

# Supplementary Material: Controlled phase synthesis of VmOn in differing oxidation states using a simplified formic acid process, quantified with a new generalized index designed for use with public domain materials process information

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## 1 Zeta potential measurements

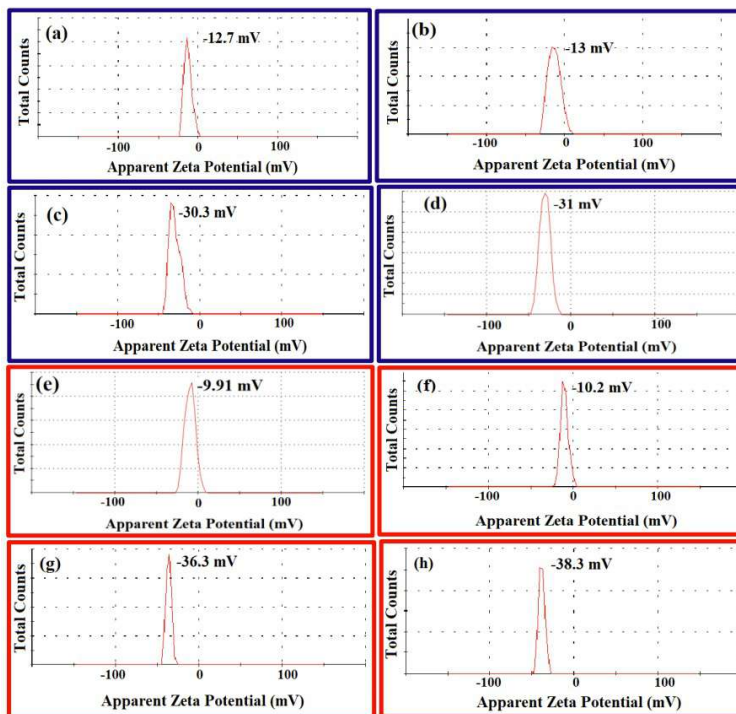


Figure 1: Zeta potential of fresh and aged  $V_2O_5$ (blue) (a) & (b) at pH=1, (c) & (d) at pH=7, fresh and aged  $VO_2$ (red) (e) & (f) at pH=1, and (g) & (h) at pH=7.

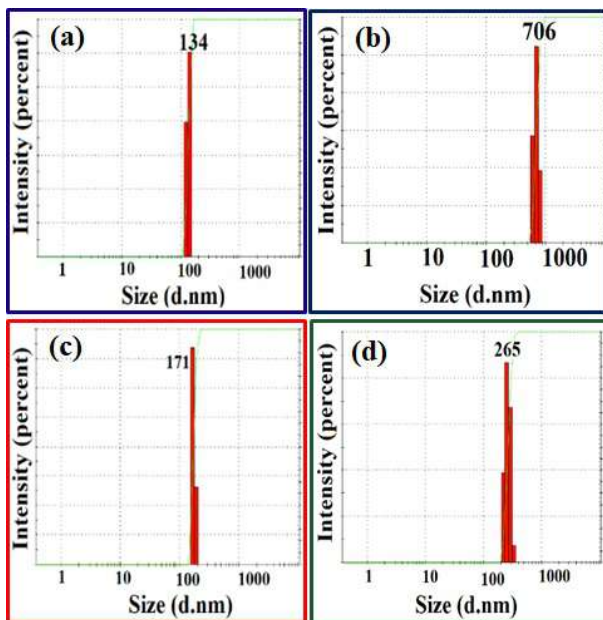


Figure 2: DLS data for (a)  $V_2O_5$ , (b) concentrated  $V_2O_5$ , (c)  $VO_2$ , and (d)  $V_2O_3$ .

## 2 Dynamic light scattering measurements

DLS data (Fig. (2)) for vanadium pentoxide yields an estimate of 134 nm (in 1.5 ml solvent) for the hydrodynamic diameters for the nanoparticles, and a different estimate (706 nm) for higher concentration (0.5 ml solvent, concentrated by evaporation). This increase can be attributed to a lower degree of separation of agglomerated nanoparticles in the more concentrated solution. A complicating factor is the non-spherical nature of the nanoparticles, which can impact the reliability of DLS measurements<sup>1</sup>.

