

Supplementary Information

Facile Synthesis of Mesoporous Silica and Titania Supraparticles by a Meniscus Templating Route on Superhydrophobic Surface and Their Application to Adsorbents

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1. Method

1.1. Preparation of superhydrophobic films

Candle soot film and fluorinated silica film were prepared as superhydrophobic surface and alumina crucible trays were used as a substrate for both of superhydrophobic films. The superhydrophobic candle soot film was readily coated on the tray by holding it on the flame of candle until yellow tray surface turned into black. Fluorinated silica films were synthesized by using the candle soot film as a template as reported by Deng et al.¹ In a typical synthesis, the candle-soot-coated alumina tray and other two trays, containing 2 mL of NH₃ (Junsei, 28%) and 2 mL of tetraethyl orthosilicate (TEOS: Aldrich, 98%), were placed into a desiccator and then vacuum was applied for 2 min. After chemical vapor deposition (CVD) was conducted for 12 h, candle soot core was removed by calcination at 600 °C for 2 h (ramping rate: 1 °C/min), resulting in hollow silica structure. Afterwards hollow silica surface was fluorinated by CVD of trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane (TPOS: Aldrich, 97%). The hollow-silica-coated tray and another alumina tray containing 0.1 mL of TPOS were placed together into a desiccator. After vacuum was applied for 2 min, fluorination was carried out for 3 h, resulting in superhydrophobic fluorinated-silica films.

1.2. Synthesis of silica sol

Silica sol with particle diameter of about 5 - 8 nm was synthesized under weak-base-

1 catalyzed condition through hydrolysis of TEOS and condensation. The molar ratio of
2 TEOS:NH₃:H₂O:EtOH was 1:0.086:53.6:40.7. A TEOS/EtOH mixture was stirred vigorously
3 at 50 °C in an oil bath, and then a NH₃/H₂O mixture was added into the TEOS/EtOH mixture
4 solution. Afterwards the final mixture solution was refluxed for 3 h resulting in transparent
5 silica sol including silica nanoparticles of about 5 nm.

6 7 **1.3. Synthesis of titania sol**

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9 100 mL of distilled water was rapidly added into a mixture of 14.8 mL titanium(IV)
10 isopropoxide (TIP: Aldrich, 97%) and 5 mL ethanol to obtain titania white precipitates,
11 followed by vigorous stirring for 30 min at ambient temperature. After 1.33 mL of
12 hydrochloric acid (Junsei, 35%) was added into the solution of titania precipitates, their
13 peptization was conducted by vigorous stirring at 90 °C for 2 h with flask mouth opened.
14 Afterwards the solution was diluted by addition of 100 mL distilled water, and then refluxed
15 at 90 °C for 18 h, resulting in titania sol with particle diameter of about 6 - 8 nm.

16 17 **1.4. Fabrication of mesoporous silica supraparticles via meniscus templating**

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19 The as-prepared silica sol needs to be enriched to increase the concentration of silica
20 nanoparticles. 200 mL of distilled water was added into 500 mL of the as-prepared silica sol,
21 followed by evaporating solvent at 100 °C till adjusting the solution volume to 240 mL. The
22 enriched silica sol was employed as mother solution for fabrication of supraparticles, and
23 sucrose was used as a porogen for mesopore formation. Sucrose was added into the enriched
24 silica sol, followed by vigorous stirring at room temperature for 10 min for formation of
25 silica-sucrose nanocomposites. The supraparticles in millimeter dimension was very easily
26 formed by dripping and drying the nanocomposite sol on superhydrophobic candle soot films
27 at ambient temperature. After supraparticles collected from candle-soot-coated trays were
28 calcined at 550 °C for 2 h (ramping rate: 1 °C/min), mesoporous silica supraparticles with
29 various morphology of millimeter scale were successfully fabricated. For preparation of
30 mesoporous silica supraparticles in micrometer dimension, the silica-sucrose nanocomposite
31 sol was sprayed on the superhydrophobic fluorinated-silica film, and was dried at room
32 temperature for 10 h, followed by calcination at 550 °C for 2 h. The mesoporous silica
33 supraparticles are designated as KIE-1 (Korea Institute of Energy research-1). Table S1
34 summarized various KIE-1 samples and their synthetic conditions.

