Electronic Supplementary Information (ESI) *for*

Smart Hybrid System of Au Nanoparticles Immobilized PDMAEMA Brushes for Thermally Adjustable Catalysis

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Experimental

Materials: All chemicals were analytical grade or of the highest purity available. Ammonium hydroxide, Methyl-2-pyrrolidinone (NMP), tetraethoxysilane (TEOS), toluene, ethanol, methanol, acetone, benzophenone (BP), $HAuCl_4$, $NaBH_4$, 4-nitrophenol and 3-aminopropyltriethoxysilane (APTES) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. 2-dimethylaminoethyl methacrylate (DMAEMA) was purchased from the Energy Chemical Company.

Preparation of bare silica NPs: Ammonium hydroxide (25 wt % in water, 15 mL) and ethanol (300 mL) were added into a two-necked round-bottom flask at ambient temperature; the mixture was stirred at 50 ^{o}C. A mixture of tetraethoxysilane (TEOS, 15 mL) and H_2O (20 mL) was added into the flask at a rate of ~1 mL/min via a dropping funnel. After stirring for 12 h at room temperature, the NPs were isolated by centrifugation at 8000 rpm. After discarding the supernatant, the sediments were redispersed in ethanol and centrifugated again. This purification cycle was repeated for four times. The obtained NPs were then dispersed and stored in 50 mL of ethanol.

Functionalization of silica with APTES: Functionalization of silica by converting most of the surface silanol groups into amino groups was carried out following a slightly modified literature procedure as follows. To a stirred suspension of dried silica (1.8 g) in dry NMP (200 mL) was added dropwise APTES (4.5 mL). The reaction mixture was stirred at room temperature for 24 h. The nanoparticles were isolated by centrifugation at 8000 rpm. After discarding the supernatant, the sediments were redispersed in toluene and centrifugated again. The above purification cycle was repeated for three times to remove excess APTES. (T. Wu, Y. F. Zhang, X. F. Wang, S. Y. Liu, *Chem. Mater.*, 2008, **20**, 101)

SIPGP: 20 mg of APTES modified silica, 2 mL of monomer (DMAEMA) and 0.005 g of benzophenone (BP) were added into a tube. The tube was placed under a UV lamp and irradiated for 40 min at room temperature. A 250 W high-pressure mercury lamp from Jiguang Co. (Shanghai, China) was used for SIPGP. Its wavelength ranged from 200 to 400 nm. The distance between the reaction mixture and the light source was 10 cm. The reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature during the irradiation. The reaction mixture was centrifuged at 8000 rpm for 5 min in methanol, which led to sedimentation of the polymer-grafted silica particles. The supernatant, which contained unreacted monomer and residual initiator, was discarded. The particulate sediment was redispersed in methanol and centrifuged two more times. To remove the ungrafted polymer, the precipitate was dispersed in acetone and centrifuged repeatedly. The offwhite polymer-grafted silica was collected and dried in vacuum at 100 ^{o}C for 24 h before characterization.

SiO_2@ PDMAEMA NPs for loading the gold NPs: The details of loading the gold NPs were as following: 0.05 g of SiO_2@ PDMAEMA NPs were dispersed in 10 mL of deionized water and 0.25 mL of 4 mM $HAuCl_4$ aqueous solution was added; then, 1 mL of 0.05 M $NaBH_4$ aqueous solution was added dropwise under the ice water bath with shaking. The reaction lasted for 1 h. The final product was purified through washing with water three times and dried under vacuum oven until constant weight.

Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol in an Aqueous Medium: A typical experiment for the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was carried out as follows: 0.1 mL of 4-NP aqueous solution (5 mM, 5×10^{-7} mol), 1.0 mL of $NaBH_4$ (0.2M, 2×10^{-4} mol) aqueous solution and 2.0 mL of water were mixed in a colorimetric tube. We introduced 0.05 mL of catalyst dispersion (1.0 mg/mL) into the mixture with gentle shaking. The bright-yellow solution faded gradually as the catalytic reaction proceeded. The catalytic activity was determined by a UV-vis spectrophotometer with a decrease at 400 nm in UV-vis absorption and a simultaneous increase in the absorption at 300 nm, indicating the formation of 4-AP.

