Supporting Information

Silica-Supported Silver Nanoparticles as an Efficient Catalyst for Aromatic C-H Alkylation and Fluoroalkylation

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Experimental

1.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) and ammonium hydroxide (28–30%) were purchased from Acros. CF_3COOH was purchased from P&M Invest and used without further purification. CH_3CN (CHROMASOLV® Plus, ≥99.9%, by Acros Organics) was used without any preliminary purification. CH_3COOH, HCF_2COOH (from Acros Organic), and C_6H_6 (CHROMASOLV® Plus, ≥99.9%, by Sigma Aldrich) were used without any preliminary purification as well.

The Ethanol and TEOS were purified by distillation.

Et_4NBF_4 was obtained by mixing an aqueous solution of Et_4NOH (30-35%) with HBF_4 for to a neutral indicator reaction. Et_4NBF_4 precipitated from the reaction mixture as white crystals, which were separated by filtering. The powder salt was further recrystallized from diethyl ether and dried for 2 to 3 days in a vacuum at 55°C for dehydration.

Synthesis of Ag@SNs

A mixture of Triton X-100 (2.38 g), *n*-heptanol (2.29 mL), cyclohexane (9.32 mL), TEOS (0.2 mL), and a 1.1 mL aqueous solution of $AgNO_3$ (C=0.01 M) was prepared and stirred for 30 min. The obtained water-in-oil (W/O) microemulsion was mixed with a mixture of Triton X-100 (2.38 g), *n*-heptanol (2.29 mL), cyclohexane (9.32 mL), and aqueous solutions of NH_3 (28-30%) with stirring. After 24 h of stirring (670 rpm), silica nanoparticles were precipitated from the microemulsion by adding acetone, centrifuging, washing by solutions of ethanol-acetone (1:1), ethanol (two times), and water (several times).

1.2. Methods

Analysis of samples was carried out in accordance with a *transmission electron microscope* Hitachi HT7700 Excellence. Sample preparation: 10 microliters of the suspension was placed on a carbon coated 3mm copper grid, drying was performed at room temperature. The grid was placed in a transmission electron microscope using special holder for microanalysis after the drying. Analysis was held at an accelerating voltage of 80 kV in TEM mode.

Content of Si and Ag in the synthesized colloids was measured using *inductively coupled plasma optical emission spectrometry* (ICP-OES) model iCAP 6300 DUO by Varian Thermo Scientific Company equipped with a CID detector. This spectrometer enables the simultaneous measurement of peak heights within the 166 to 867 nm range. The optical resolution is less than 0.007 nm to 200 nm. The working frequency is 27.12 MHz. Together, the radial and axial view configurations enable optimal peak height measurements with suppressed spectral noises. The experimentally observed Ag (spectral line – 328.068 nm) and Si (spectral line - 251.611 nm) concentrations are summarized in Table 1.
The UV-Vis spectra were recorded on a Lambda 35 spectrophotometer (Perkin-Elmer).

Electrosynthesis

Preparative electrolysises were performed using a B5-49 direct current source in a thermostatically controlled, cylindrical, sectioned 100 mL electrolyser (a three-electrode cell). Platinum with a surface area of 20 cm^2 was used for the cathodes and a platinum rod was used as the anode. The working electrode potential was determined using reference electrode Ag/AgCl. During electrolysis, the electrolyte was stirred using a magnetic stirrer, the saturated Et_4NBF_4 solution in CH_3CN was used as an analyte, and the anode compartment was separated by ceramic membrane. The mass spectra were then recorded in EI mode using ThermoQuest TRACE MS.

NMR measurements

A NMR measurements were performed in the NMR department (A.E. Arbuzov Institute Organic and Physical Chemistry) of the Federal Collective Spectral Analysis Center for physical and chemical studies on the structure, properties, and composition of matter and materials. NMR experiments were conducted using Bruker spectrometers AVANCE-400 (400.1 MHz (^{1}H), 376.5MHz (^{19}F), 100.6 MHz (^{13}C)) and AVANCE-600 (600.1 MHz (^{1}H), 150.9 MHz (^{13}C) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm^{-1}. All spectra were acquired in a 5 mm gradient inverse broad band probe head. As a result, chemical shifts were reported on the δ (ppm) scale relative to the residual ^{1}H and ^{13}C C_6D_6 signal resulting in external C_6F_6 (-164.9 ppm) for ^{19}F NMR spectra.