## 3 IV hysteresis data

The IV characteristics (hysteresis loop) of all the three vanadium oxides (a)  $V_2O_5$  (b)  $VO_2$  and (c)  $V_2O_3$  (unannealed (U) and annealed (P)) are in Figure. 3 respectively.

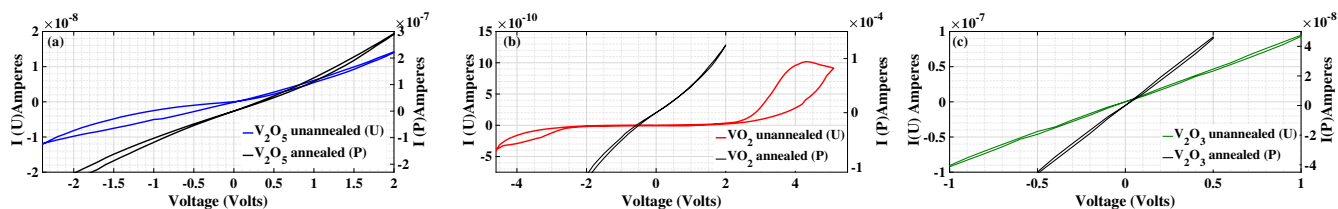


Figure 3: IV characteristics of (a)  $V_2O_5$ , (b)  $VO_2$  and (c)  $V_2O_3$  for unannealed (U) and annealed (P) devices.

## 4 Relation of greenness index to the 12 guiding principles for green synthesis

In our proposal of a more accessible greenness index that can be employed in academic research labs for obtaining estimates of relative greenness against published literature, we have defined the following normalized

dimensionless quantities:

1.  $U_s$  (Health, special and flammability hazard).
2.  $E_c$  (Process thermal energy conversion index).
3.  $L_s$  (Shelf-life).
4.  $A$  (Atom economy).
5.  $C_s$  (Use of surfactants).
6.  $R_s$  (Derivability of reactants from agricultural products, or renewable feedstocks).
7.  $M_f$  (Metal criticality/scarcity/use of catalysts).

We now attempt to relate the above factors to the 12 principles laid down by Anastas and Warner<sup>2,3</sup>.

1. Prevention is better than cure, and
2. Atom economy.

The E-factor<sup>4</sup> relates the weight of waste/byproducts co-produced to the weight of the desired product. Process mass intensity<sup>5</sup> has been introduced by the ACS Green Chemistry Institute Pharmaceutical Roundtable which prefers to use the ratio of weight of all materials used to the weight of the drug ingredient produced.<sup>6</sup> This measure has proven to be extremely useful in industry in boosting the efficiency of the production. However, given that the mass of solvents is often unknown in literature or not reported, it becomes difficult to compare the efficiencies of published processes, which is often the first step in selecting processes for scale up and industrial use. We use a measure of  $A$  (atom economy) here, defined similarly to the one in literature<sup>2</sup>, as an imperfect indicator for efficiency of use of minimal reactants as a fraction of products. A process that uses too many unnecessary reagents (impacting prevention) would necessarily suffer from a low  $A$  value.

3. Less hazardous chemical synthesis, designing safer chemicals, and inherently safer chemicals for accident prevention.

Hazards posed by chemicals take many forms: toxicity, physical damage (such as corrosiveness), flammability, radiological risk, etc, which is an involved consideration depending on the degree of exposure, demographic profile of personnel exposed, and is a strong function of the nature of the hazard<sup>3,7</sup>. To address this using information that is commonly available to researchers, we have used the National Fire Protection Association (NFPA) Hazard identification system<sup>8</sup> diamond to define the factor  $U_s$  above for the reagents used. The safety of chemicals also is related to the shelf-life of the reagents as safer (more physically stable) chemicals tend to have a longer shelf-life. We account for this using factor  $L_s$ .