Characterizations: Fourier transform infrared (FTIR) Spectroscopy (Nicolet 6700, Thermoscientific, USA): The spectra were measured with a spectrometer. Absorbance spectra were collected using a spectral resolution of 4 cm^{-1} at room temperature over a frequency range of 4000-500 cm^{-1}. The background spectra were recorded on corresponding KBr. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO-TGA/DSC I instrument with a heating rate of 10 ^{o}C min^{-1} in flowing N_2 and a sample of 3-5 mg. The morphology and size of the samples were investigated using transmission electron microscopy (TEM, Tecnai F20 S-TWIN (FEI), accelerating voltage of 200 kV). TEM samples were prepared by dropping a diluted aqueous solution (5μL) of samples onto carbon-coated copper grids and were dried in air for 1h. UV-vis absorption spectra of the samples were recorded using a Lambda 950 spectrophotometer (Perkin-Elmer). Measurements of the solutions were taken in 3mL quartz cuvettes.

Figures

For example, in the spectrum of pure SiO_2 particles, the absorption bands at 3400 cm^{-1} and 958 cm^{-1} were the characteristic peaks of Si-OH, the absorption band at 1600 cm^{-1} was the characteristic peak of bonding water, and the absorption bands at 1100 cm^{-1} and 800 cm^{-1} were the characteristic peaks of Si-O-Si group. In the spectrum of neat PDMAEMA, an intense increase of the absorption peak appears at 1730 cm^{-1} corresponding to the stretching vibration of ester carbonyl group in the PDMAEMA. By comparing the FTIR spectra of amino modified silica and pure PDMAEMA in **Fig. S1**, in the spectrum of SiO_2@PDMAEMA, the bands at 2925 and 2853 cm^{-1} are observed for amine functionalized NPs. The presence of asymmetric and symmetric stretching vibrations of $-CH_2$ on amino modified silica indicates the grafting of aminopropyl groups on the surface of silica. The characteristic bands located at 1620-1650 cm^{-1} were assigned to the bending vibrations of aliphatic amine (N-H) groups.

As seen in **Fig. S1,** the spectrum of SiO_2@PDMAEMA/Au was similar to that of the SiO_2@PDMAEMA, however, the wavenumbers and the relative intensities are slightly different with each other. These slight changes in IR spectrum may come from the interaction between SiO_2@PDMAEMA and gold NPs. The obvious difference between the two IR spectra was the disappearance of the peak at 2780 cm^{-1}, which was in assignment of C-H stretching vibrations of the $N-CH_3$ groups of PDMAEMA brushes. Moreover, this disappeared absorption further implied that the $N-CH_3$ group was reduced to quaternary amine salts or other coordination compounds. Therefore, the end tertiary amine groups of PDMAEMA were thought to be the primary role in the reductive reaction between PDMAEMA and $HAuCl_4$.

