1	<b>Electronic Supporting Information (ESI)</b>
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3	Superior Dye Adsorption Capacity of Amorphous WO <sub>3</sub> Sub-
4	micrometer Rods Fabricated by Glancing-Angle Deposition
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# 1 S.I WO<sub>3</sub> Sub-micrometer Rod (SMR) Samples Preparation

2 The source material, Tungsten Oxide pieces, WO<sub>3</sub> (99.99+%, metal base), was purchased 3 from Kurt J. Lesker (Clairton, PA) and used without further purification. The WO<sub>3</sub> SMR 4 arrays were fabricated by a custom designed vacuum deposition system equipped with an 5 electron-beam evaporation source (Torr International, Inc.). Both cleaned glass 6 microscope slides (Gold Seal ® Catalog No. 3010) and Si (100) wafer (Montco Silicon 7 Technologies Inc.) were used as substrates. The glass substrates were cut into sizes of 9.0 8 mm  $\times$  27.0 mm while Si substrates were cut into size of 10.0 mm  $\times$  10.0 mm. Glass 9 substrates were cleaned with a mixture of sulfuric acid  $(H_2SO_4)$  and hydrogen peroxide 10  $(H_2O_2)$  solution, in a 4:1 ratio, by boiling about 15 mins and dried with nitrogen  $(N_2)$ 11 flow. Si wafers were cleaned in a mixture solution of de-ionized (DI) water, H<sub>2</sub>O<sub>2</sub>, and 12 ammonium hydroxide (NH<sub>4</sub>OH) in a ratio of 5:1:1, boiling for 15 mins and dried with  $N_2$ 13 flow. For glancing angle deposition (GLAD), the deposition angle, the angle between the 14 substrate surface normal and the incident vapor direction, was fixed to 86°. Prior to the deposition, the vacuum chamber was evacuated to a pressure of less than  $1 \times 10^{-6}$  Torr 15 16 whereas during the deposition, the pressure was maintained to be in the range of  $(3-7) \times$ 17  $10^{-6}$  Torr. During the deposition, the substrate holder was rotated continuously and 18 azimuthally at a speed of 0.25 rpm. The deposition rate and the deposited thickness were 19 monitored by a quartz crystal microbalance (QCM) positioned directly facing the incident 20 vapor. The deposition rate was maintained at 0.4 nm/s, and the final QCM thicknesses 21 reading was 3 µm. The mass of the deposited materials was estimated by weighing the 22 substrates before and after deposition using a high precision electron microbalance 23 (Model: XP56, METTLER TOLEDO).

# 1 S.II Characterization of As-deposited WO<sub>3</sub> SMRs

As-deposited WO<sub>3</sub> SMRs on glass substrates were used for X-ray diffraction (XRD) analysis and UV-Vis characterization while samples deposited on Si wafer were used for scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Figure S1 shows the XRD patterns of as-deposited WO<sub>3</sub> SMRs. No crystalline peaks are presented in the spectrum indicating that the as-deposited WO<sub>3</sub> SMRs are in amorphous phase.



Fig.S1 A representative XRD spectrum of as-deposited WO<sub>3</sub> SMRs on glass substrate.

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- 1 Figure S2 shows the EDX spectrum of as-deposited WO3 SMRs. Besides a strong Si
- 2 peak coming from the Si substrate, the EDX spectrum only consists of O and W peaks.



