

Supporting Information

Preparation of Highly Uniform 1-Dimensional α - Ag_2WO_4 Nanostructures with Controllable Aspect Ratio and Study of the Growth Mechanism

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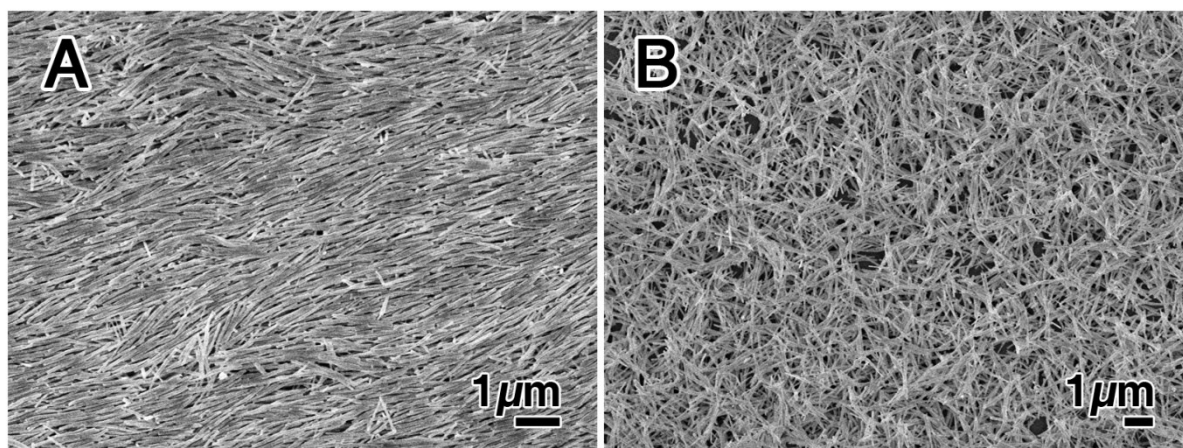


Figure S1. SEM image showing (A) uniformly aligned and (B) randomly deposited nanowires obtained for $t_{\text{stir}} = 0$ s.