Electrochemistry

Electrochemical measurements were taken on a BASiEpsilonE2P electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A conventional three-electrode system was used with glassy carbon for carbon paste electrode (CPE) solutions for powder samples as the working electrode, the Ag/AgCl (0.01M) electrode as the reference electrode, and a Pt wire as the counter electrode. 0.1 M Et_4NBF_4 was used as the supporting electrolyte to determine the current–voltage characteristics.

To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) composite electrode was prepared using a grinding a mixture of graphite powder and phosphonium salt with a 90/10 (w/w) ratio in mortar giving it a homogeneous mass [1-2]. A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the $Ag@SiO_2$ powder under study. As a result, a portion of the resulting paste was packed firmly into the (3 mm in diameter) a Teflon holder cavity.

Scanning electron microscopy analysis

In this case, an immobilized catalyst was studied using electron microscopy analysis before and after a alkylation reaction. The solutions were applied to the titanium foil surface previously cleared using sonification in acetone. Then, the sample was exsiccated at low heat (no higher than 40 °C). The morphology of the sample surfaces was characterized by an SEM plan-view using a high-resolution microscope that Merlin Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for an energy-dispersive x-ray spectroscopy (EDX) analysis with an AZTEC X-MAX energy-dispersion spectrometer by Oxford Instruments.

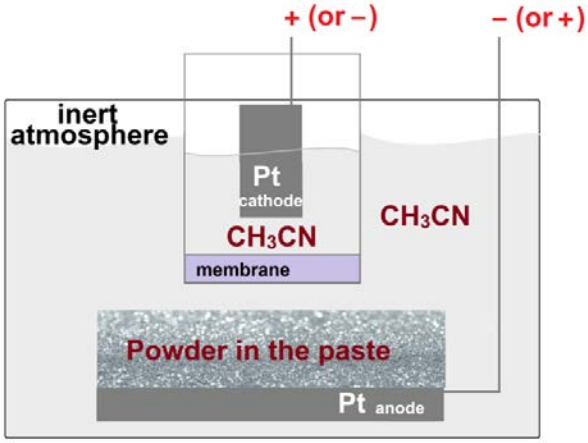
ESR experiments

Oxygen was removed from liquid samples by three cycles of "freezing in liquid nitrogen—evacuation—thawing" and after the last cycle, the electrolysis cell was filled with gaseous helium. Platinum was used as auxiliary electrode , Ag/AgCl equipped with a carbon slate-pencil bridge was applies as reference electrode, and a gold wire 0.5 mm in diameter served as the working electrode. Electrochemical experiments were conducted in CH_3CN using 0.1 M Bu_4NBF_4 as a supporting electrolyte, the potential sweep E(t) being 0.1 V s^{-1}. Measurements were taken on an apparatus program complex featuring an analog electrochemical system with a potentiostat and PWR-3 programmer, an ELEXSYS E500 ESR x-range spectrometer, an E14-440 analog-to-digital and digital-to-analog modulus (L-Card), a fourth-generation computer, and a unique three-electrode helical cell [3-4]. Finally, ESR spectra were simulated using the WinSim 0.96 program (developed by NIEHS).

Synthesis

I. Condition 1: Stepwise synthesis: A) Electrochemical oxidation of $Ag^0@SiO_2$ B) the subsequent chemical reaction using $Ag^I@SiO_2$.

Step 1 – Electrochemical generation of $Ag^I@SiO_2$ in ionic gel on a platinum plate (a working electrode) with an applied thin paste layer of a mixture of dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate and silica nanoparticles $Ag^0@SiO_2$. The working electrode was placed in a solution of acetonitrile and background salt. Following that, electrolysis was performed in an electrochemical cell, separating the anode and cathode compartments at ambient temperature in an argon atmosphere with a working electrode potential of 1.29 V vs. Ag/AgCl. The amount of electricity that passed through the electrolyte was 1,2F per mole of Ag. The paste was dissolved in acetonitrile with the use of an ultrasonic bath. Then silica nanoparticles were separated from the solution by centrifugation. The separated nanoparticles were dried in a high vacuum. The oxidized nanoparticles $Ag^I@SiO_2$ can be stored for month at least without any special protection.