1 Figure S3 shows the UV-Vis extinction spectroscopy of the as-deposited WO<sub>3</sub> SMRs.



2 The apparent absorption edge of WO<sub>3</sub> SMRs is around 390 nm.

# **1** S.III Dye Adsorption Experiment

2 All the adsorption experiments were performed at room temperature ( $25 \pm 1$  °C) with 3 predetermined WO<sub>3</sub> SMR mass  $m = 1.52 \pm 0.04$  mg and a fixed methylene blue (MB) 4 solution volume V = 14 mL. The MB powder ( $C_{16}H_{18}CIN_3S$ ) was purchased from Alfa 5 Aesar Company (CAS #122965-43-9), and was used without further purification. The 6 prepared MB aqueous solutions were observed to have maximum absorbance at 7 wavelength,  $\lambda_{\text{max}} = 664$  nm (see the UV-Vis spectra in section S.V, below). A stock 8 solution of MB was prepared by dissolving the accurately weighed quantity of MB 9 powder, m = 64 mg, in DI water (18 MQ·cm) to make 200  $\mu$ M (initial concentration,  $C_0$ ). 10 To make a homogeneous solution, it was magnetically stirred for 12 h at room 11 temperature. Experimental solutions of the desired concentrations of 50, 70, 80, 90 and 12 100 µM were obtained by sequentially diluting the base solution with DI water. The pH 13 values of as-prepared MB aqueous solutions of 100 µM and 50 µM were slightly acidic, 14 in the range of pH 6.2-6.7, respectively. A 50 ml glass bottle was used to perform the 15 adsorption experiment with MB solutions. The bottle with a mixture of WO<sub>3</sub> SMRs (with 16 glass substrate) and MB solution, of known mass and concentration, was shaken 17 immediately (i.e. after immersing the glass-deposited  $WO_3$  SMR sample in the MB 18 solution) on an orbital shaker (Southwest Digital Shaker, Model: SBT300) at 300 rpm for 19 the predetermined time. For lower concentrations ( $C_0 \leq 70 \ \mu$ M), the shaking time was chosen to be every 5 min while for higher concentrations,  $C_0 \ge 80 \ \mu\text{M}$  it was chosen to be 20 21 every 10 min, until the adsorption get saturated. An aliquot sample (2 ml; solution 22 mixture of WO<sub>3</sub> SMRs and MB solution) was taken out at every predetermined time, as 23 mentioned above, and was measured the absorbance spectrum (UV-Vis

1 spectrophotometer, Model: JASCO V 570). Two successive experiments were performed 2 in order to obtain the absorbance spectra of aliquot samples. In one experiment UV-Vis 3 absorbance measurements were performed without centrifuging (WOC) the aliquot 4 samples, and in the other experiment, the absorbance measurements were performed with 5 centrifuging (WC) the aliquot samples at 15, 000 rpm (Eppendorf Centrifuge, Model: 6 5424). Then supernatant solution was taken out gently for the absorbance measurement, 7 and repeated the same procedure for absorbance measurements of all WC experiments. 8 Two- to four-fold dilutions of the aliquot samples were performed, before absorbance 9 measurements, if the expected concentration was higher than 30  $\mu$ M, i.e., to make the 10 concentration of MB solution  $\leq$  30  $\mu$ M. As demonstrated by the MB solution calibration 11 curve (section S.V), 30 µM was a concentration limit below which we can apply a linear 12 calibration curve to estimate the concentration. All the adsorption experiments were 13 conducted in duplicates, and only the mean values of remaining MB solution 14 concentrations were reported for each concentration profile, C(t). The maximum 15 deviation in the remaining concentrations values, in our experiments, was usually less 16 than 5%. The control adsorption experiments without WO<sub>3</sub> SMR samples were also 17 conducted to ensure that the decrease in the concentration was actually due to the 18 adsorption of WO<sub>3</sub> SMRs.

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# 1 S.IV Properties of MB-adsorbed WO<sub>3</sub> SMRs

# 4 S.IV.1 The FT-IR spectra of MB/WO<sub>3</sub> Complex

Figure S4 shows the FT-IR spectra of the WO<sub>3</sub> SMRs, MB, and MB-adsorbed WO<sub>3</sub> SMRs (MB/ WO<sub>3</sub> complex). For FT-IR measurements, we used the as-deposited WO<sub>3</sub> SMRs sonicated off from the substrate in de-ionized (DI) water and MB solution, 50 µM. About 50 µL of each sample solution was pipetted on three-individual cleaned glass substrates and air dried. The same process was repeated about 10 times to form multiple layers of each type sample on the substrates before the measurements were performed. Then the FT-IR spectra were recorded for 500- 4000 cm<sup>-1</sup> at 120 scans with a spectral resolution of 2 cm<sup>-1</sup> using Thermo-Nicolet 6700. Comparing the spectra of WO<sub>3</sub> SMRs, pure MB and MB/WO<sub>3</sub> complex, the MB/WO<sub>3</sub> complex spectrum confirms the adsorption of MB and shows a ring stretched vibrational mode at 1603 cm<sup>-1</sup>.<sup>1, 2</sup> 