4. Safer solvents and auxiliaries.

This involves avoiding the use of solvents, separation agents (such as reduce derivatives), and use of benign auxiliaries whenever possible<sup>2,5</sup>. This overlaps with our definition of  $U_s$ , and  $C_s$ .

5. Energy efficiency.

Energy requirements and environmental impact need to be accounted for in process design, and synthesis should be conducted at ambient temperatures as far as is practicable<sup>2,5</sup>. Our definition of the  $E_c$  (process thermal energy conversion index) explicitly measures deviations from the room temperature (298K) at different process steps.

6. Renewable feedstocks.

To avoid depleting precious natural resources, the use of renewable feedstocks is desirable<sup>2,9</sup>. We have defined a factor  $R_s$  that explicitly measures the fraction of reagents that are sourceable in principle from renewable feedstocks.

7. Reduce derivatives.

Use of blocking group/protecting group/ any chemical that can alter physical/ chemical process like Methoxymethyl ether (MOM), Methoxytrityl [(4-methoxyphenyl)diphenylmethyl] (MMT), p-Methoxybenzyl ether (PMB), p-Methoxyphenyl ether (PMP) etc. should be avoided as far as possible<sup>2,9</sup>.

We are counting this factor as surfactants ( $C_s$ ). However, the greenness index has been defined in a manner that clearly admits of future extension. In the synthesis of  $V_2O_5$  and  $VO_2$ , examples of enzymatic synthesis were not readily found.

8. Catalysis.

While role of catalysis is encouraged in discussions<sup>2,10</sup> as it reduces activation energy of the reaction, and also enables the use of simple reducing agents in certain cases, a matter of concern is that metals involved in catalysis tend to be found only rarely in the Earth's crust and oceans. The low natural abundances argue against the use of catalysis in certain cases where its avoidance does not impose a large energy cost. In our treatment, we have elected to treat use of catalysis as an undesirable factor ( $M_f$ ) since  $G$  explicitly and separately accounts for thermal energy usage explicitly, in recognition of the fact that the choice of catalysis is driven by multiple considerations.

9. Design for degradation.

This aspect relates to the desirability of spontaneous breakdown of chemical products at the end of their desired function<sup>2,9</sup>. Given that how long the functionality of a synthesized material is needed depends strongly on the application, we have elected not to account for this specific principle in  $G$ .

10. Real-time analysis for pollution prevention.

This principle relates to the need for in-process monitoring of synthetic processes<sup>2,9</sup>, and control prior to the formation of hazardous substances. Given that this principle asks for information that is highly specific to the process involved, and concerns information that rarely makes it into scientific literature, we have chosen not to include it in  $G$ .

11. Inherently safer chemistry for accident prevention.

This principle relates to the need for use of chemistry and phase of chemicals that is inherently safer<sup>2,5</sup>. There is a significant overlap between this principle and the one recommending less hazardous synthesis. We have addressed this through the factor  $U_s$  in  $G$ .

As can be seen above, we have made an attempt to account for 8 of the above 11 principles in the definition of  $G$ . These principles, which are intended as guiding principles towards the design of chemical processes, can only be imperfectly captured by different greenness indices. Each index has its own natural strengths. We have attempted to construct a greenness index that can be informally used in graduate research laboratories, and can employ the usually low degree of process detail expressed in scientific literature to produce estimators of greenness.

Table 1: Greenness index of  $V_2O_5$  synthesis. Constituent terms have been estimated for each of the referenced works primarily from published data. This has been supplemented with public domain material safety data sheet (MSDS) data for the precursor safety, which has been used where appropriate, as described in the manuscript.