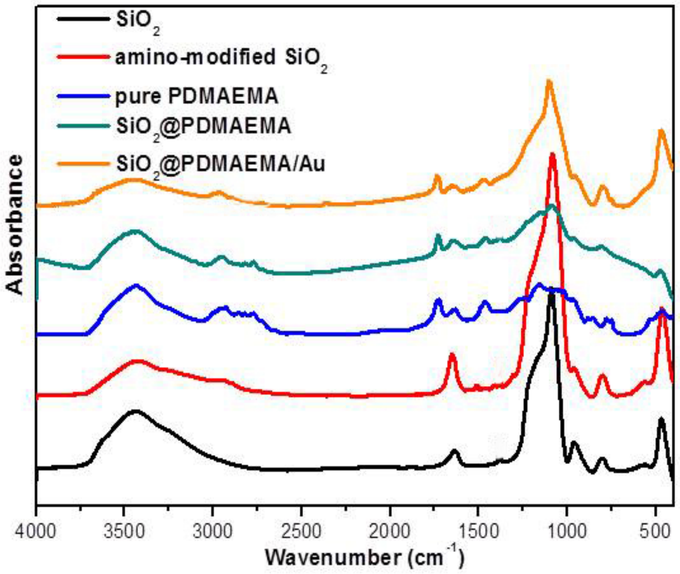

Fig. S1 FT-IR spectra of (black) SiO_2, (red) amino-modified SiO_2, (blue) pure PDMAEMA, (green) SiO_2@PDMAEMA and (orange) SiO_2@PDMAEMA/Au.

As shown in **Fig. S2.**, a weight loss of 5% for the SiO_2 NPs was assigned to the physically adsorbed water on the silica surface. Pure PDMAEMA exhibited a two-stage weight-loss process between 200 and 500 °C as expected. [16] For the resultant SiO_2@PDMAEMA microspheres with the grafted PDMAEMA brushes, the weight loss was 30% with two distinct weight loss stages between 200 and 600 ^{o}C. The first weight loss until 200 ^{o}C was also due to the evaporation of the physically adsorbed water or solvent, and the second major weight loss from 200 to 600 ^{o}C was due to the decomposition of the polymer component in the shell layer of the corresponding microspheres.

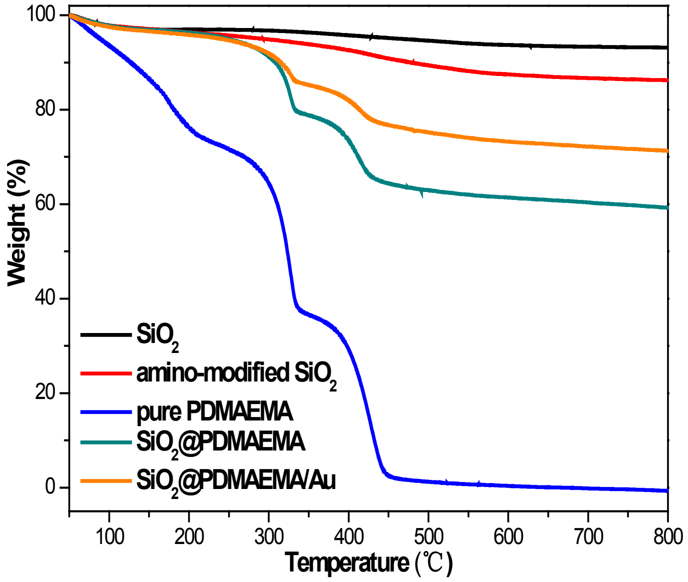

Fig. S2 TGA spectra of (black) SiO_2, (red) amino-modified SiO_2, (blue) pure PDMAEMA, (green) SiO_2@PDMAEMA and (orange) SiO_2@PDMAEMA/Au.

Furthermore, in order to corroborate residual weight is only due to the gold present in the samples, DTG analysis of core-shell composites before loading Au NPs (black) and after loading Au NPs (red) were made. These two distinct weight loss stages of SiO_2@PDMAEMA and SiO_2@PDMAEMA/Au between 200 and 500 °C are very similar, as shown in **Fig. S3**, which illustrates that SiO_2@PDMAEMA/Au hybird system remained high thermostability.