### 1 S.IV.2 Time-dependent UV-Vis Spectra of MB Solutions with WO<sub>3</sub> SMRs

The time dependent UV-Vis absorbance spectra of the MB solutions with WO<sub>3</sub> SMRs

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4 were observed to be strongly dependent on both the initial MB concentration and mass of 5  $WO_3$  SMR loadings. For example, for a fixed mass loading (0.48 mg) in the 3 ml MB 6 solution, the MB absorbance peaks at  $\lambda = 664$  nm and its shoulder peak at  $\lambda = 612$  nm (as 7 shown in Fig. S5, below) were observed to be decreased rapidly at lower concentrations 8  $(C_0 \leq 70 \ \mu\text{M})$ . However, increasing the initial concentration of MB solution, the 9 decreasing rate of these absorbance peaks were observed to decrease. More interestingly, 10 the shapes of UV-Vis absorbance spectra of MB solution were also observed to change 11 rapidly and drastically at lower concentration, especially for  $C_0 \leq 30 \ \mu M$  (as shown in Fig. S5 (a) for 20  $\mu$ M). However, at higher MB solution concentrations,  $C_0 \ge 50 \mu$ M, and 12 13 with the same WO<sub>3</sub> SMR mass loadings, the UV-Vis absorbance spectra of MB solutions 14 were observed to maintain the same shape. In other words, the MB peaks were not 15 observed to be blue-shifted as observed for lower concentrations (as shown in Fig. S5 (b) 16 for 70 µM). The spectra, shown in Figures S5 (a) and S5 (b), were recorded for various 17 time intervals for each concentration and with a constant mass loading as mentioned 18 above. As seen in Fig.S5 (a), the blue-shifted peaks were attributed to the aggregation of MB molecules onto the WO<sub>3</sub> SMRs such that the peak is shifted due to more 19 20 concentrations in the WO<sub>3</sub> SMR surface (than remaining MB molecules in the aqueous-21 media). However, adsorption of MB molecules was observed to be dominating at higher 22 concentrations such that the shapes of absorbance spectra were not observed to change 23 during the adsorption experiments providing  $C_0 \ge 50 \ \mu M$  (as shown in Fig. S5 (b)). 24 Similarly, we did not observe any change in the UV-Vis spectra performing the

(figures are not shown here).

1 adsorption experiment starting with higher concentrations of MB solutions,  $C_0 \ge 50 \ \mu M$ 



Fig.S5 Time-dependent absorbance spectra of MB solutions with WO<sub>3</sub> SMRs, in liquid phase, starting with different concentrations of MB solutions: (a) 20 μM and (b) 50 μM.
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Similar results due to the effect of MB concentration on aggregation were reported by Sagiv<sup>3</sup> and Adachi *et.al.*<sup>4</sup> Note that the absorbance peaks at  $\lambda = 664$ , 605 to 608 and 574-580 nm can respectively be regarded as due to monomer  $(MB^+)$ , dimer  $(MB^+)_2$  and trimer  $(MB^+)_3$  MB species.<sup>4, 5</sup> 