Process	A	$R_s$	$E_c$	$U_s$	$L_s$	$C_s$	$M_f$	$G = \frac{1}{7} \times (A + R_s + U_s + E_c + L_s + C_s + M_f)$
<b>Present work</b>	0.649	0.5	0.646	0.548	0.864	1	1	0.744
<b>Thermal decomposition<sup>11</sup></b>	0.777	0	0.335	0.7	0.950	1	1	0.680
<b>Solvothermal<sup>12</sup></b>	0.614	1	0.630	0.616	0.950	1	1	0.830
<b>Hydrogen peroxide<sup>13</sup></b>	0.492	0	0.646	0.6	0.864	0	0.0003	0.371
<b>Hydrothermal<sup>14</sup></b>	0.547	0	0.728	0.699	0.950	1	0.284	0.601
<b>Polyol<sup>15</sup></b>	0.614	1	0.589	0.616	0.950	1	1	0.824

Table 2: Greenness index of  $VO_2$  synthesis.

Process	A	$R_s$	$E_c$	$U_s$	$L_s$	$C_s$	$M_f$	$G = \frac{1}{7} \times (A + R_s + U_s + E_c + L_s + C_s + M_f)$
<b>Present work</b>	0.508	0.666	0.738	0.555	0.632	0	1	0.585
<b>Gram scale<sup>16</sup></b>	0.471	0	0.532	0.472	0.632	0	0.284	0.341
<b>Colloidal<sup>17</sup></b>	0.560	0.25	0.293	0.386	0.632	1	1	0.588
<b>Hydrothermal<sup>18</sup></b>	0.458	0.5	0.638	0.561	0.993	0	1	0.592

## 5 Calculations for $G$ and its constituent terms

The tables that provide values for various terms used in the greenness index: A(atom economy): Table 3( $V_2O_5$ ) and 4( $VO_2$ ),  $R_s$ (renewable feedstocks): Table 5( $V_2O_5$ ) and 6( $VO_2$ ),  $E_c$ (energy conversion index): Table 7( $V_2O_5$ ) and 8( $VO_2$ ),  $U_s$ (total hazard): Table 9, 10( $V_2O_5$ ) and 11( $VO_2$ ),  $L_s$ (shelf life):Table 9, Table 12( $V_2O_5$ ) and Table 13( $VO_2$ ),  $M_f$ (standardised metal scarcity):Table 9 .

## References

- [1] P. Arenas-Guerrero, Á. V. Delgado, K. J. Donovan, K. Scott, T. Bellini, F. Mantegazza and M. L. Jiménez, *Sci Rep*, 2018, **8**, 9502.
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- [3] P. T. Anastas and J. Charles Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.
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Table 3: Calculation of A for V<sub>2</sub>O<sub>5</sub> synthesis.

Synthesis	Reactants	Molecular weight (amu)	Desired product	Molecular weight (amu)	A
<b>Present work</b>	2NH <sub>4</sub> VO <sub>3</sub> +HCOOH	279.99	V <sub>2</sub> O <sub>5</sub>	181.88	0.649
<b>Thermal decomposition</b> <sup>11,19</sup>	12NH <sub>4</sub> VO <sub>3</sub>	1403.76	6V <sub>2</sub> O <sub>5</sub>	1091.28	0.777
<b>Solvothermal synthesis</b> <sup>12</sup>	2NH <sub>4</sub> VO <sub>3</sub> +H <sub>6</sub> C <sub>2</sub> O <sub>2</sub>	296.03	V <sub>2</sub> O <sub>5</sub>	181.88	0.614
<b>Peroxide method</b> <sup>13</sup>	2NH <sub>4</sub> VO <sub>3</sub> +4H <sub>2</sub> O <sub>2</sub> + HNO <sub>3</sub>	368.97	V <sub>2</sub> O <sub>5</sub>	181.88	0.492
<b>Hydrothermal</b> <sup>14</sup>	2NH <sub>4</sub> VO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub>	332.03	V <sub>2</sub> O <sub>5</sub>	181.88	0.547
<b>Polyol route</b> <sup>15</sup>	2NH <sub>4</sub> VO <sub>3</sub> +H <sub>6</sub> C <sub>2</sub> O <sub>2</sub>	296.03	V <sub>2</sub> O <sub>5</sub>	181.88	0.614

Table 4: Calculation of A for VO<sub>2</sub> synthesis.