35 36 **1.5. Fabrication of mesoporous titania supraparticles via meniscus templating**

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38 Mother solution for synthesis of mesoporous titania supraparticles was prepared by

1 enriching the as-prepared titania sol. 100 mL of distilled water was added into 220 mL of the
2 as-prepared titania sol, followed by evaporating solvent at 100 °C till adjusting the solution
3 volume to 150 mL. Sucrose was added into the enriched titania sol, followed by vigorous
4 stirring at room temperature for 10 min for formation of titania-sucrose nanocomposites.
5 Mesoporous titania supraparticles were prepared with titania-sucrose nanocomposite sol
6 through the same procedure as silica supraparticles except for calcination temperature of 350
7 °C. The mesoporous titania supraparticles are designated as KIE-2 (Korea Institute of Energy
8 research-2). Their synthetic conditions were summarized in Table S1.

9 10 **1.6. Characterization**

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12 Contact angles of water droplets (8-10 µL per each droplet) on the superhydrophobic films
13 were measured by using a PHODNIX-300 (SEO, Korea) instrument. The mesopore
14 properties of silica and titania supraparticles were taken by nitrogen sorption tests with a
15 Micromeritics ASAP 2420 instrument. Degassing of samples was conducted at 200 °C for 7 h.
16 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses
17 were carried out by employing a HITACHI S-4700 and a FEI/TECNAI G2 instrument. X-ray
18 diffraction (XRD) patterns were collected on a Rigaku D/MAX-2200V instrument operated at
19 1.6 kW.

20 21 **1.7. Amine-functionalization of KIE-1**

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23 0.05 g of calcined KIE-1-d/0.18 was added into 30 mL of toluene, followed by addition of
24 0.35 mL of 3-aminopropyl trimethoxysilane (APTMS: Aldrich, 97%). The final mixture was
25 refluxed without stirring for 3 h at 110 °C. After filtering and washing unreacted APTMS
26 with toluene, the amine-functionalized KIC-1-d/0.18 was successfully prepared. Amine
27 functionalization of KIE-1 was confirmed by fourier transform infrared (FTIR) analysis,
28 which was conducted by using a Thermo Nicolet 5700 instrument.

29 30 **1.8. Acid blue 25 adsorption tests of KIE-1**

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32 0.003 g of Acid blue 25 (or eriochrome blue black B: Aldrich) was dissolved in 40 mL of
33 distilled water. After complete dissolution, 0.015 g of KIE-1-d/0.18-a was added into the Acid
34 blue 25 solution. After the solution was allowed to equilibrate at ambient temperature for 7
35 days without stirring, the KIE-1 adsorbents were easily separated from the solution by using a
36 scoop net. The dye concentration after adsorption was measured by using a UV/visible
37 spectrophotometer (SCINCO S-4100).

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1 1.9. Cr(VI) adsorption tests of KIE-2

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3 Potassium dichromate solution with initial Cr(VI) concentration of 8 mg/L was prepared
4 by mixing 0.184 mL of potassium dichromate solution (SAMCHUN, 1/60 M) and 40 mL of
5 0.1 M nitric acid aqueous solution. For Cr(VI) adsorption tests of KIE-2, 0.04 g of calcined
6 KIE-2-d/0.13 was added into 40 mL of potassium dichromate solution with initial Cr(VI)
7 concentration of 8 mg/L. After the solution was allowed to equilibrate at ambient temperature
8 for 7 days without stirring, the KIE-2 was easily separated from the solution by using a scoop
9 net. The Cr(VI) concentration after adsorption was measured by using ICP-OES (Inductively
10 Coupled Plasma-Optical Emission Spectrometer: Optima 5300 DV).