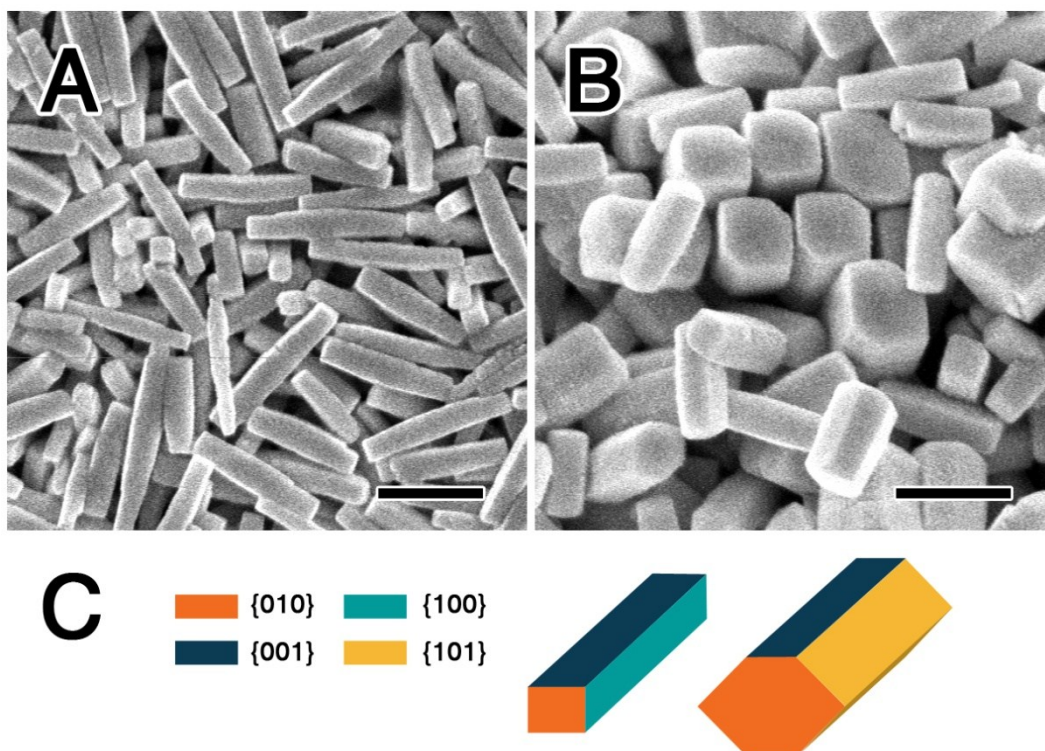


Figure S2. Angled SEM profiles showing (A) a rectangular cross section for the nanowires and nanorods, and (B) a hexagonal cross section for the sub-micrometer