Synthesis	Reactants	Molecular weight (amu)	Desired product	Molecular weight (amu)	A
<b>Present work</b>	2NH <sub>4</sub> VO <sub>3</sub> +2HCOOH	326.02	2VO <sub>2</sub>	165.88	0.508
<b>Gram</b> <sup>16</sup>	V <sub>2</sub> O <sub>5</sub> +H <sub>2</sub> SO <sub>4</sub> +N <sub>2</sub> H <sub>4</sub> + NaOH	351.99	2VO <sub>2</sub>	165.88	0.471
<b>Colloidal</b> <sup>17</sup>	2NH <sub>4</sub> VO <sub>3</sub> + H <sub>6</sub> C <sub>2</sub> O <sub>2</sub> +C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	296.03	2VO <sub>2</sub>	165.88	0.560
<b>Hydrothermal</b> <sup>18,20</sup>	V <sub>2</sub> O <sub>5</sub> +2C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	361.94	2VO <sub>2</sub>	165.88	0.458

Table 5: Calculation of R<sub>s</sub> for V<sub>2</sub>O<sub>5</sub> synthesis.

Synthesis	Number of renewable reactants	Number of non-renewable reactants	R <sub>s</sub>
<b>Present work</b>	1	1	0.5
<b>Thermal decomposition</b>	0	1	0
<b>Solvothermal</b>	1	0	1
<b>Hydrogen peroxide</b>	0	1	0
<b>Hydrothermal</b>	0	1	0
<b>Polyol</b>	1	0	1

Table 6: Calculation of  $R_s$  for  $\text{VO}_2$  synthesis

Synthesis	Number of renewable reactants	Number of non-renewable reactants	$R_s$
<b>Present work</b>	2	1	0.66
<b>Gram Scale</b>	0	1	0
<b>Colloidal</b>	1	3	0.25
<b>Hydrothermal</b>	1	1	0.5

Table 7: Process steps in  $\text{V}_2\text{O}_5$  synthesis are defined using a (process temperature (K), time (minutes)) vector. Quantity  $e_{c,i} \equiv |T_i - 298K| \times \Delta t_i (\times 10^4) (K.min)$  is calculated in columns below for the  $i^{th}$  process step.

Study	Step 1	$e_{c,1}$	Step 2	$e_{c,2}$	Step 3	$e_{c,3}$	$Y = \frac{\sum_i e_{c,i}}{298K \times \sum_i \Delta t_i}$	$E_c \equiv e^{-Y}$
Present work	(353.15, 180)	0.99	(343.15, 360)	1.625	(673.15, 180)	6.75	0.43	0.64
Thermal decomposition <sup>11</sup>	(623.15, 300)	9.75	(0, 0)	0	(0, 0)	0	1.09	0.33
Solvothermal synthesis <sup>12</sup>	(453.15, 1440)	22.34	(298.15, 480)	0.007	(773.15, 120)	5.70	0.46	0.63
Hydrogen peroxide <sup>13</sup>	(453.15, 1440)	22.34	(333.15, 600)	2.109	(773.15, 60)	2.85	0.43	0.64
Hydrothermal <sup>14</sup>	(393.15, 1440)	13.70	(343.15, 480)	2.167	(773.15, 60)	2.85	0.31	0.72
Polyol route <sup>15</sup>	(433.15, 60)	0.81	(353.15, 360)	1.985	(773.15, 120)	5.70	0.52	0.58

Table 8: Process steps in  $\text{VO}_2$  synthesis are defined using a (process temperature (K), time (minutes)) vector. Quantity  $e_{c,i} \equiv |T_i - 298K| \times \Delta t_i (\times 10^4) (K.min)$  is calculated in columns below for the  $i^{th}$  process step.