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13 2. Supporting tables and figures

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15 **Table S1.** Various KIE-1 and KIE-2 samples and their synthetic conditions.

sample code	inorganic source	droplet formation method	sucrose/ inorganic source/ water molar ratio [-]	dilution ratio [-]	initial droplet diameter before drying [mm]	density of initial droplets before drying [g/cm ³]
KIE-1-d/0	SiO ₂	dripping	0/1/94	-	4.5	1.028
KIE-1-d/0.18	SiO ₂	dripping	0.18/1/94	0	4.5	1.050
KIE-1-d/0.18/2	SiO ₂	dripping	0.18/1/188	2	4.5	1.026
KIE-1-d/0.18/8	SiO ₂	dripping	0.18/1/752	8	4.5	1.010
KIE-1-d/0.67	SiO ₂	dripping	0.67/1/94	-	4.5	1.096
KIE-1-s/0.18	SiO ₂	spraying	0.18/1/94	-	0.05-0.35	1.050
KIE-2-d/0	TiO ₂	dripping	0/1/175	-	4.3	1.032
KIE-2-d/0.13	TiO ₂	dripping	0.13/1/175	-	4.3	1.046
KIE-2-d/0.65	TiO ₂	dripping	0.65/1/175	-	4.3	1.066
KIE-2-s/0.13	TiO ₂	spraying	0.13/1/175	-	0.07-0.72	1.046

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1 **Table S2.** A macroscopic morphology summary of KIE-1 and KIE-2 samples before
 2 calcination.

sample code	diameter of supra-particles [mm]	cap structure of supraparticles	bottom structure of supraparticles	contact circle diameter at the bottom of supraparticles
KIE-1-d/0	1.57	bagel	dimpled	0.91
KIE-1-d/0.18 ^a	1.68	round	dimpled	1.11
KIE-1-d/0.18/2 ^a	1.29	round	dimpled	0.80
KIE-1-d/0.18/8	1.03	wrinkled	crumpled concave	nm ^b
KIE-1-d/0.67	2.28	round	flat	1.51
KIE-1-s/0.18	0.016-0.125	round	round	fs ^c
KIE-2-d/0	1.49	bagel	dimpled	0.97
KIE-2-d/0.13	1.86	bagel	dimpled	1.39
KIE-2-d/0.65	2.42	pizza	dimpled	1.79
KIE-2-s/0.13	0.026-0.312	round	round	fs

3 ^a Core structure is solid, because the evaporative flux of solvent at periphery of droplets
 4 (three phase contact line) is much faster than that for gas-liquid interface on the top of
 5 droplets.

6 ^b It could not be measured due to its crumpled structure.

7 ^c there are no contact circles because supraparticles are full sphere.

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9 **Table S3.** Mesopore properties of KIE-1 and KIE-2 samples after calcination.

Sample code	S _{BET} [m ² /g] ^a	S _{micro} [m ² /g] ^b	V _{tot} [cm ³ /g] ^c	D [nm] ^d
KIE-1-d/0	510	98	0.604	4.5
KIE-1-d/0.18	490	77	0.726	5.5
KIE-1-d/0.67	460	110	0.859	6.8
KIE-2-d/0	110	6	0.131	3.4
KIE-2-d/0.13	160	4	0.263	4.9
KIE-2-d/0.65	170	3	0.339	5.8