rods. (C) Schematic representations of the morphology and facet composition of the nanowires/ rods and sub-micrometer rods.

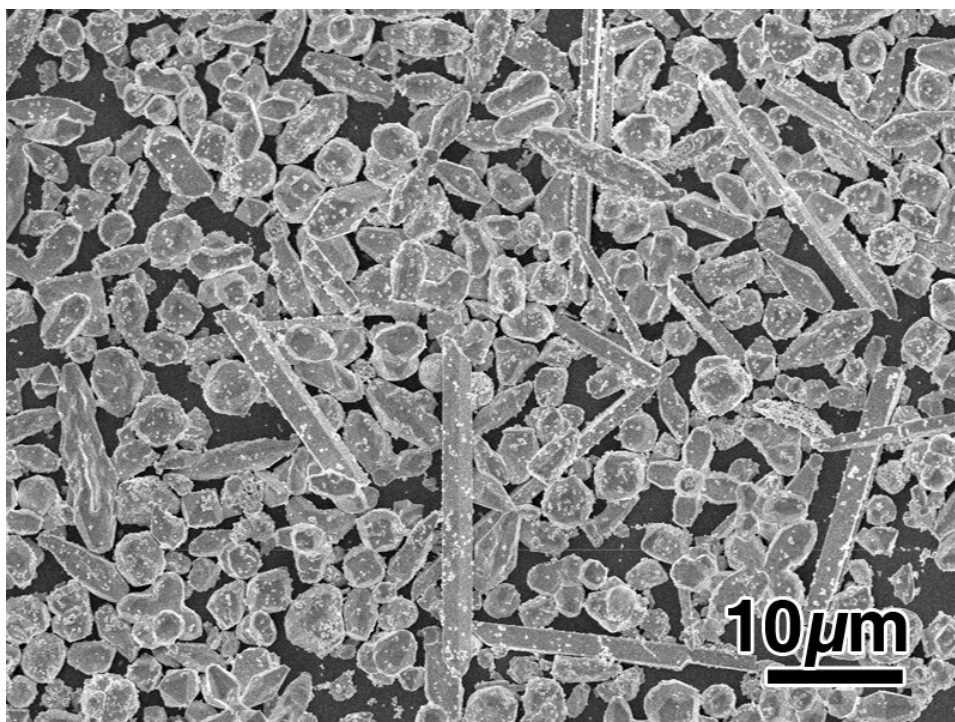
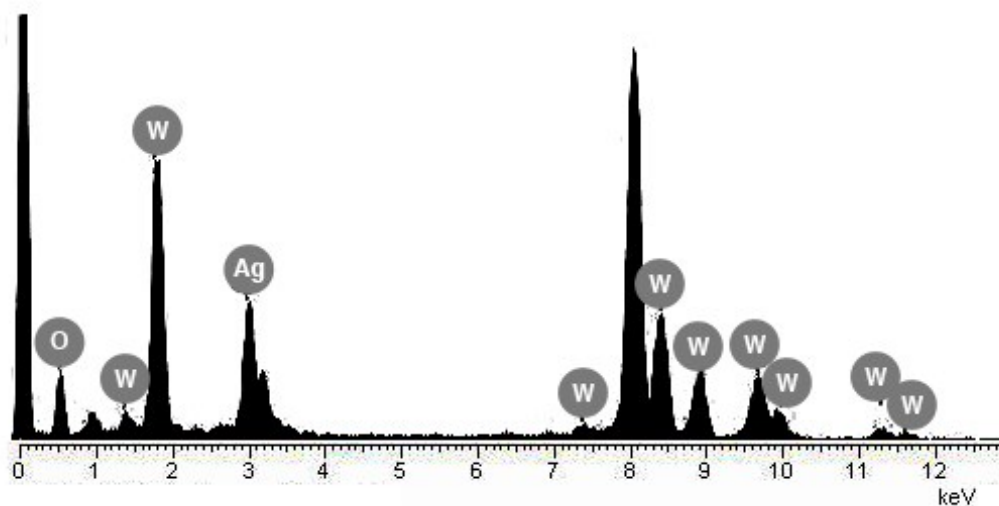