Study	Step 1	$e_{c,1}$	Step 2	$e_{c,2}$	Step 3	$e_{c,3}$	Step 4	$e_{c,4}$	$Y = \frac{\sum_i e_{c,i}}{298K \times \sum_i \Delta t_i}$	$E_c \equiv e^{-Y}$
Present work	(353.15, 1440)	7.94	(333.15, 360)	1.26	(973.15, 120)	8.10	-	-	0.30	0.73
Thermal decomposition <sup>11</sup>	(493.15, 2880)	56.20	(333.15, 10)	0.03	(1073.15, 60)	4.65	(333.15, 360)	1.26	0.63	0.53
Solvothermal synthesis <sup>12</sup>	(433.15, 60)	0.81	(473.15, 30)	0.52	(473.15, 30)	0.52	(873.15, 120)	6.90	1.22	0.29
Hydrogen peroxide <sup>13</sup>	(453.15, 2880)	44.68	(298.15, 20)	0.0003	(333.15, 600)	2.10	-	-	0.44	0.63

Table 9:  $H_i$  (Health),  $T_f$ (flash temperature),  $S_i$  (special hazard factors)<sup>8</sup>,  $L_s$  (shelf life) and  $M_f$  (standardised metal scarcity) for the reagents used. For materials whose flash temperature, health and special hazard is not available, we have assigned zero.

Substances	$H_i$	$T_f(K)$	$S_i$	$h_1 = \frac{H_i+S_i}{5}$	$h_2 = e^{-\frac{T_f}{343}}$	t=shelf life in months	$L_s$	$M_f = M_s/1 \times 10^{-7}$
H <sub>2</sub> O	0	0	0	0	0	0	0	1
H <sub>2</sub> SO <sub>4</sub> <sup>21</sup>	3	0	1	0.8	0	36	0.95	0.28
HNO <sub>3</sub> <sup>22</sup>	4	0	1	1	0	36	0.95	$2.6 \times 10^{-6}$
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> <sup>21,23</sup>	1	384.15	0	0.2	0.32	60	0.99	1
HCOOH <sup>21,24</sup>	3	342.15	0	0.6	0.36	24	0.86	1
H <sub>2</sub> O <sub>2</sub> <sup>21,25</sup>	3	0	1	0.8	0	24	0.86	$3 \times 10^{-4}$
NaCl <sup>26</sup>	0	0	0	0	0	60	0.99	1
NaOH <sup>26,27</sup>	3	0	1	0.8	0	12	0.63	1
NH <sub>4</sub> VO <sub>3</sub>	4	0	0	0.8	0	36	0.95	1
NH <sub>4</sub> Cl <sup>26</sup>	2	0	0	0.4	0	12	0.63	1
NO <sup>28</sup>	3	0	1	0.8	0	13.92	0.68	1
NO <sub>2</sub> <sup>28</sup>	3	0	1	0.8	0	3.99	0.28	1
SO <sub>2</sub> <sup>28</sup>	3	0	0	0.6	0	18	0.77	1
Ca(OH) <sub>2</sub> <sup>26</sup>	3	0	0	0.6	0	12	0.63	1
NH <sub>3</sub> <sup>28</sup>	3	0	0	0.6	0	13.92	0.68	1
CO <sub>2</sub> <sup>28</sup>	2	0	0	0.4	0	27.6	0.89	1
CO <sup>28</sup>	3	82.15	0	0.6	0.787	27.6	0.89	1
CH <sub>4</sub>	2	85.15	0	0.4	0.78	0	0	1
H <sub>2</sub>	0	0	0	0	0	0	0	1
HSO <sub>4</sub> <sup>-</sup>	1	0	0	0.2	0	0	0	1
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> <sup>26,29</sup>	3	439.15	0	0.6	0.27	60	0.99	1
N <sub>2</sub> H <sub>4</sub> <sup>30</sup>	4	325.15	0	0.8	0.38	60	0.99	1
C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> <sup>31</sup>	0	462.15	0	0	0.25	12	0.63	1
Citric acid <sup>26,32</sup>	1	0	0	0.2	0	12	0.63	1
Na	3	0	0	0.6	0	0	0	1
V <sub>2</sub> O <sub>5</sub>	4	0	0	0.8	0	60	0.99	1
PVP	0	0	0	0	0	48	0.98	1



Table 10:  $U_s$  calculation for  $V_2O_5$ .  $n$  represents the number of reagents.