10 ^a BET surface area

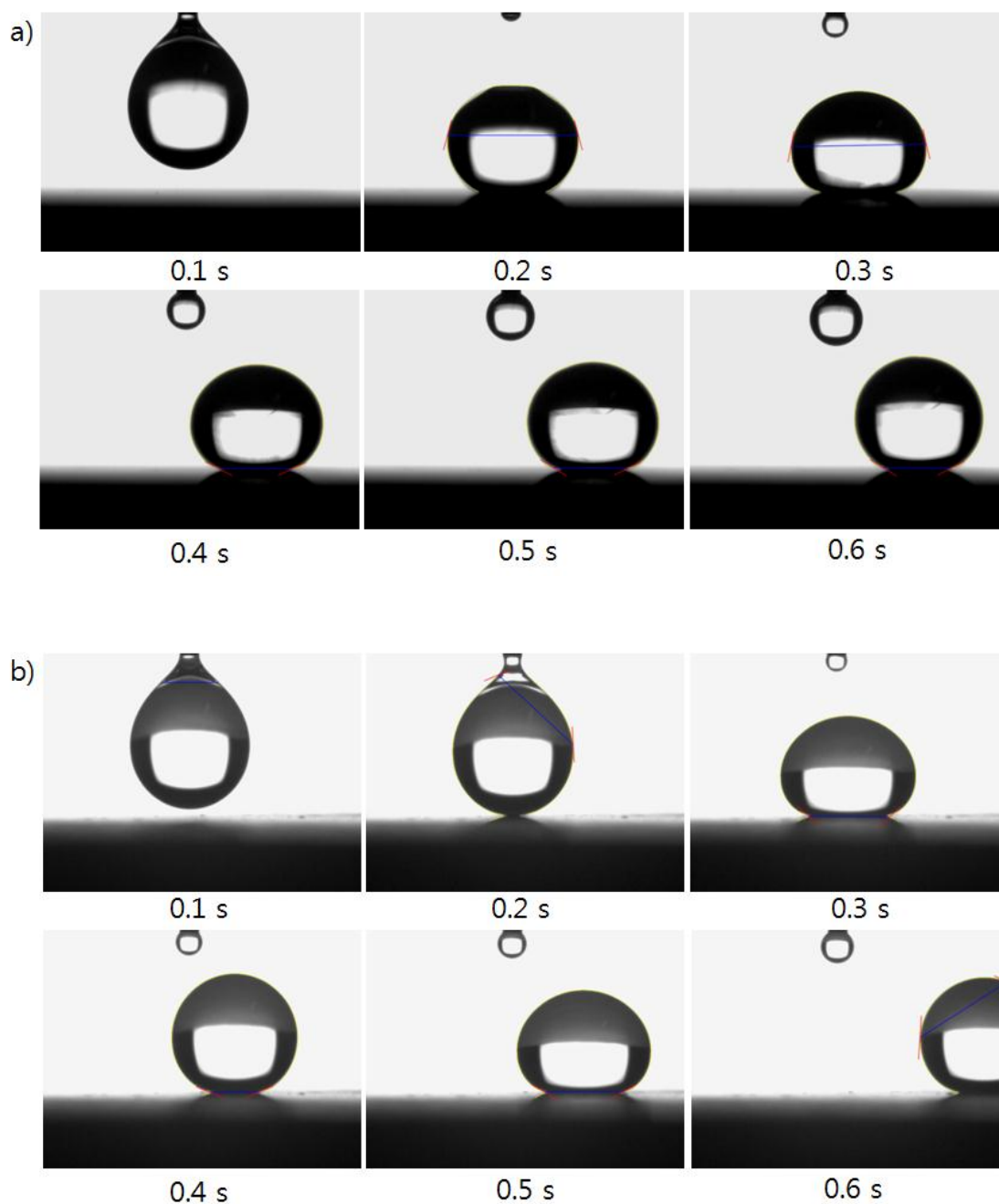
11 ^b micropore surface area calculated from a t-plot

12 ^c total pore volume taken from the volume of nitrogen adsorbed at P/P₀=0.995

13 ^d BJH desorption average pore diameter

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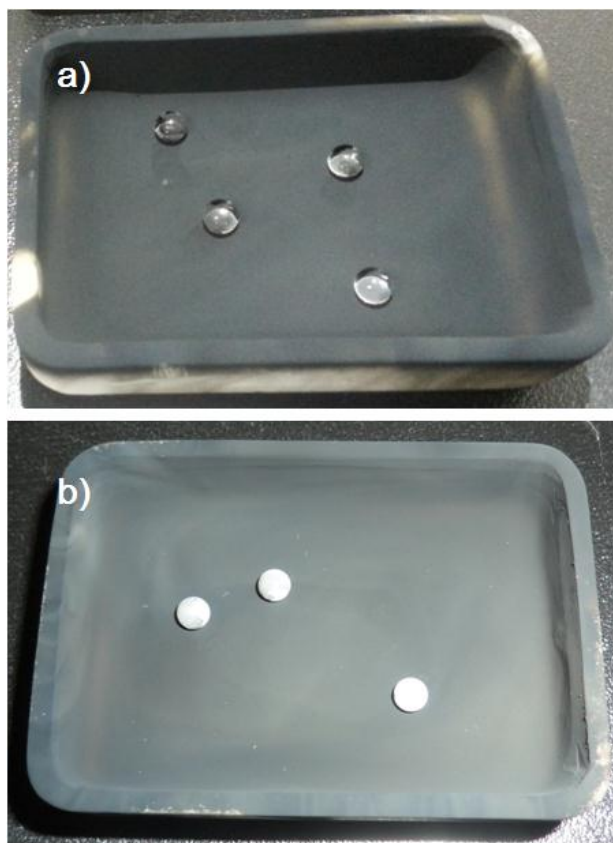


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Fig. S1. Digital images of water droplet movements on a) candle soot and b) fluorinated silica films.