# S.IV.3 Effect of UV-irradiation on Concentration Profile of MB Solution with WO<sub>3</sub> SMRs

Figure S6 show the concentration profile of MB solution recorded with and without the UV-irradiation during adsorption experiment for  $C_0 = 50 \ \mu M$ . These experiments were performed under the same conditions for without centrifuging (WOC). An UV lamp ( $\lambda =$ 365 nm, UV; BLAK-RAY, Model B 100AP) was used for illumination. The incident UV light intensity on sample was kept constant, 10 mW/cm<sup>2</sup>, measured by an optical power meter (Thorlabs PM100D/S310C). And the UV-Vis absorbance spectra of the MB solution with WO<sub>3</sub> SMRs were recorded in time acquisition mode by using an Ocean Optics spectrophotometer (Model: USB2000). The change in the intensity of the MB absorbance peak at  $\lambda_{max} = 664$  nm was, converted into concentration profile for each measurement (see section S.V for the calibration process). Reduction rate of MB concentration was observed to be faster noticeably after about 30 min UV irradiation as shown in Fig. S6. In addition, an additional reduction of MB concentration was also observed with the UV-illumination. This enhancement could be contributed to the fact that the WO<sub>3</sub> SMRs (semiconductor) absorbs UV light and then generate electron-hole pairs that will participate in photocatalytic reaction.<sup>6</sup> 



# 1 S.V MB Solution Concentration: Calibration Curve

2 A calibration curve, shown below, was used to compute the concentration MB solutions 3 through optical absorbance measurements. UV-Vis absorbance spectra of the MB 4 solutions with different known concentrations (5 to  $60 \mu$ M) were measured as shown in Fig. S7. Fig. S7 (b) shows that the maximum absorbance at  $\lambda_{max} = 644$  nm, is a linear 5 6 function of concentration below a critical value. For instance, we observe a linear relationship between the peak absorbance,  $A_{664}$  (i.e. at  $\lambda_{max} = 664$  nm) versus  $C_0$  for  $C_0 \leq$ 7 30  $\mu$ M. Thus, we can use the peak absorbance value  $A_{664}$  to estimate the concentration of 8 9 MB solution from their calibration curve (Fig. S7 (b)). For higher concentrated MB solutions ( $C_0 \ge 30 \ \mu$ M), we performed 2- to 4-folds dilutions to bring the concentrations 10 11 down to  $\leq$  30  $\mu$ M, and then used the UV-Vis absorption spectra to evaluate the MB 12 concentration. It is worthy to mention that the absorbance value of glass-deposited  $WO_3$ 13 SMRs at the above mentioned wavelength is negligible, as shown in Fig. S.3. However, 14 to avoid the possible errors due to WO<sub>3</sub> SMRs, we used the GRAMS/AI software 15 (Thermo Scientific), subtracted the baseline, carried out the peak fittings, and obtained 16  $A_{664}$ .

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### 1 S.VI Change in morphology of WO<sub>3</sub> SMRs after MB Adsorption Experiments

The morphology of as-prepared amorphous WO<sub>3</sub> SMRs was observed to change when centrifuged at 15,000 rpm during the adsorption experiments. The new morphology of the SMRs was observed to be a sponge-like nanostructure as shown in Fig. S8 (b). Conversely the morphology of these SMRs was not observed to change without the mechanical agitation as shown in Fig. S8 (a). In addition, to confirm the braking of these WO<sub>3</sub> SMRs was only due to the severe mechanical force applied, we took the SEM and TEM images of SMRs after immersing and centrifuging in pure DI water, and the same phenomena were observed. Although Lee *et. al.*<sup>7</sup>, and Hidayat *et. al.*<sup>8</sup> reported that the amorphous WO<sub>3</sub> undergo high dissolution in acidic solutions, the GLAD deposited amorphous WO<sub>3</sub> SMRs are considerably stable in slightly acidic media, i.e. in MB solutions over the pH range of 6.2- 6.7. It is worthy to mention that the pH scale reported by Lee et. al.<sup>7</sup> was comparatively much smaller (1 M H<sub>2</sub>SO<sub>4</sub> of pH 0.96). 