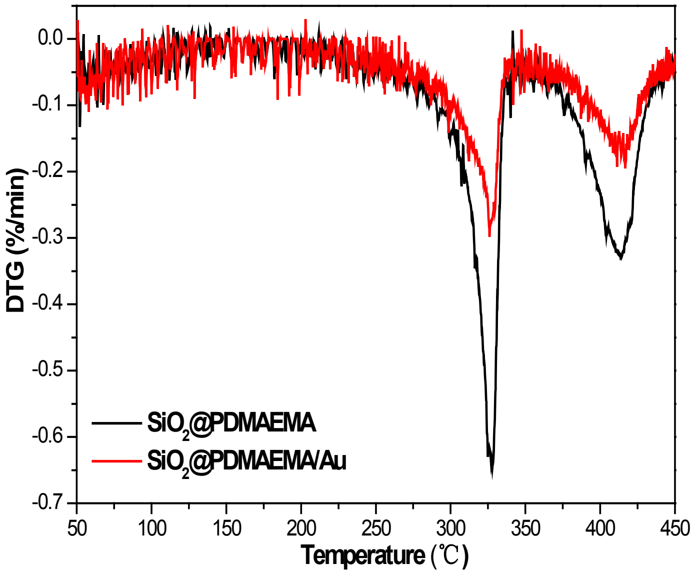

Fig. S3 DTG of SiO_2@PDMAEMA and SiO_2@PDMAEMA/Au.

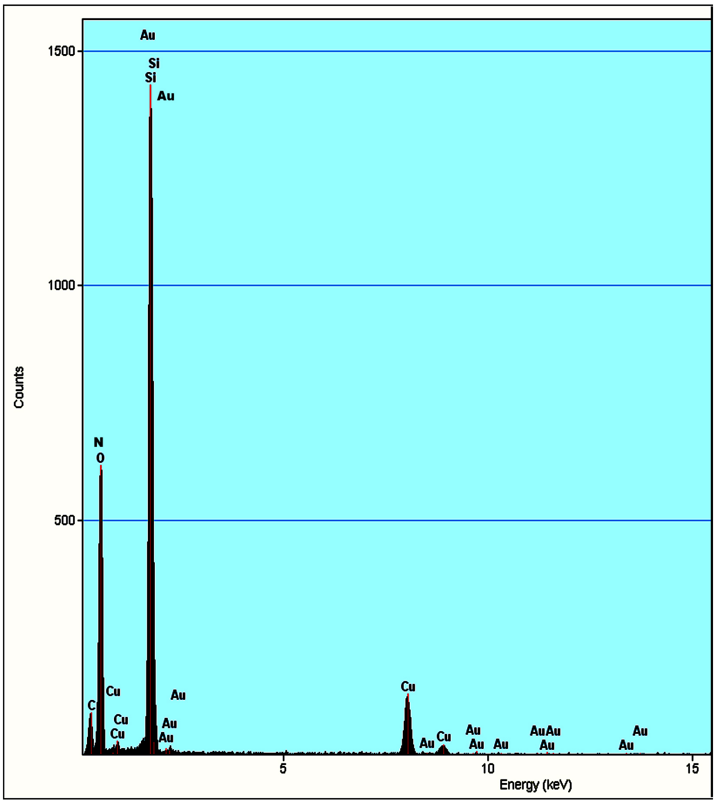

Fig. S4 EDX spectrum of SiO_2@PDMAEMA/Au. The copper peaks are from the copper grid used as support in the measurements.

