$  photocatalysis, *Appl. Catal. B: Environ.* 2012, 111-112, 555-561.
6. R. Delisi, R. Ciriminna, F. Parrino, L. Palmisano, Y.-J. Xu, M. Pagliaro, One-Pot, Clean Synthesis of Vanillic Acid from Ferulic Acid, *ChemistrySelect* 2016, 1, 626-629.
7. Y. Zhang, R. Ciriminna, G. Palmisano, Y.-J. Xu, M. Pagliaro, Sol-gel entrapped visible light photocatalysts for selective conversions, *RSC Adv.* 2014, 4, 18341-18346.
8. R. Ciriminna, R. Delisi, F. Parrino, L. Palmisano, M. Pagliaro, Tuning the Photocatalytic Activity of Bismuth Wolframate: Towards Selective Oxidations for the Biorefinery Driven by Solar-Light, *Chem. Commun.* 2017, 53, 7521-7524.
9. N. Zhang, R. Ciriminna, M. Pagliaro, Y.-J. Xu, Nanochemistry-Derived  $\text{Bi}_2\text{WO}_6$  Nanostructures: Towards Sustainable Chemicals and Fuels Production Induced by Visible Light, *Chem. Soc. Rev.* 2014, 43, 5276-5287. ■

## YMC STATIONARY PHASES FOR SFC

The highly robust stationary phases of **YMC** are the ideal choice for **SFC**! Available with different selectivities for achiral (including diol, amino, cyano, PFP, C18 and silica) and chiral applications (immobilised and coated cellulose-/amylose-derivatives), **YMC**'s stationary phases cover the full range of applications. The wide range of pore sizes (6, 12, 20 or 30 nm) and particle sizes (from 1.9  $\mu\text{m}$  up to 50  $\mu\text{m}$ ) allows maximum flexibility.

Virtually any dimension for pre-packed columns is possible, from analytical scale up to industrial scale **SFC** applications. Full **SFC** compatibility has been approved. The well-known **YMC** reproducibility comes with its renown outstanding stability and reliability.

In addition to typical technical demands such as robustness, reproducibility, longevity and capacity, aspects such as regulatory support, cost-effectiveness and reliability are indispensable in the large-scale preparative context. As a competent partner **YMC** can provide an all-around support throughout a product's lifecycle.

Since its foundation, **YMC** has been providing high-purity preparative media for industrial-scale applications. For the last 35 years we have lived up to this mission, gathering knowledge and building a formidable reputation for quality and reliability. With this background **YMC** is able to ensure a safe supply of top-quality products for your preparative processes.

For further information see: <https://ymc.de/sfc-columns.html>



## NEWS