# 1 S.VII Effects of Crystallization on MB Adsorption

2 We annealed the as-prepared  $WO_3$  SMRs (deposited on glass substrates) at various 3 temperatures, T = 300, 400, 500 and 550 °C, respectively, in a quartz tube furnace 4 (Lindberg/Blue M Company) for 4 h in air. Note that we could not anneal the glass-5 deposited WO<sub>3</sub> SMR samples at T > 550 °C due to the temperature limitation of glass. 6 Figure S9 (a) shows the XRD patterns of annealed  $WO_3$  SMR samples (spectrum of as-7 prepared samples has also included to for a comparison). The as-deposited samples 8 exhibited the amorphous phase while annealed samples exhibited the polycrystalline 9 WO<sub>3</sub> phases (mixed phases of Monoclinic (JCPDS ref: 43-1035), Orthorhombic (JCPDS 10 ref: 20-1324) and Hexagonal phases (JCPDS ref: 85-2459)). A slight evidence of emergence of monoclinic phase was observed with a noticeable peak at  $2\theta = 23.12^{\circ}$  for 11 12 T = 300 °C annealed samples, and was followed by above mentioned mixed phases with all discern peaks for  $T \ge 300$  °C (up to T = 550 °C). For samples annealed at higher 13 14 temperatures, i.e. 400 °C  $< T \le 550$  °C, hexagonal phase appeared to be dominating by 15 comparing the relative peak intensity ratios. Figure S9(b) below shows the MB 16 adsorption capability versus samples annealed at different temperature. With increased 17 annealing temperature, the MB adsorption decreases. This could be primarily due to the 18 decrease in total surface area of nanostructure via crystallization and coarsening of the 19 rods. To support this argument, a quantitative comparison of crystalline sizes obtained 20 from XRD using the well-known Scheerer's formula (at  $2\theta = 23.12^{\circ}$ ) is conducted. The 21 crystal size changes from ~ 12.6 nm (T = 300 °C) to 17.3 nm (T = 400 °C) and then to 22 25.8 nm (T = 500 °C). It is noteworthy to mention that the equilibrium adsorption time,

1  $t_{\rm e}$ , was also observed to increase with annealing temperature due to the difficulty of MB



2 penetrating (diffusing) into the films.

# S.VIII Equilibrium Adsorption Capacity Comparisons for Cationic and Anionic Dyes

3 The extra pure Rhodamine 6G (R6G) (99%), high purity Methyl Orange (MO), and 4 analytical grade Phenol (Ph) ( $\geq$  99%) were purchased from ACROS ORGANICS 5 (AC41901-0250), Alfa-Aesar (CAS #547-58-0), and Sigma Aldrich Company (CAS 6 #108-95-2) respectively. Dye aqueous solutions, of predetermined concentrations (shown 7 in figures below; where MB spectra used for a comparison), were prepared by following 8 the above mentioned protocols. The initial pH of the as-prepared MB, R6G, MO and Ph 9 aqueous solutions were 6.2, 7.5, 6.4 and 6.6, respectively. The maximum absorbance 10 peaks were observed at  $\lambda = 526$  nm for R6G, 270 nm for Ph and 480 nm for MO aqueous 11 solutions, as shown in Figure S10 below. And these maximum absorbance peaks were 12 utilized to estimate the concentration profiles for each dye. A summary of experimental parameters for dye adsorptions and  $q_e$  that was estimated by using Eq. 1 is listed in Table 13 14 S1.

15 The adsorption process for cationic dyes (both MB and R6G) is instantaneous and 16 attained equilibrium within 30 minutes (see Figures S10 (a) & (b)). The estimated  $q_e$  of 17 R6G and MB solutions were 176.5 mg/g and 149.8 mg/g, respectively, with a loaded 18 mass of adsorbent (amorphous WO<sub>3</sub> SMRs)  $m = 0.48 \pm 0.04$  mg and volume, V = 3.0 ml 19 (and  $C_0 = 50 \,\mu\text{M}$ ) for both dyes, and those values are significant. However, no substantial 20 adsorption of MO and Ph were observed even for longer adsorption time (i.e.  $t \ge 40$  min; 21 see Figures S10(c) & (d)). Unlike the spectra for MO, we observed an extra peak 22 appeared for Ph, at  $\lambda = 320$  nm, when the adsorption time exceeded about 20 min. 23 However, we could not recognize this characterizing peak. Similar peak was also

observed by F. He and L.-C. Lei when Ph was irradiated under UV light in H<sub>2</sub>O<sub>2</sub>.<sup>9</sup> The  $q_{\rm e}$  values for these anionic dyes were estimated to be  $\leq 3.0$  mg/g after 1 h adsorption. This suggests that the dye adsorption process onto WO<sub>3</sub> SMR surfaces, in the slightly acidic and basic solutions, is dominated by the electrostatic interaction. In other words, the negative surface charge of WO<sub>3</sub> SMRs (zeta potential,  $\zeta = -39$  mV at pH 8.1) could be regarded as a primary source for such a high adsorption for cationic dyes. 