Figure S3. SEM image of the products obtained under prolonged stirring durations ($t_{\text{stir}} > 5$ min)



Element	Weight %	Atomic %
O K	7.02	38.93
Ag L	47.67	39.21
W M	45.31	21.86

Figure S4. Representative EDX spectrum of α -Ag₂WO₄ crystals. The unlabeled peaks in the EDX plot are Cu signals which belong to the Cu grid used for particle deposition.

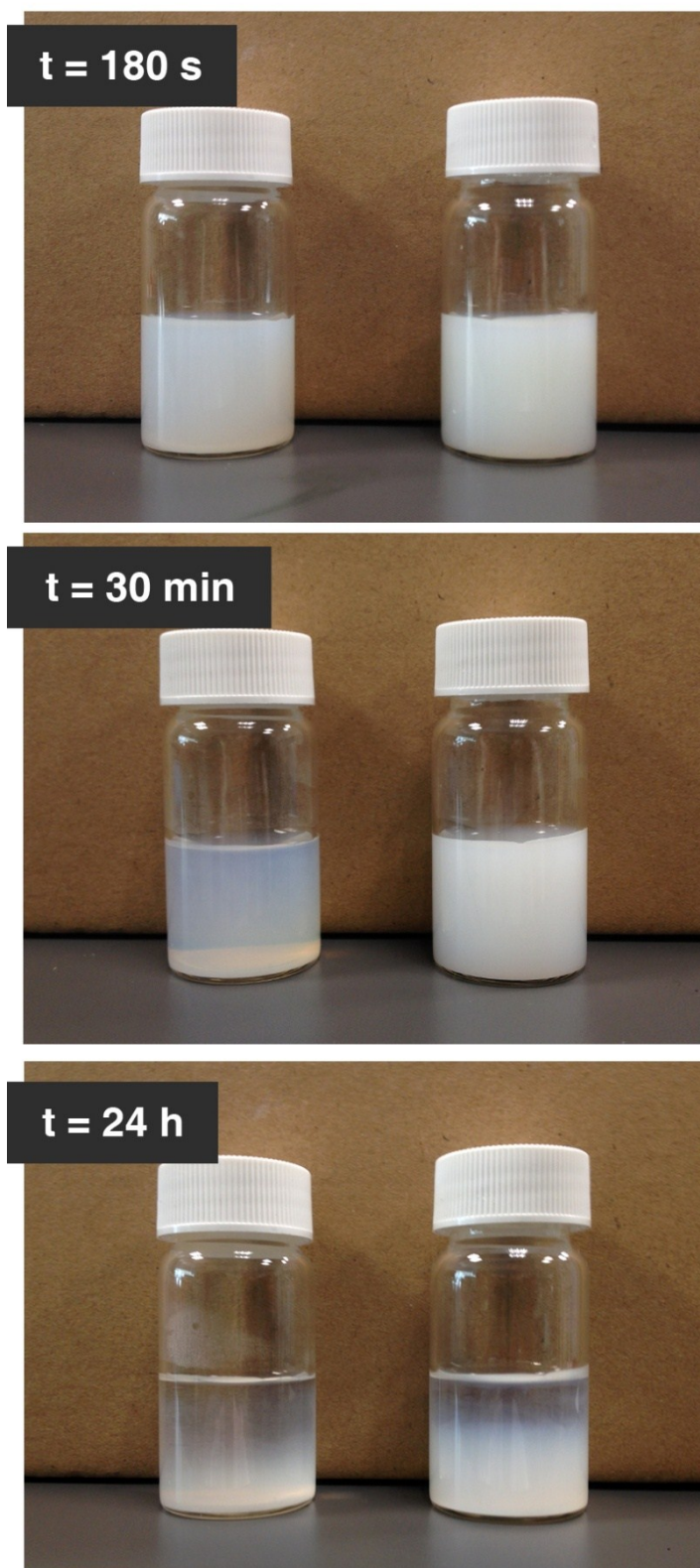


Figure S5. Photos illustrating the appearance of the reaction mixtures for the synthesis for $t_{\text{stir}} = 180 \text{ s}$ (left) and $t_{\text{stir}} = 0 \text{ s}$ (right) at different ageing times (t_{age}) as labelled.

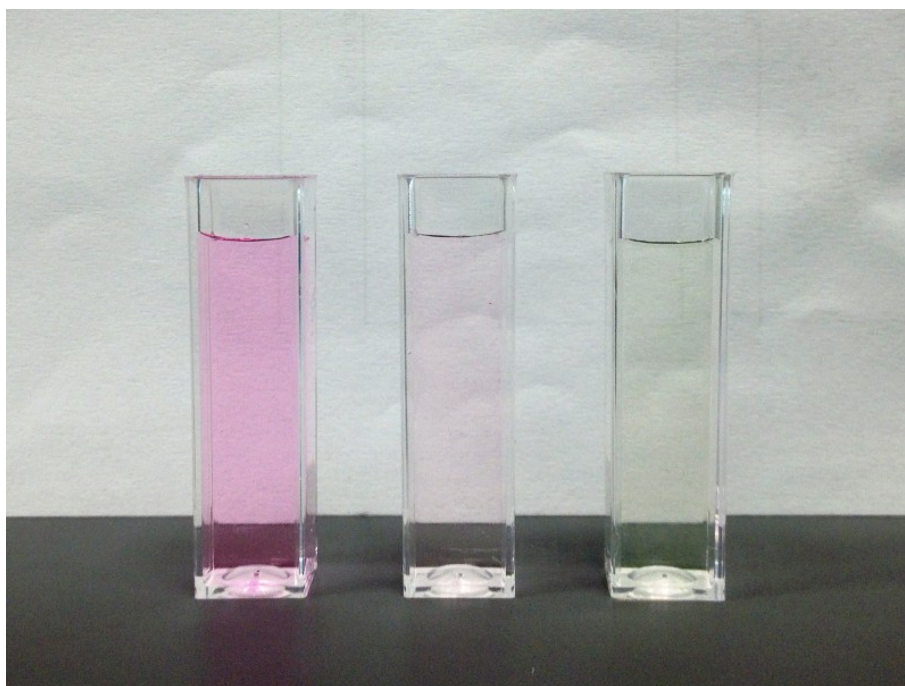


Figure S6. Photos illustrating the appearance of 5 ppm aqueous RhB (left) and the solutions after 3 h of visible-light irradiation for α - Ag_2WO_4 sub-micrometer rods (center) and nanowires (right). The α - Ag_2WO_4 crystals have been removed via centrifugation.