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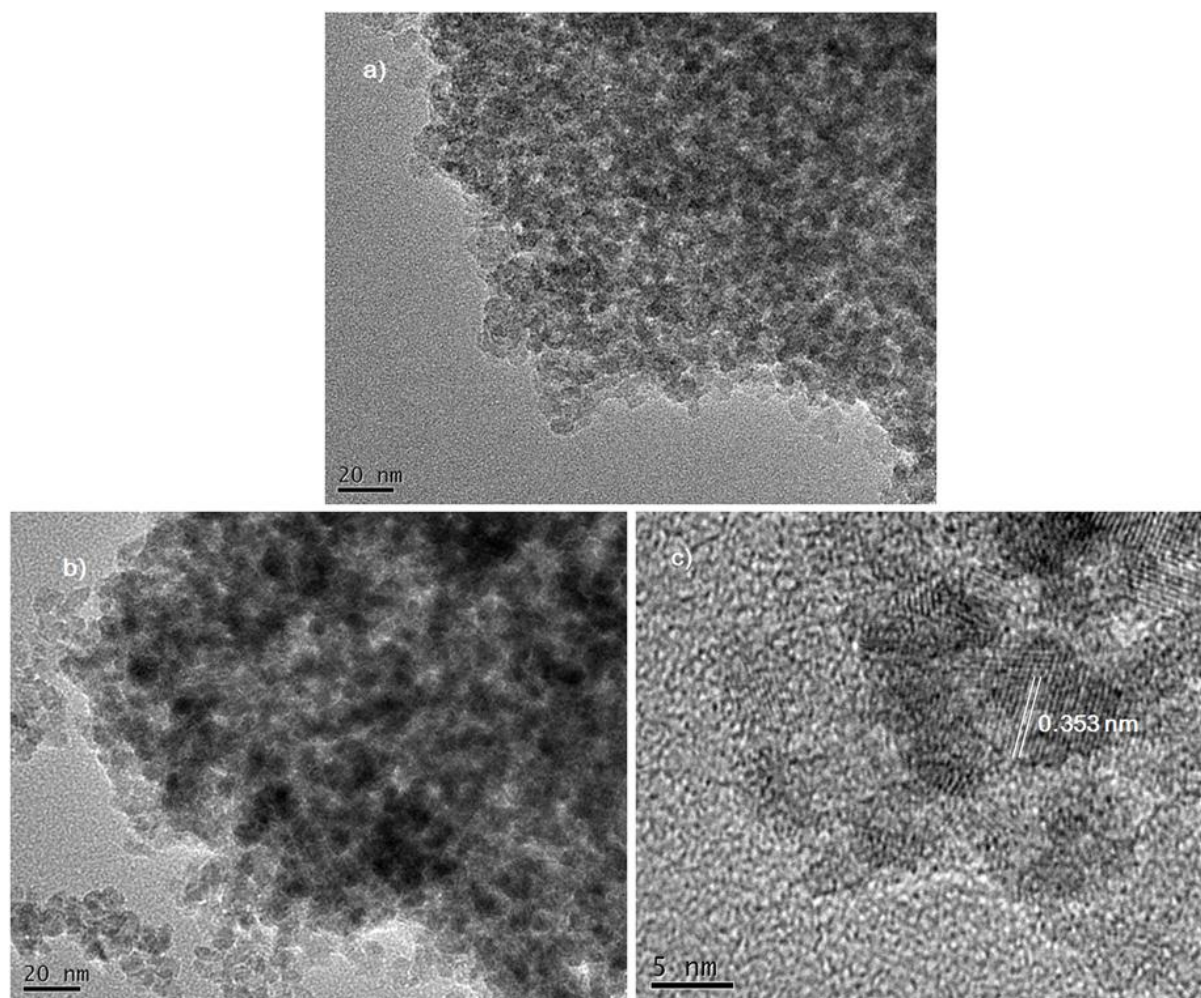
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4 **Fig. S2.** Photographs for droplets of a) silica-sucrose (KIE-1-d/0.18) and b) titania-sucrose
5 (KIE-2-d/0.13) nanocomposite sol on candle soot films.