Scheme S1. Solid state oxidation of nanoparticles $Ag@SiO_2$

Step 2 - A solution was prepared for synthesis by mixing $4.6 \cdot 10^{-2}$ mmol of Ag-doped silica nanoparticles, $9.2 \cdot 10^{-3}$ mmol of arene (benzene or pyridine), and $9.2 \cdot 10^{-3}$ mmol of acid in CH_3CN (50 ml). Synthesis was performed in a round-bottomed flask at ambient temperature. Before starting the reaction, the reaction mixture was purged with argon, then tightly stoppered. The synthesis was performed over 24 hours. After completing the reaction, the oxidant was separated by centrifugation. The yields of the product were evaluated using GC-MS (EA).

II. Condition 2: Electrosynthesis based on $Ag^{+1}@SiO_2$ (5%) generation and regeneration in situ in the presence of coupling partners

A solution was prepared for synthesis by mixing 0.1 g ($0.15 \cdot 10^{-4}$ mol) of Ag-doped silica nanoparticles, 0.3 mmol of arene (benzene or pyridine), and 0.3 mmol of acid (CF_3COOH or HCF_2COOH or CH_3COOH) in CH_3CN (50 ml). Electrolysis was performed in an electrochemical cell, separating the anode and cathode compartments at ambient temperature in an argon atmosphere with a working electrode potential of 1.40-1.60 V vs. Ag/AgCl. The amount of electricity that ended up passing through the electrolyte was 2F per mole of acid. After completing the electrolysis, the immobilized catalyst was separated by centrifugation. The yields of the product were evaluated using GC-MS (EA).

Table 1. Yields of the alkylated arenes (1-6) in conditions **I** (stoichiometric quantity of the nanocatalyst) and **II** (catalytic quantity of the nanocatalyst). Blank SiO_2 indicates blank test with empty, naked SiO_2.

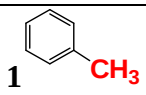
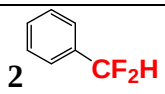
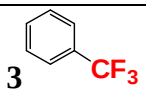
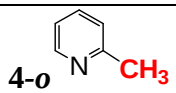
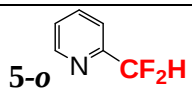
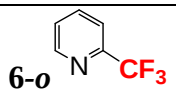
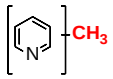
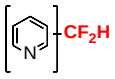
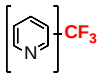
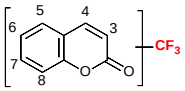
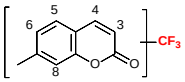
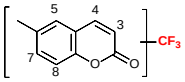
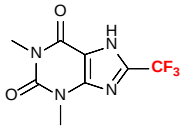
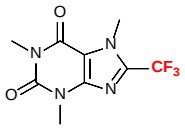
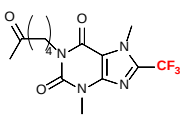
Compound	Conditions	Product yield [%] in repeated synthesis				
		1st	2nd	3rd	4th	5th
1 	I / II	75/55	75/55	75/54	75/53	75/53
	Blank silica nanoparticles	12	-			
2 	I / II	52/45	55/43	54/39	52/35	50/33
	Blank silica nanoparticles	10	-			
3 	I / II	56/47	55/42	54/39	53/35	52/30
	Blank silica nanoparticles	11	-			
4-*o* 	I / II	53/45	53/45	53/44	53/43	53/43
	Blank silica nanoparticles	14	-			
5-*o* 	I / II	57/49	55/48	54/45	52/55	50/40
	Blank silica nanoparticles	9	-			
6-*o* 	I / II	55/45	54/42	54/45	53/45	53/40
	Blank silica nanoparticles	10	-			

Table 4. Total yields and selectivity of the alkylated heteroarenes (4-12) in the conditions **II** using 5 % of the nanocatalyst.

Product	[a]Total product yield [%]	[b]Isomer ratio (substitution position)
4 	79	4:1:1*(o,m,p)*
5 	85	4:1:1*(o,m,p)*
6 	82	4:1:1*(o,m,p)*
7 	75	8:2:1:1*(3,4,6,7)*
8 	77	9:2:1*(3,4,6)*
9 	75	5:1:1*(3,4,7)*
10 	83	-
11 	87	-
12 	81	-

[a]NMR yields and [b]selectivity were obtained by ^{19}F NMR analysis and (GC-MS was used for products 4 *(o,m,p)*) of the crude reaction mixtures.