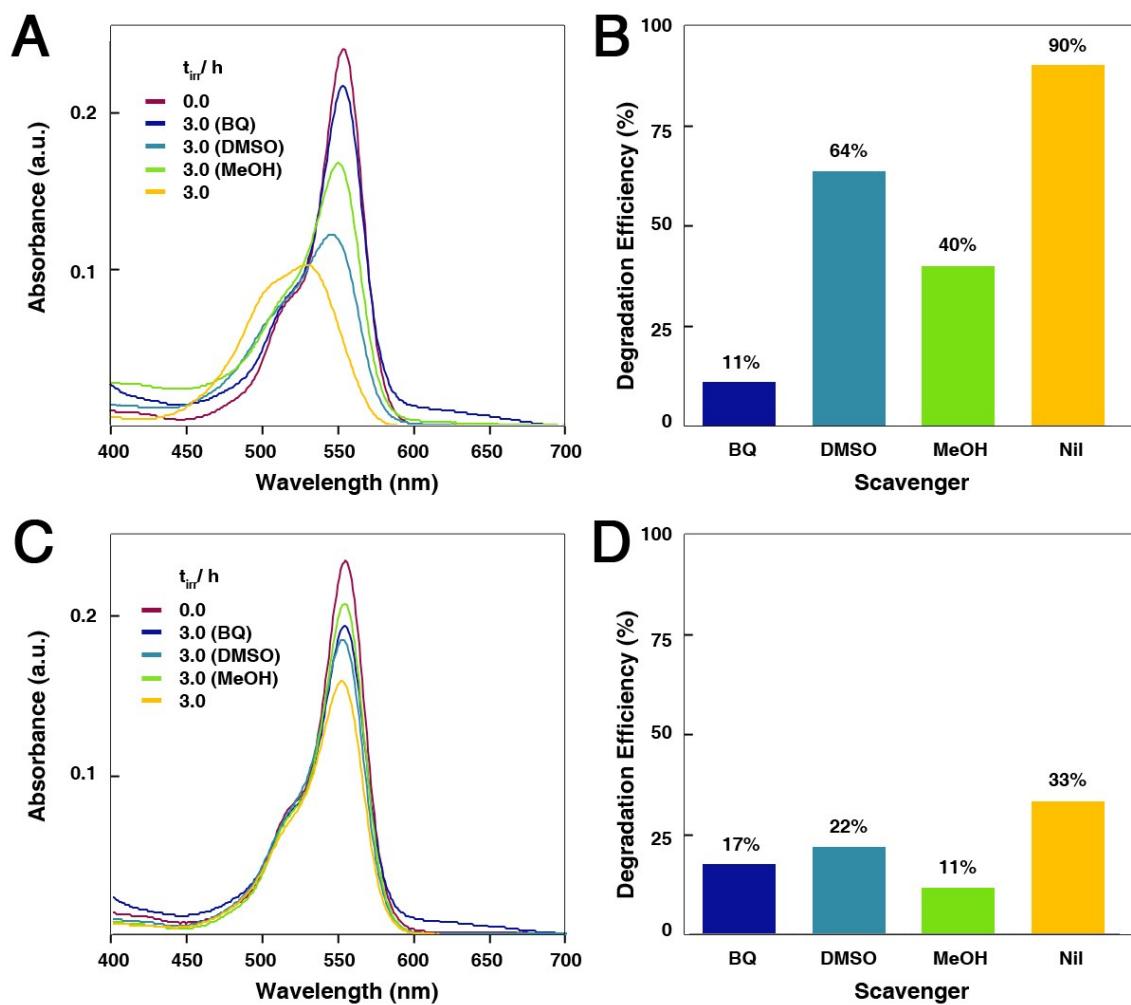
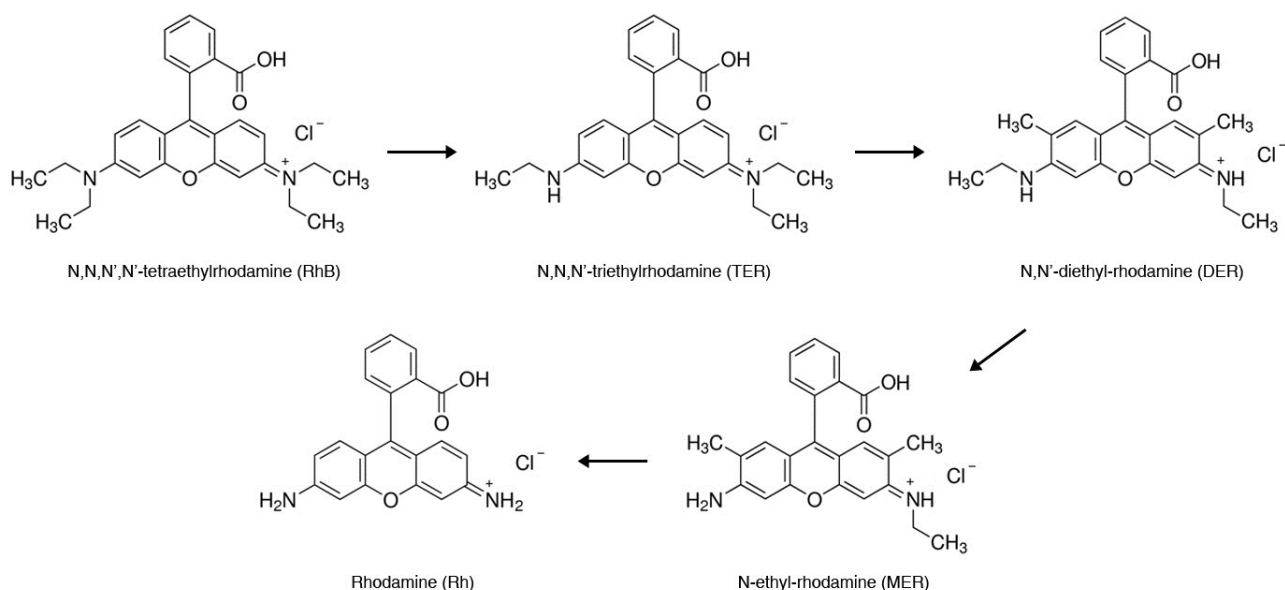