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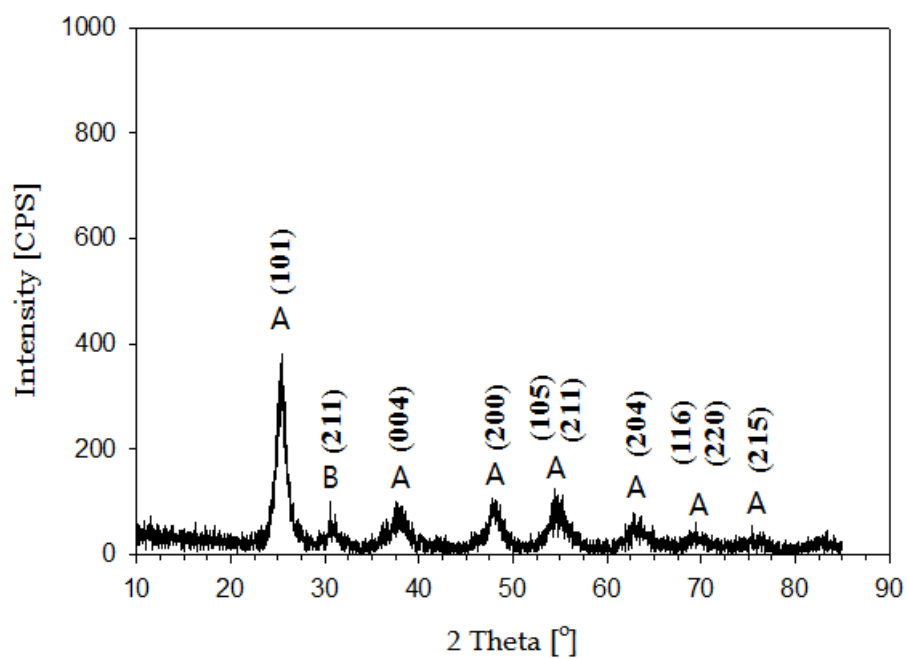
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4 **Fig. S3.** TEM images of KIE-1-d/0.67 and KIE-2-d/0.65 after calcination: a) a low
5 magnification image of KIE-1-d/0.67, b) a low magnification image of KIE-2-d/0.65, (c) a
6 high magnification image of KIE-2-d/0.65.