Study	Materials	$\frac{h_1}{n}$	$h_2$	$\frac{h_1}{n} + h_2$	$T = \frac{1}{2} \left( \frac{h_1}{n} + h_2 \right)$	$U_s$
<b>Present work</b>	HCOOH, CO <sub>2</sub> , NH <sub>3</sub>	0.53	0.368	0.902	0.451	0.548
<b>Thermal</b>	NH <sub>3</sub>	0.6	0	0.6	0.3	0.7
<b>Solvothermal</b>	H <sub>6</sub> C <sub>2</sub> O <sub>2</sub> , NH <sub>3</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub>	0.44	0.326	0.766	0.383	0.616
<b>Hydrogen peroxide</b>	H <sub>2</sub> O <sub>2</sub> , HNO <sub>3</sub> , NH <sub>3</sub>	0.8	0	0.8	0.4	0.6
<b>Hydrothermal</b>	H <sub>2</sub> SO <sub>4</sub> , NH <sub>3</sub> , HSO <sub>4</sub> <sup>-</sup>	0.46	0.134	0.601	0.300	0.699
<b>Polyol</b>	H <sub>6</sub> C <sub>2</sub> O <sub>2</sub> , NH <sub>3</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub>	0.44	0.326	0.766	0.383	0.616

Table 11:  $U_s$  calculation for VO<sub>2</sub>.  $n$  represents the number of reagents.

Study	Materials	$\frac{h_1}{n}$	$h_2$	$\frac{h_1}{n} + h_2$	$T = \frac{1}{2} \left( \frac{h_1}{n} + h_2 \right)$	$U_s$
<b>Present work</b>	HCOOH, citric acid, NH <sub>4</sub> VO <sub>3</sub> , NH <sub>3</sub> , CO <sub>2</sub>	0.52	0.368	0.888	0.444	0.555
<b>Gram</b>	V <sub>2</sub> O <sub>5</sub> , H <sub>2</sub> SO <sub>4</sub> , N <sub>2</sub> H <sub>4</sub> , NaOH, Na <sup>+</sup> , HSO <sub>4</sub> <sup>-</sup>	0.66	0.387	1.054	0.527	0.472
<b>Colloidal</b>	NH <sub>4</sub> VO <sub>3</sub> , H <sub>6</sub> C <sub>2</sub> O <sub>2</sub> , C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> , NH <sub>3</sub> , CO	0.44	0.787	1.227	0.613	0.386
<b>Hydrothermal</b>	V <sub>2</sub> O <sub>5</sub> , C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> , CO <sub>2</sub> , CO	0.60	0.277	0.877	0.438	0.561

Table 12: Calculation of  $L_s$  for V<sub>2</sub>O<sub>5</sub> synthesis. The shelf life is governed by the material with the lowest shelf life.

Synthesis type	Material with lowest shelf life	$t_s$ (min)	$L_s$
<b>Present work</b>	HCOOH	2	0.864
<b>Thermal</b>	NH <sub>4</sub> VO <sub>3</sub>	3	0.950
<b>Solvothermal</b>	NH <sub>4</sub> VO <sub>3</sub>	3	0.950
<b>Hydrogen peroxide</b>	H <sub>2</sub> O <sub>2</sub>	2	0.864
<b>Hydrothermal</b>	NH <sub>4</sub> VO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	3	0.950
<b>Polyol</b>	NH <sub>4</sub> VO <sub>3</sub>	3	0.950

Table 13: Calculation of  $L_s$  for  $\text{VO}_2$  synthesis. The shelf life is governed by the material with the lowest shelf life.

Synthesis type	Material with lowest shelf life	$t_s$ (min)	$L_s$
Present work	citric acid	1	0.632
Gram	NaOH	1	0.632
Colloidal	$\text{C}_{18}\text{H}_{34}\text{O}_2$	1	0.632
Hydrothermal	$\text{V}_2\text{O}_5/\text{C}_2\text{H}_2\text{O}_4$	5	0.993

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