Figure S7. Spectral changes of RhB after $t_{irr} = 3h$ and degradation efficiency in the absence and the presence of $O_2^{\cdot-}$, $\cdot OH$ and h^+ scavengers (i.e. BQ, DMSO, MeOH respectively) for α - Ag_2WO_4 (A,B) nanowires and (C,D) sub-micrometer rods.

Details of the method for spectra deconvolution. The degradation for RhB via N-deethylation is known to occur stepwise via TER, DER, MER and Rh.



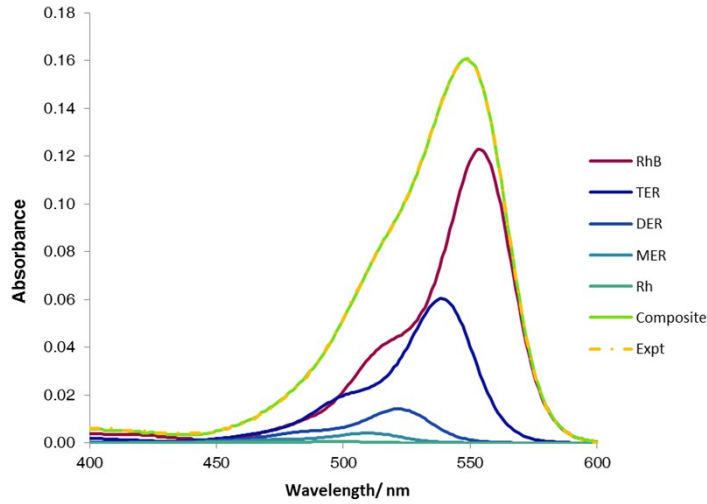
At any given time, the resulting spectrum will consist of some linear combination of the RhB, TER, DER, MER and Rh spectra. Based on previous work by Watanabe *et al.*, it can be seen that the rhodamine species have similar absorption profiles, differing only by the wavelength of peak absorbance (λ_{\max}) and molar absorbance coefficient (ϵ_{\max}).¹ Hence, the individual spectra of TER, DER, MER and Rh were approximated by scaling and shifting a measured spectrum of RhB (5 ppm) based on the reported λ_{\max} and ϵ_{\max} . The composite spectrum can then be simulated using the concentration values of each species. The concentrations of each component at the various time points were obtained using the Solver routine in Microsoft Excel to minimize the sum squared error between the calculated spectrum (from $\lambda = 400$ to 600 nm) and the experimentally observed spectrum, by refining the estimates of the RhB, TER, DER, MER and Rh concentrations.

Table S1 summarises the temporal-concentration profiles of RhB, TER, DER, MER, Rh, as well as the total chromophoric rhodamine ($\sum\text{Rh}$). As shown in the spectral illustrations, good agreement was typically obtained between the calculated and experimental spectra. The increase in the $\sum\text{Rh}$ concentration with irradiation time was also observed in the photodegradation of RhB with Ag@AgCl embedded on reduced graphene oxide and is attributed to the desorption of the deethylated products from the semiconductor surface into the solution.² Since a net decrease in $\sum\text{Rh}$ concentration was not observed during the experiment, it further suggests that degradation of RhB in the presence of $\alpha\text{-Ag}_2\text{WO}_4$ nanowires had occurred primarily via N-deethylation.