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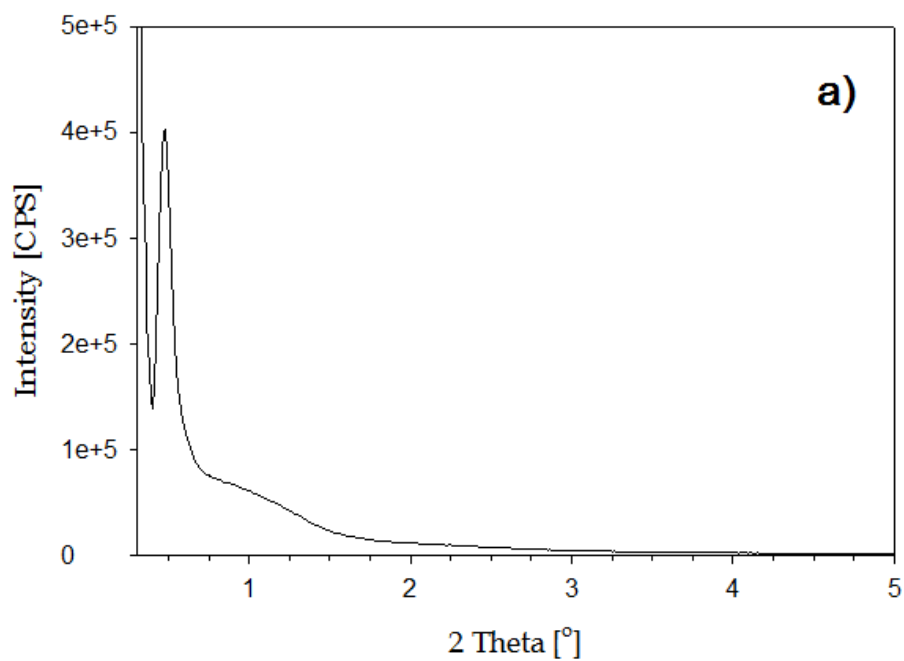
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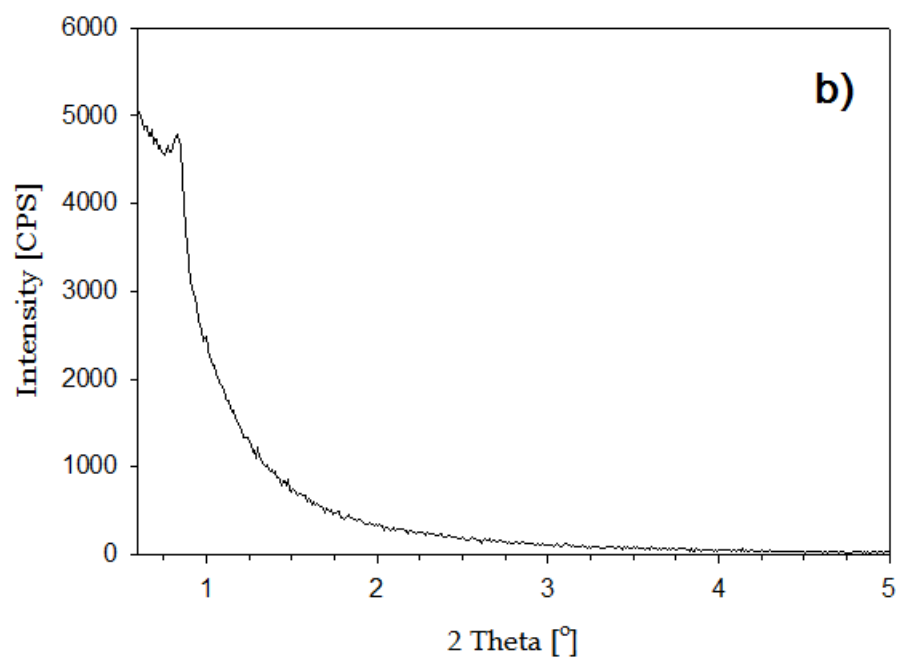
Fig. S4. XRD pattern of KIE-2-d/0.13 after calcination. (A: anatase, B: brookite)

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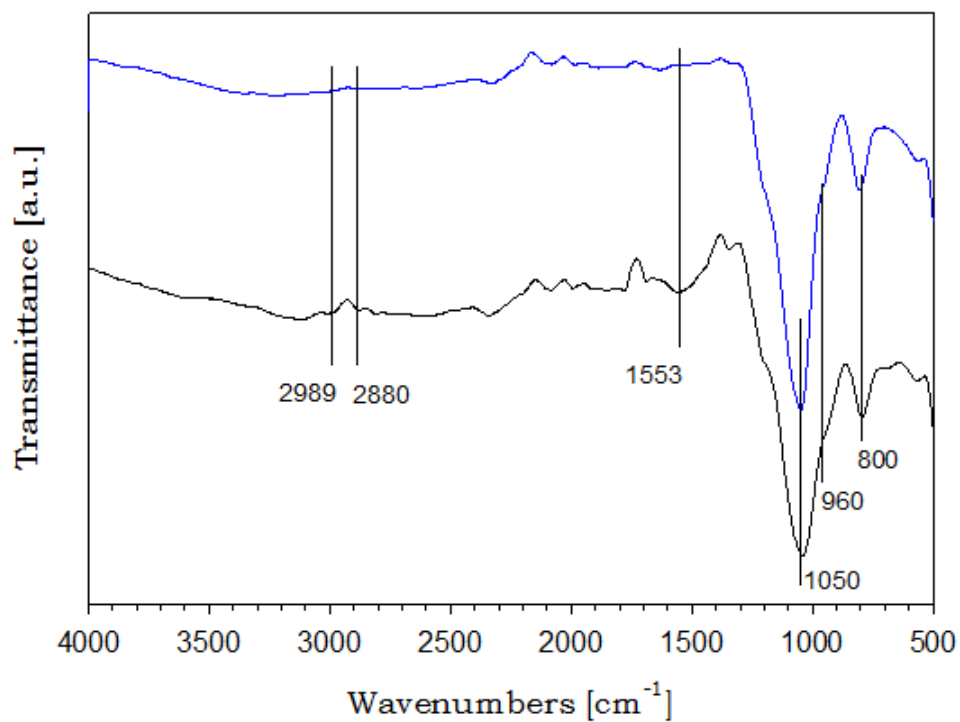
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6 **Fig. S5.** Low angle XRD patterns of a) KIE-1-d/0.18 and b) KIE-2-d/0.13 after calcination.