Preparative synthesis

After completing the electrolysis (condition II), the solution was washed with distilled water (100 ml) and extracted with benzene (3×100 ml). The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Residue was purified by column chromatography (SiO2; hexane:EtOAc) to afford product (table 4)

3-(Trifluoromethyl)-2*H*-chromen-2-one (7-*3*)

(SiO_2; hexane:EtOAc = 5:1) White crystals, m.p. 130—133 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.17 (s, 1H, C(4)H); 7.69 (t, 1H, ArH, J = 7.9 Hz); 7.63 (d, 1H, ArH, J = 7.9 Hz); 7.42—7.37 (m, 2 H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 155.9, 154.6, 143.4, 134.4, 129.5, 125.3, 121.3, 117.6, 116.7, 115.9. ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: –66.3 (s, 3 F). MS, m/z: 214.56 [M]+. Found (%): C, 56.12; H, 2.31. $C_{10}H_5F_3O_2$. Calculated (%): C, 56.09; H, 2.35. Physicochemical characteristics of **7-*3*** correspond to the literature data. [1]

7-Methyl-3-(trifluoromethyl)-2*H*-chromen-2-one (8-*3*)

(SiO_2; hexane:EtOAc = 10:1) White crystals, m.p. 120—122 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.11 (s, ^{1}H, C(4)H); 7.49 (d, 1H, ArH, J=8.0 Hz); 7.18 (d, 2H, ArH, J=7.6 Hz); 2.5 (s, 3H, C(7)Me). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.2, 154.8, 146.4, 143.2, 129.1, 126.5, 121.5, 117.5, 116.4, 114.4, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$), δ: –65.5 (s, 3F). MS, m/z: 229.05 [M]+. Found (%): C, 57.95; H, 3.00. $C_{11}H_8F_3O_2$. Calculated (%): C, 57.90; H, 3.09. Physicochemical characteristics of **8-*3*** correspond to the literature data. [1]

6-Methyl-3-(trifluoromethyl)-2*H*-chromen-2-one (9-*3*)

(SiO_2; hexane:EtOAc = 8:1) White crystals, m.p. 140—143 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.09 (s, 1H, C(4)H); 7.48 (d, 1 H, ArH, J = 8.5 Hz); 7.39 (s, 1 H, ArH); 7.29 (d, 1H, ArH, J = 8.5 Hz); 2.44 (s, 3H, C(6)Me). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.2, 152.8, 143.3, 135.5, 135.2, 129.1, 121.4, 117.5, 116.8, 116.5, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$), δ: –65.3 (s, 3 F). MS, m/z: 228.98 [M]+. Found (%): C, 57.93; H, 3.02. $C_{11}H_8F_3O_2$. Calculated (%): C, 57.90; H, 3.09. Physicochemical characteristics of **9-*3*** correspond to the literature data. [1]

1,3-dimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (10)

(SiO_2; hexane:EtOAc = 5:1) White crystals; m.p. 233—237 ºC; ^{1}H NMR (600 MHz, CD_3OD), δ: 3.54 (s, 3H), 3.36 (s, 3H) ppm; ^{13}C NMR (150 MHz, CD_3OD) δ 159.5, 153.8, 150.2, 145.4 (q, J = 38 Hz), 121.6 (q, J = 269 Hz), 116.0, 30.8, 28.4 ppm; ^{19}F NMR (376 MHz, CD_3OD) δ: -64.7; IR (KBr, ν(cm^{-1})): 3484, 2965, 1695, 1640, 1272, 1160, 1114, 1061, 1033, 751; HRMS (ESI-TOF), m/z: 262.98 $[M]^{+\cdot}$ Found (%): C, 38.79; H, 2.76 N, 23.02; $C_8H_7F_3N_4O_2$ Calculated (%): C, 38.72; H, 2.84; F, 22.97; N, 22.58; O, 12.89 Physicochemical characteristics of **10** correspond to the literature data. [2]

1,3,7-trimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (11)

(SiO_2; hexane:EtOAc = 5:1) White crystals, mp 130-133^{0}C ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.12 (s, 3H), 3.55 (s, 3 H), 3.38 (s, 3 H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.5, 151.4, 146.6, 139.0, 118.3, 109.7, 33.3, 30.0, 28.3; ^{19}F NMR (376 MHz, $CDCl_3$), δ -62.7 ppm; IR (KBr, ν(cm^{-1})): 3379, 2958, 1709, 1661, 1609, 1510, 1459, 1404, 1367, 1181, 1025, 978, 821, 683; HRMS (ESI-TOF), m/z: 262.98 $[M]^{+\cdot}$ Found (%): C, 41.27; H, 3.35 N, 21.80; $C_9H_9F_3N_4O_2$ Calculated (%): C, 41.23; H, 3.46; F, 21.74; N, 21.37; O, 12.20 Physicochemical characteristics of **11** correspond to the literature data. [2]