Table S1. Decconvoluted spectra and estimated concentrations of RhB, TER, DER, MER, Rh and Σ Rh at different irradiation times (t_{irr}).

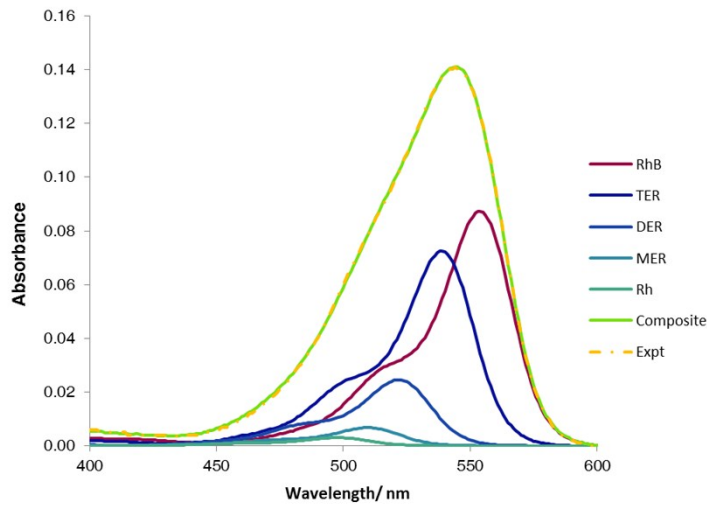
Time/ h	Decconvoluted Spectrum	Concentration of Species/ ppm												
0		<table border="1"> <tr> <td>RhB</td> <td>3.60</td> </tr> <tr> <td>TER</td> <td>0.00</td> </tr> <tr> <td>DER</td> <td>0.00</td> </tr> <tr> <td>MER</td> <td>0.00</td> </tr> <tr> <td>Rh</td> <td>0.00</td> </tr> <tr> <td>ΣRh</td> <td>3.60</td> </tr> </table>	RhB	3.60	TER	0.00	DER	0.00	MER	0.00	Rh	0.00	Σ Rh	3.60
RhB	3.60													
TER	0.00													
DER	0.00													
MER	0.00													
Rh	0.00													
Σ Rh	3.60													
0.08		<table border="1"> <tr> <td>RhB</td> <td>3.22</td> </tr> <tr> <td>TER</td> <td>0.88</td> </tr> <tr> <td>DER</td> <td>0.10</td> </tr> <tr> <td>MER</td> <td>0.00</td> </tr> <tr> <td>Rh</td> <td>0.00</td> </tr> <tr> <td>ΣRh</td> <td>4.21</td> </tr> </table>	RhB	3.22	TER	0.88	DER	0.10	MER	0.00	Rh	0.00	Σ Rh	4.21
RhB	3.22													
TER	0.88													
DER	0.10													
MER	0.00													
Rh	0.00													
Σ Rh	4.21													
0.25		<table border="1"> <tr> <td>RhB</td> <td>2.58</td> </tr> <tr> <td>TER</td> <td>1.72</td> </tr> <tr> <td>DER</td> <td>0.25</td> </tr> <tr> <td>MER</td> <td>0.07</td> </tr> <tr> <td>Rh</td> <td>0.00</td> </tr> <tr> <td>ΣRh</td> <td>4.62</td> </tr> </table>	RhB	2.58	TER	1.72	DER	0.25	MER	0.07	Rh	0.00	Σ Rh	4.62
RhB	2.58													
TER	1.72													
DER	0.25													
MER	0.07													
Rh	0.00													
Σ Rh	4.62													