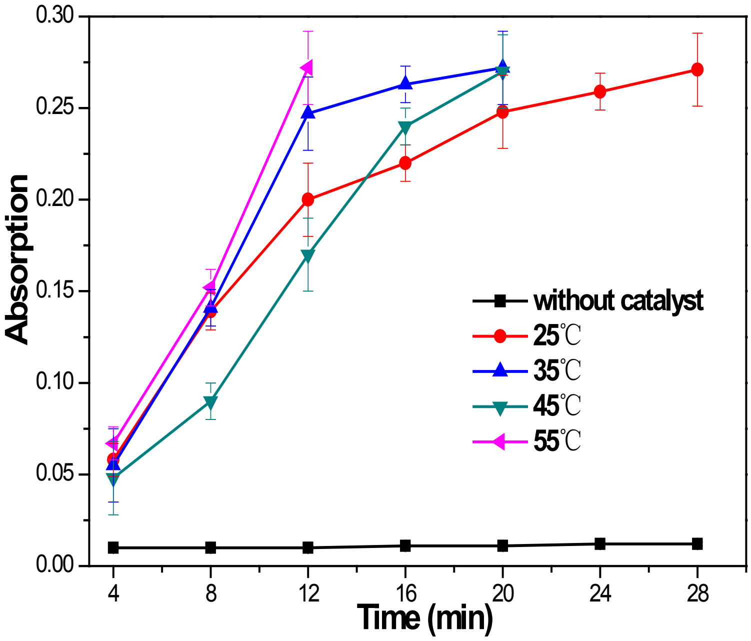

Fig. S5 Reduction of 4-NP in aqueous solution recorded by UV-vis spectroscopy every 4 min using the SiO_2@PDMAEMA/Au hybrid system as a catalyst at different temperature. (The absorption peak is 300nm)

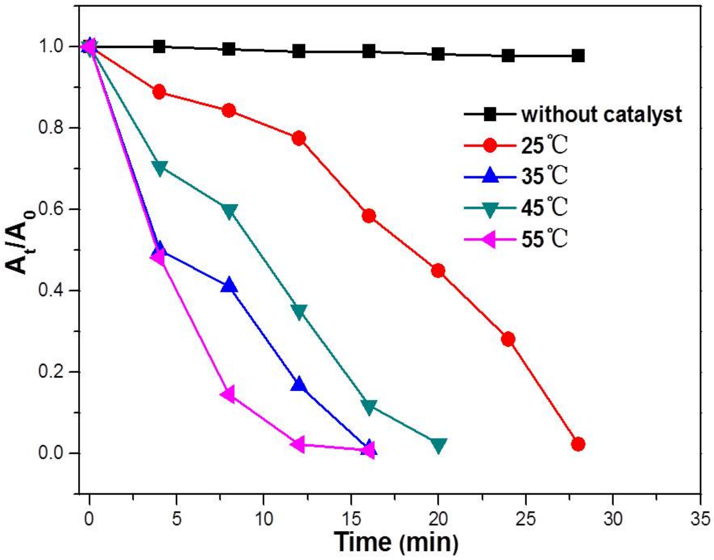

Fig. S6 A_t/A_0 *versus* reaction time for the reduction of 4-NP over no catalyst and SiO_2@PDMAEMA/Au at different temperatures. A_0 and A_t are the absorption peak at 400 nm initially and at time *t*.

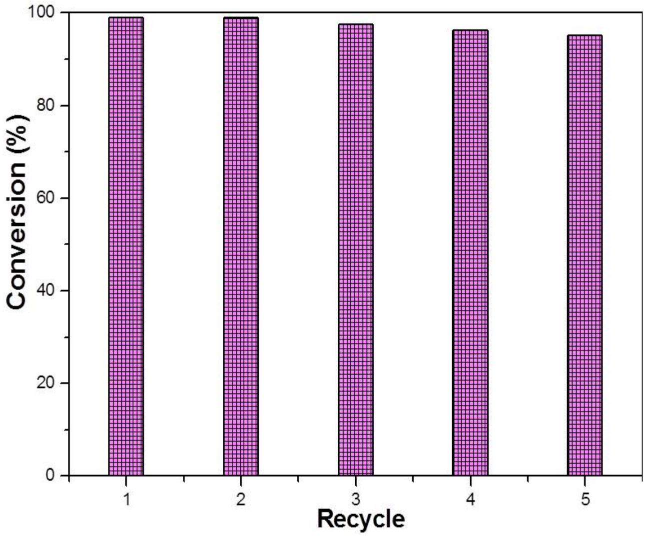

Fig. S7 Reusability of the SiO_2@PDMAEMA/Au as a catalyst for the reduction of 4-NP with $NaBH_4$.