3,7-dimethyl-1-(5-oxohexyl)-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (12)

(SiO2; hexane:EtOAc = 5:1) White crystals; m.p.: 67—69 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.13 (s, 3H), 4.01 (t, J =7.1 Hz, 2H), 3.57 (s, 3H), 2.49 (t, J = 7.1 Hz, 2 H), 2.13 (s, 3H), 1.68 – 1.60 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 208.7, 155.4, 151.2, 146.7, 139.1, 118.3, 109.8, 43.2, 41.3, 33.3, 30.1, 30.0, 27.4, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; IR (KBr, ν(cm^{-1})): 1712, 1652, 1608, 1459, 1379, 1244, 1201, 748, 600; HRMS (ESI-TOF), m/z: 347.01 $[M]^{+\cdot}$ Found (%): C, 48.62; H, 4.89 N, 16.20; $C_{14}H_{17}F_3N_4O_3$ Calculated (%): C, 48.56; H, 4.95; F, 16.46; N, 16.18; O, 13.86. Physicochemical characteristics of **12** correspond to the literature data. [2]

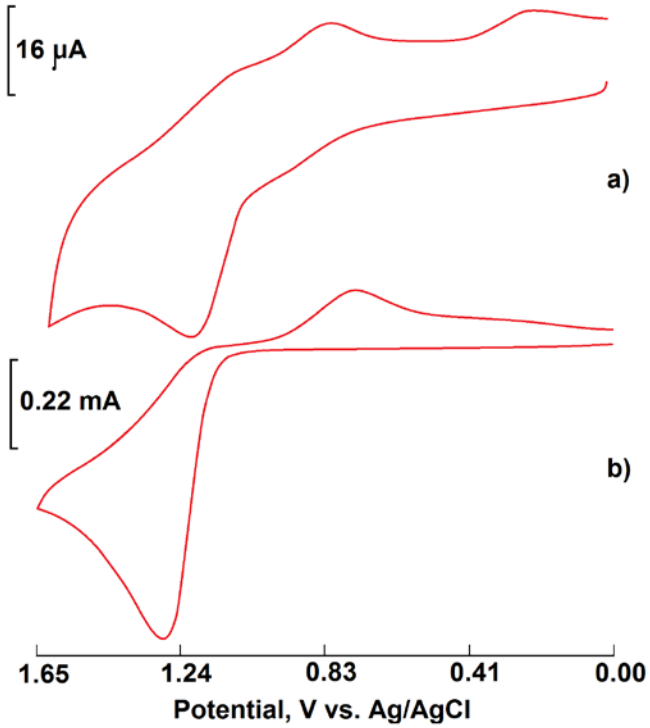


Fig. S1. Oxidation CVs of Ag@SiO2 (5mg) in the suspension (CH_3CN 1ml) on GC (a); Ag@SiO_2 (5mg) in the paste[1,2] on the CPE (b).

Preparative oxidation

For the preparative oxidation the paste-like mixture of dried Ag^0@SNs and phosphonium salt as binder was coated onto the anode (for the detailed Scheme S1, Fig. S2). The current was passed through the mixture at 1.3 V. The oxidation peak (Ag^0 to Ag^+) disappears after the passing of 1.2 F, while the reduction of the oxidized silver (I) occurs at -0.174V (Fig. S2).