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4 **Fig. S6.** FTIR spectra of KIE-1-d/0.18 (blue line) and amine-functionalized KIE-1-d/0.18
5 (black line).

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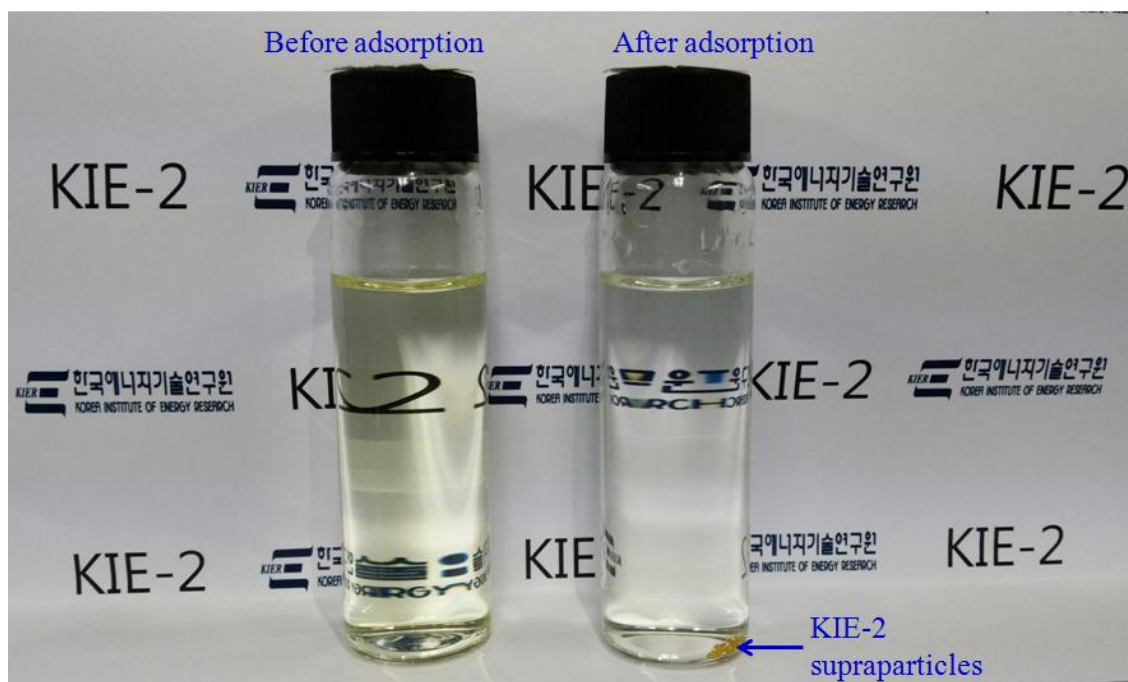
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4 **Fig. S7.** A photograph for Acid blue 25 solutions before and after adsorption with amine-
5 functionalized KIE-1-d/0.18.

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10 **Fig. S8.** A photograph for potassium dichromate solutions before and after adsorption with
11 KIE-2-d/0.13.

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1 **3. Supporting references**

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3 1. X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, *Science* 2012, **335**, 67-70.

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