0.5



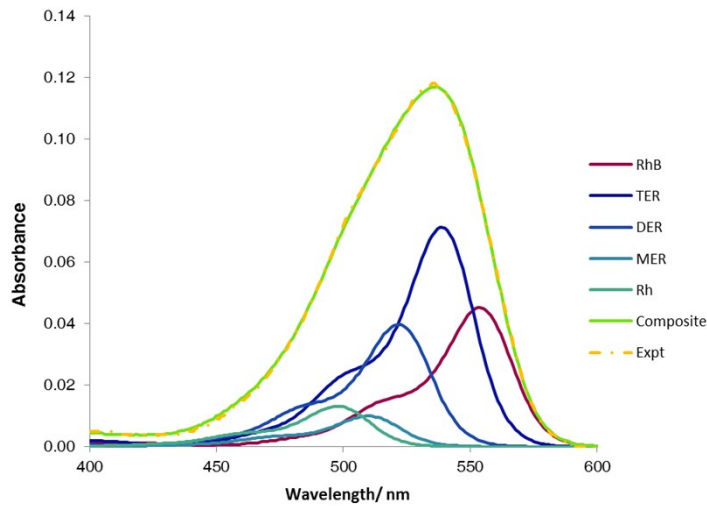
RhB	2.18
TER	2.23
DER	0.40
MER	0.14
Rh	0.01
Σ Rh	4.96

1.0



RhB	1.54
TER	2.69
DER	0.70
MER	0.23
Rh	0.07
Σ Rh	5.23

2.0



RhB	0.80
TER	2.65
DER	1.13
MER	0.33
Rh	0.32
Σ Rh	5.22

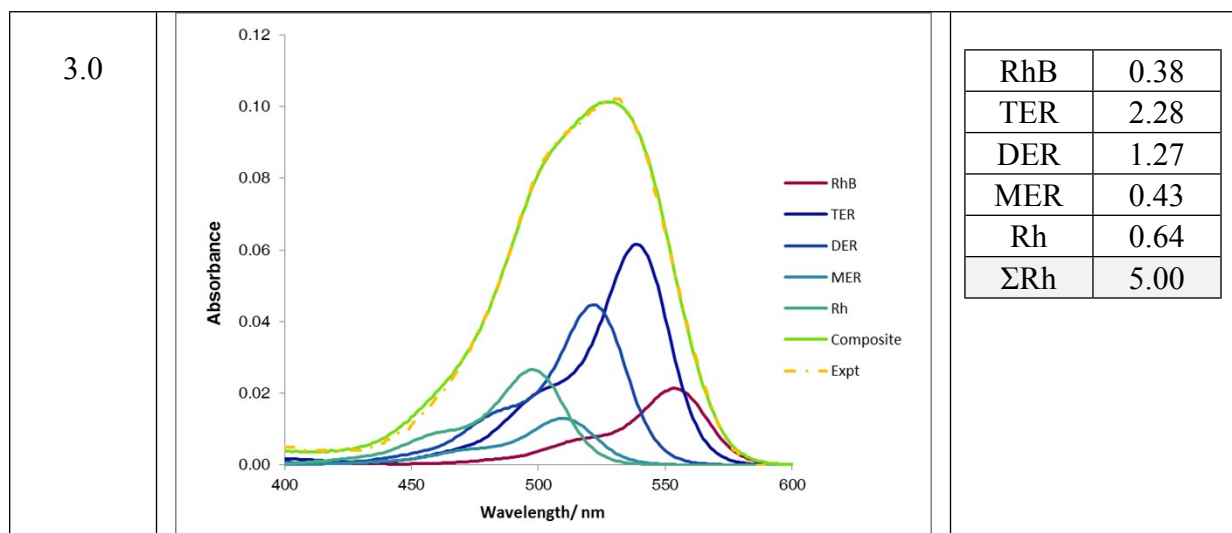


Table S2. Experimental rate constants (k_{expt}), specific surface areas (S_{BET}) and normalized rate constants (k_{norm}) for the different catalysts.

	k_{expt} (h^{-1})	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	k_{norm} ($\text{h}^{-1} \text{m}^{-2} \text{g}$)
$\alpha\text{-Ag}_2\text{WO}_4$ nanowires	0.724	4.90	0.148
$\alpha\text{-Ag}_2\text{WO}_4$ sub-micrometer rods	0.139	1.23	0.113

REFERNCES

- (1) Watanabe, T.; Takizawa, T.; Honda, K. *J. Phys. Chem.* **1977**, *81*, 1845.
- (2) Miller, C. J.; Yu, H.; Waite, T. D. *Colloids Surfaces A Physicochem. Eng. Asp.* **2013**, *435*, 147.