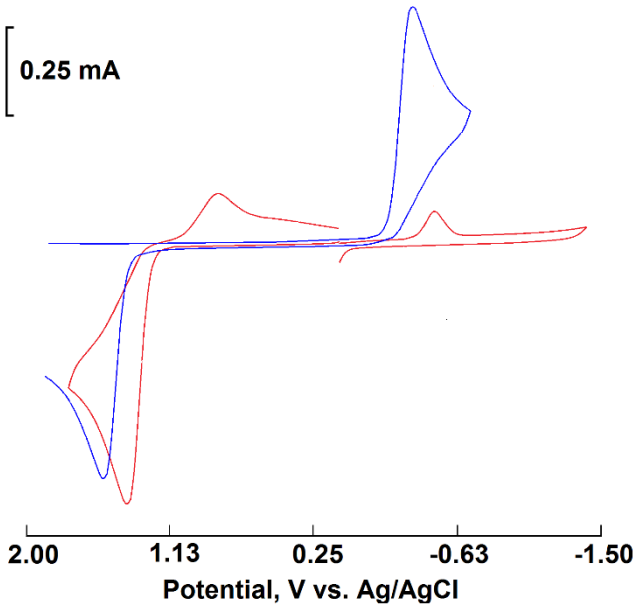


Fig. S2. CVs for $Ag^0@SiO_2$ (5mg) at CPE a) before preparative oxidation and b) after preparative oxidation (1.2F)

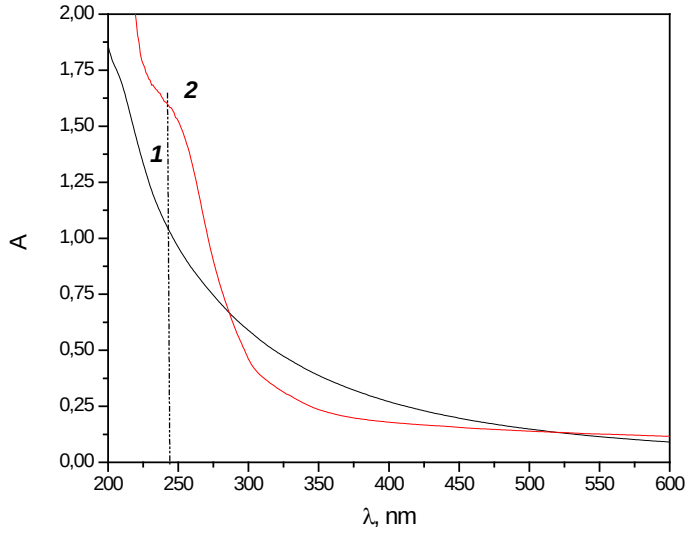


Fig. S3. UV-VIS spectra (1) $Ag^0@SiO_2$ in CH_3CN (C=0.1 g L^{-1}), (b) $Ag^{+1}@SiO_2$ in CH_3CN (C=0.17 g L^{-1}).

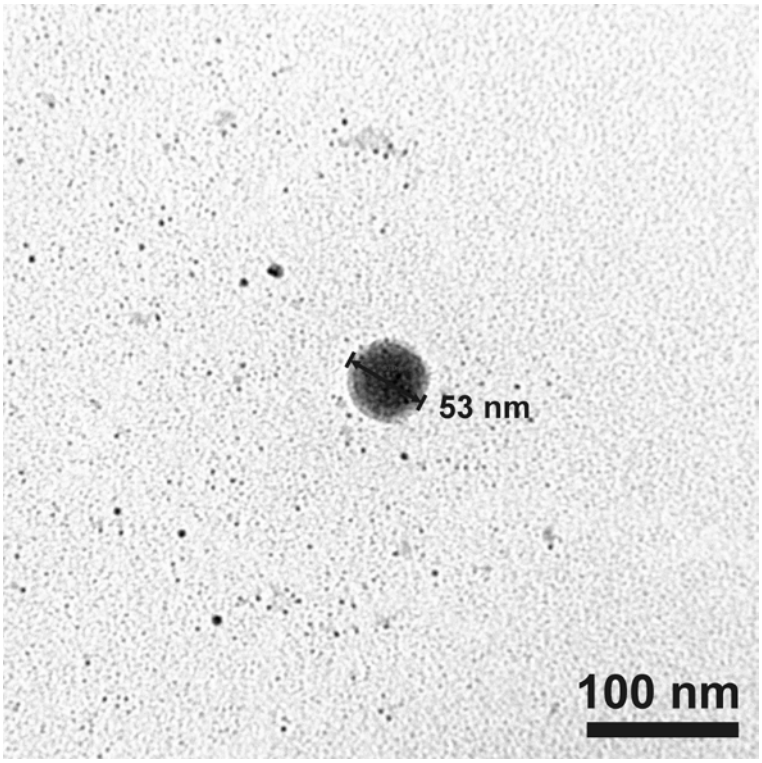


Fig. S4 TEM images of $Ag^0@SiO_2$ after five catalytic cycle of reaction with CH_3COOH.

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