Table S1. Summary of  $q_e$  and other experimental parameters for cationic and anionic dye adsorptions.

-	Dy	/e	Mass of adsorbent, $m$ (mg)	Equil. ads. cap., $q_e$
-	(fixed volum	$\frac{\text{ne, } l = 3 \text{ ml}}{1000 \text{ ml}}$	(amorphous WO <sub>3</sub> )	(mg/g)
-	Dye/ type	Initial Conc. $(C_0)$		
	MB/ cationic	50 µM	$0.48 \pm 0.04$	149.8
	R6G/ cationic	50 µM	$0.48 \pm 0.04$	176.5
	MO/ anionic	20 µM	$0.48\pm0.04$	2.5
	Ph/ anionic	50 µM	$0.48\pm0.04$	3.0
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### 1 S.IX Kinetics of adsorption Models

Various kinetic models have been introduced to describe the liquid-phase adsorption of dyes onto solid adsorbents.<sup>10-12</sup> Two simplified kinetic models respectively pseudo-firstorder and pseudo-second-order equations are analyzed and tested for MB adsorption. The pseudo-first-order model was suggested by Lagergren that describes the adsorption of solutes from a solution and it can be expressed as,<sup>13</sup>

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t.$$
 (1)

9 The linear plot of  $\log(q_e - q_t)$  versus t gives  $K_1$  as well as  $q_e$  from slope and intercept 10 respectively. Thus, we used the Eq. (1) to estimate the  $K_1$  values using known  $q_t$  and  $q_e$ 11 values, obtained for all different adsorption experiments (plots are not shown here).

12 The rate law for the pseudo-second-order kinetic model is described in the main content; 13 and the Figure S.11 (a)-(g), below, show the  $t/q_t$  versus t plots. The fitting parameters are 14 summarized in Table S2.

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1 Table S2. Adsorption kinetics parameter for the adsorption of MB onto WO<sub>3</sub> SMRs for

2 different initial concentrations  $(C_0)$  for both the WO and WOC cases.

4	Initial parameter, $C_0$ ( $\mu$ M), and sample description	1 <sup>st</sup> order kinetics		2 <sup>nd</sup> order kinetics		
5		<i>K</i> <sub>1</sub> (h <sup>-1</sup> )	Adj. R <sup>2</sup>	h (= $K_2 q_e^2$ ) (µmol g <sup>-1</sup> h <sup>-1</sup> )	<i>K</i> <sub>2</sub> (g μmol <sup>-1</sup> .h <sup>-1</sup> )	Adj. R <sup>2</sup>
6	50 -WOC	5.23	0.921	4425	0.016	0.971
_	50 -WC	5.61	0.915	5193	0.020	0.980
7	55 -WOC	8.02	0.944	4969	0.016	0.985
	55 -WC	6.25	0.962	5567	0.017	0.990
8	60 -WOC	4.69	0.976	5262	0.018	0.999
	60 -WC	4.21	0.965	5463	0.018	0.998
9	70 -WOC	3.40	0.960	2819	0.006	0.999
	70 -WC	3.47	0.965	3580	0.007	0.998
10	80 -WOC	3.46	0.944	2216	0.003	0.980
	80 -WC	3.34	0.959	2780	0.004	0.994
11	90 -WOC	3.63	0.985	1313	0.001	0.979
	90 -WC	2.96	0.986	1551	0.001	0.982
12	100 -WOC	2.46	0.980	1571	0.001	0.967
	100 -WC	2.46	0.997	1838	0.002	0.994

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